

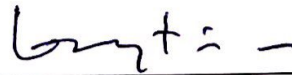
APPLICATION OF TRIBOELECTRIC CHARGING EFFECT FOR ENGINE LUBRICATING OIL DEGRADATION MONITORING

A THESIS SUBMITTED TO
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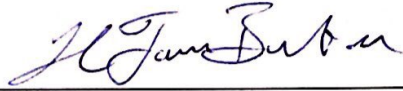
By
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January 2019

Application of triboelectric charging effect for engine lubricating oil
degradation monitoring
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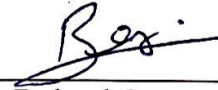
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ABSTRACT

APPLICATION OF TRIBOELECTRIC CHARGING EFFECT FOR ENGINE LUBRICATING OIL DEGRADATION MONITORING

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M.S. in Materials Science and Nanotechnology

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January 2019

Lubrication of machine parts is necessary to prevent friction and wear in machine operation. Even the slightest reduction of friction and wear cause a huge positive impact in the economy since almost all machines in our current industry suffer from the energy and material losses caused by these events. Therefore, maintaining good and stabilized lubrication is vital for this purpose. However, oxidation of lubricants upon operation brings about unwanted changes in its chemical and physical properties and causes lubrication performance to deteriorate. Thus, a better understanding of lubricant condition and its variation under different parameters can enable technologists to make informed decisions to ensure lubrication excellence and optimization of the lubricant's renewal time. However, current methods for detection of oil deterioration lack practicality and flexibility. In this study, a novel method was put forward to estimate the remaining service life of several types of commercially available engine lubricants using triboelectrification. A Triboelectric sensor (TES) was developed and this TES was given different open circuit voltage (Voc) values according to the different oxidation time of lubricant oils. These results were then correlated with FTIR-ATR analyses of the oils. Additionally, we reported the dynamic viscosity changes of engine oil samples upon oxidation. We believe the results presented in this thesis convey the basis for establishing a TES for straightforward detection of deterioration of engine oil.

Keywords: Lubricant oil, Combustion, Tribochemical Reactions, Triboelectric sensor.

ÖZET

MOTOR KAYGANLAŞTIRICI YAĞLARIN BOZUNMA İZLENİMİ İÇİN TRIBOELEKTRİK ŞARJ ETKİSİNİN UYGULANMASI

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Makine çalışmasında sürtünmeyi ve aşınmayı önlemek için makine parçalarının yağlanması gerekir. Sürtünme ve aşınmanın en ufak bir azalması bile ekonomide büyük bir olumlu etkiye neden olur çünkü mevcut endüstrimizdeki neredeyse tüm makineler bu olayların neden olduğu enerji ve malzeme kayıplarından muzdariptir. Bu nedenle, iyi ve dengeli yağlamanın korunması bu amaç için hayati öneme sahiptir. Bununla birlikte, çalışma sırasında yağlama maddelerinin oksidasyonu kimyasal ve fiziksel özelliklerinde istenmeyen değişiklikler meydana getirir ve yağlama performansının bozulmasına neden olur. Bu nedenle, yağlama koşulunun daha iyi anlaşılması ve farklı parametrelerdeki değişkenliği, teknoloji uzmanlarının yağlama mükemmelliğini ve yağlama maddesinin yenileme zamanının optimizasyonunu sağlamak için bilinçli kararlar vermelerini sağlayabilir. Bununla birlikte, yağ bozulmasının tespiti için mevcut yöntemler pratiklik ve esneklik açısından yeterli değildir. Bu çalışmada, triboelektrifikasyon konsepti kullanılarak ticari olarak satılan çeşitli motor yağlama maddelerinin kalan servis ömrünü tahmin etmek için yeni bir teknoloji geliştirilmiştir ve Triboelektrik sensör (TES) adı verilen bir cihaz geliştirildi. TES ile, kayganlaştırıcı yağların farklı oksidasyon sürelerine göre farklı açık devre voltaj (Voc) değerleri verdiği tespit edildi. Bu sonuçlar daha sonra yağ örneklerinin FTIR-ATR analizleriyle ilişkilendirildi. Ek olarak, oksidasyon sonrası motor yağı örneklerinin dinamik viskozite değişimleri rapor edilmiştir. Bu tezde sunulan sonuçların, motor yağının bozulmasını doğrudan tespit etmek için bir TES'in temelini oluşturduğuna inanıyoruz.

Anahtar sözcükler: Kayganlaştırıcı yağ, Yanma, Tribokimyasal reaksiyonlar, Triboelektrik sensör.

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To My Daughter

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List of Abbreviations

API	American Petroleum Institute
ATIEL	Association Technique de l'Industrie Europeenne de
ATR	Lubricants Attenuated Total Reectance
EP	Extreme Pressure
IDT	Interdigital transducers/electrodes
IR	Infrared
OCP	Olefin copolymer
OEMs	Original Equipment Manufacturers
PET	Polyethylene terephthalate
PIB	Polyisobutylene
PMA	Polymethacrylates
PPDs	Pour Point Depressants
PSU	Polysulfone
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene fluoride
TAN	Total acid number
TES	Triboelectric Sensor
TSM	Thickness shear mode
VMs	Viscosity modifiers
Voc	Open Circuit Voltage
ZDDP	Zinc Dialkyl Dithio Phosphate

Chapter 1

Introduction

1.1 General Introduction & Motivation

Oil has been vital for human society for more than ten thousand years. People were taking oil into plenty of practical application [1]. Lubrication of the wheel, one of the famous invention of the earliest ancestors, is the best example for this. Ever since people keep excavating the materiality of lubricating oil. Different coatings have been developed to minimize the unwanted friction or wear on different aspects of life [1]. Lubrication oils have become part and parcel for many applications in modern society as well [2]. According to the working domains, lubricants are mainly falling into two categories: automotive lubricants, which comprises engine and gear oils, and industrial lubricants that has three major classes, working fluids, hydraulic oils, and turbine oils [2]. With the increasing popularity of motor vehicles since the early 1930s [3], engine lubricating oil becomes an indispensable part of the automobile industry. Since after, engine lubricating oil has been turned into an all-important element in any motor (engine) based machine such as the car, motorcycle, engine based generator etc. It has the lubricating function in internal combustion engines which can decrease energy wastes for the reason of friction between the machine parts, prevent parts

from damaging quickly by wearing. Thereby, engine lubricant oil has an important role in the efficiency of fuel using, perve the working life of the engine and relative components. However, the useful life of engine oil is limited. Engine oil will lose its usable viscosity level, contaminated with metal shavings and other particles after a certain period. This is mainly due to the oxidation/combustion by the high temperature which is generated by the friction of engine movement. If not carrying out proper estimation periodically, it would be given rise to both oil costs and oil disposal costs, at the same time it may arouse environmental concerns [3]. But most importantly, a vast amount of usable engine oil would be wasted. Moreover, the wasted oil is a high pollutant material that calls for very rigorous management [4]. Without proper treatment, the waste engine oil would be dumped into the soil or the water streams [4]. This would lead to serious groundwater and soil pollution [4]. One of the viable solutions for this issue is a proper prediction of the remaining service life of engine oil. Multiple approaches, such as kinematic viscometer and dielectric constant sensors based technique with a particle filtering algorithm [5], model-based approach [3], soot modeling approach [5], the hybrid approach using MEMS technologies [5] have been committed for monitoring oil condition and determining the remaining use-ful life of engine oil. However, a common disadvantage of these approaches is requiring highly sensitive devices. Moreover, the high complexity of parameter analysis, long time consumption, and challenges for portability of sensor devices are another shortcomings of these approaches. Most notably, all these methods need the external power source. It is necessary to develop simple and rapid methods for creating a prediction system for the remaining useful life of engine oil. In the meantime, it should be with high simplicity in the interpretation of the result.

In this thesis study, we will present a completely novel method which is upon the triboelectric effect, and this triboelectric sensor can be used for the detection of the oxidation level of engine oil. Thereby, it is a very helpful induction system for the estimation and prediction of remaining useful life of used engine oil.

1.2 Tribology: friction, lubrication and wear

The relative motion between two surfaces is very common in the operation of almost any device with mechanical components. Efficiency and performance of these device components are determined by their tribology. Tribology is defined as the science and technology of interacting surfaces in relative motion [6]. Tribology can be used in explaining everyday phenomena such as skating on ice, and it has been used since the invention of the first wooden wheel. Today, it is used immensely in industry and transportation. Dynamic power generation, automobile, machinery, hydraulics etc. almost all the today's industry is somehow bound up with tribology. Tribology is referring to friction, wear, and lubrication of surfaces [7]. Even though these three main elements of tribology are under the same roof, they all have their disparate mechanism. Friction and wear are two correlated subjects and can be investigated on their own in unlubricated or lubricated contacts. The overall subject of tribology is visualized in Figure 1.1, for which lubrication is an indispensable, supplemental area [16]. Tribology plays a major role in the sustainable growth of industry and society [16]. Without the proper control of friction and wear in systems, energy consumption is high and the life of the system shortens. Sustainability of one system can be achieved by decreasing the consumption of raw materials and lubricants, and lowering the amount of toxic or environmentally harmful surface materials generated upon continuous contact [16]. Therefore, reduction in friction and lengthened usability of lubricants on the system would yield significant economic and environmental savings. So far, plenty of studies were dedicated to achieve these, aiming to reduce energy loss and to uprate performance of the machine. Besides friction, wear of material from a surface can lead to severe damage and failure of the component and/or the machine [24]. So far the most common approach to minimize friction, protect component from wear and to save machine components (or the machine itself) from severe destruction is by proper selections of materials and lubricants.

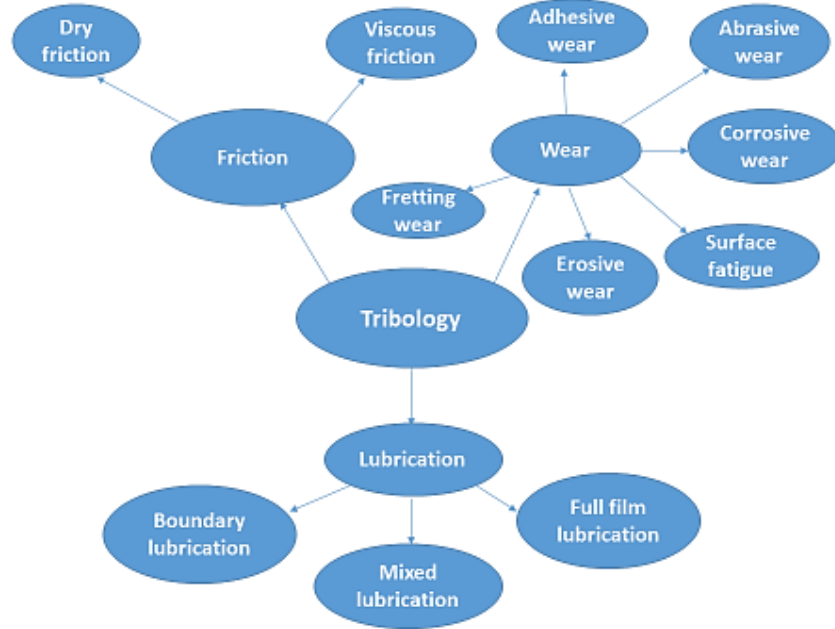


Figure 1.1: The different domains of tribology: friction, wear and lubrication [16]

1.3 Lubrication tribological system

It is well known that the primary purpose of lubrication is to decrease wear, friction and heat generation between contacting surfaces in relative movement. Lubrication is a crucial segment in machinery processing because it helps reducing oxidation and preventing metallic rust. Lubricants also serve for specific purpose as well, such as separating the parts that in relative motion, transferring heat or power, reducing friction, protecting against wear, preventing corrosion, carrying away contaminants and debris, sealing for gases, reducing noise and vibrations [16].

As shown in figure 1.2, the function of lubricants changes with the film parameter of the film the lubricant forms between the surfaces. The surfaces are said to be in contact in boundary lubrication regime, and the full-film lubrication starts at higher film parameter values. This full-film lubrication in the regime in which depletion of friction and wear are the most efficient. In some cases, the additive

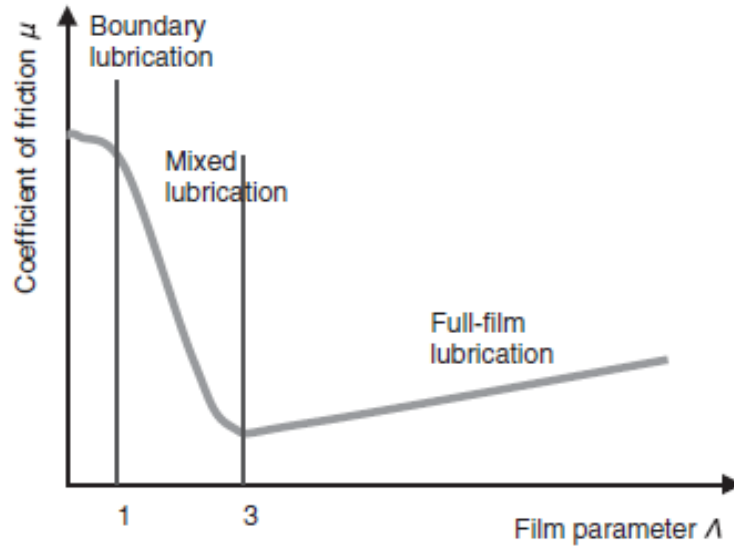


Figure 1.2: Coefficient of friction μ versus film parameter Λ in lubricated sliding contacts [16]

film could not be formed as good as expected due to the specific operating condition, this may cause adhesive wear. In the ideal full film lubrication regime, the surfaces are completely separated by the lubricant film, that is to say, no wear would happen. The main aim is to separate the surfaces at the lowest possible values of film parameter that provides this full-film behavior [16].

Lubricants can be divided into three classes on the basis of their physical state: liquid lubricants, semi-solid lubricants, solid and dry lubricants.

- **Semi-liquid lubricants:** In some operation conditions, liquid lubricants are not proper for utilizing, e.g. liquid lubricant cannot stay in contact. Therefore, semi-liquid lubricants play an important role instead of liquid lubricants. One of the widely used semi-liquid lubricants is grease, which is very popular in many fields. It is comprised of base oils with 5-30% thickener. The base oil components have the lubrication with good contact and protection against contamination [25].

- **Solid and dry lubricants:** This type of lubricants must be used when fluid/liquid lubricants are not able to keep in contact due to operating condition, e.g., contact pressure or high temperature becomes too high. Different

types of materials are used as solid lubricants in industry, such as Teflon (Polytetrafluoroethylene), molybdenum disulfide, graphite etc. [16]. In general, they are applied as a coating or as solid additives in powder form for reducing wear and friction on surfaces [16]. Next, we will state some liquid lubricants with their sorts, components and chemical structural properties in details.

1.3.1 Base oil

Base oil (or so-called base fluid) is the fundamental component of modern liquid lubricant. Base oil is generally used to lessen friction and wear by creating a fluid film layer and separate surfaces in relative motion [18]. The properties of base oil can be enhanced or new functions can be added to its functions by adding particular chemical additives in it. For instance, anti-oxidation and degradation properties are promoted by antioxidants additive whilst extreme pressure, EP; Antiwear property can be created by adding special additives in base fluids [18].

The general source of lubricant base fluids is refined crude oil. Approximately 35 Mt petroleum base oils were demanded in 1990 according to total worldwide estimation value [26]. The chemical form of crude oil is complicated. It is a mixture of organic chemicals ranging from simple gases such as methane to very high molecular weight asphaltic components [18]. The base oil is obtained through a series of refining processes of crude petroleum oil. In the following section, we will present the composition, categorization of base oil, and refining process of crude oil to obtain base oil.

1.3.1.1 Base oil composition

Although the components of crude oil are categorized into several base classes, primarily they are divided as hydrocarbons and non-hydrocarbons. Basically, hydrocarbons are comprised of carbon atoms and hydrogen atoms as shown in Figure 1.3, and they are classified as saturated and unsaturated hydrocarbon [17]. According to the structures of hydrocarbon present in base oils, it is subdivided

into several designations: paraffin, olefins, naphthenes, and aromatics. Paraffins have two main structure types: saturated linear or branched-chain structures [3]. Olefins have unsaturated molecules. The fraction of the latter is relatively low in crude oils. However, by cracking or dehydrogenation with certain refining processes produce large amounts of alkenes, naphthenes (saturated cyclic structures based on five- and six-membered rings), and aromatics (mainly derivatives of the six-membered benzene ring). Chemical structures of these classes of compounds are shown in figure 1.4 [18].

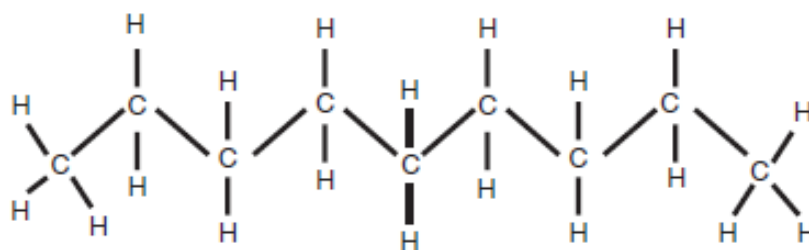


Figure 1.3: The bonds of the carbon and hydrogen atoms [17]

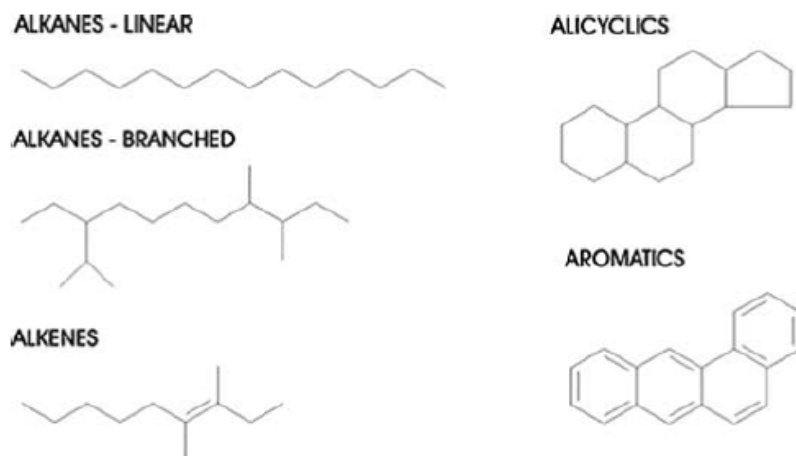


Figure 1.4: Examples of straight- and branched-chain aliphatic, alkenes, alicyclic and aromatic hydrocarbon structures [18]

1.3.1.2 Base oil categorization

Classification of base oils depends on their specific uses. Base oils are used in manufacturing of lubricants that are used mainly in the automotive industry. Lubricants for automotive go through very rigid control processes to ensure the quality and performance of lubrication function. All examination processes are done by ‘Original Equipment Manufacturers’ (OEMs), which have very strict requirements for automotive lubricants. OEMs authorization is crucial for offering of a global base fluid. Base oils used in automotive industry are divided into groups that are denoted by roman numbers; I, II, III, IV, and V. This classification and the characteristics of the different groups are defined by American Petroleum Institute (API) and Association Technique de l’Industrie Europeenne des Lubrifiants (ATIEL) [27].

Group	Description
I	Saturated hydrocarbons $< 90\%$, sulfur $> 0.03\%$, $80 \leq VI \leq 120$
II	Saturated hydrocarbons $\geq 90\%$, sulfur $\leq 0.03\%$, $80 \leq VI < 120$
III	Saturated hydrocarbons $\geq 90\%$, sulfur $\leq 0.03\%$, $VI \geq 120$
IV	PAOs (Polyalphaolefins)
V	All others, but groups I, II, III and IV: e.g.naphthenics, synthetic and natural esters

Table 1.1: Description of base oil categorization according to API and ATIEL [27]

1.3.1.2.1 The refining process of crude oils The usable base oil lubrication products are produced by a refining of crude oil. The schematic plan of the refining process is presented in figure 1.5. The different components in crude oil are separated in the process. Basically unwanted parts are removed

and the desirable substances are kept. Sulfur, a natural antioxidant, belongs to desirables. Process starts with distillation under atmospheric pressure. The crude oil flow is heated and when it crosses the distillation tower which has the temperature difference between the top and down. The low molecular weight molecules in crude oil that have high evaporability move towards the top of the distillation column upon heating and high-molecular weight molecules stay at the bottom parts of it. This process results in different components in crude oil to be separated (see Figure 1.5) [19, 28, 29].

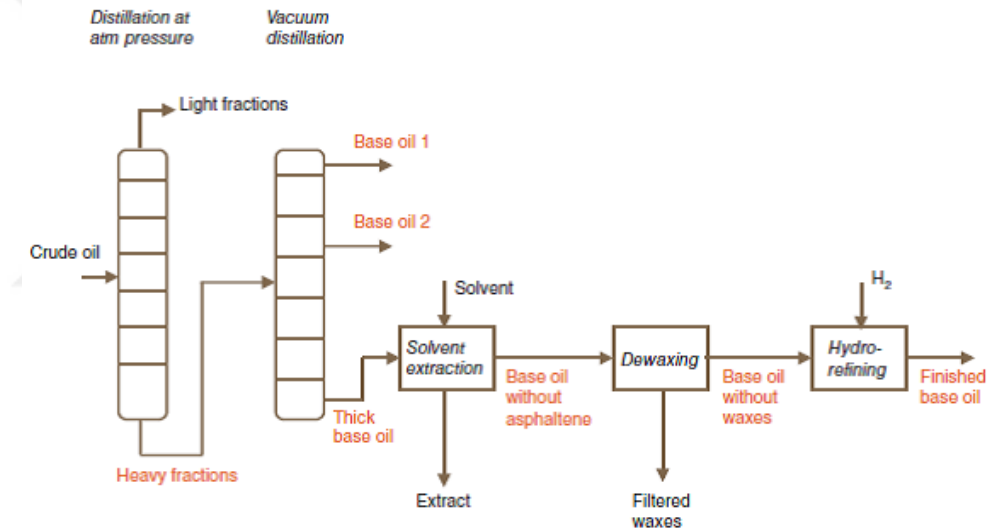


Figure 1.5: A simplified schematic map of the crude oil refining process [19]

1.3.2 Engine Oil Lubricants

Base oil has already had the lubrication function, e.g. decreasing friction and wear, because of it can form a film on metal surfaces. However, for engine lubrication, base oils are not sufficient alone. The base oil is therefore ‘augmented’ by addition of various additives. In addition to the base oil’s existing properties such as viscosity, viscosity index, pour point, and oxidation resistance, new properties such as cleaning and suspending ability, antiwear performance, and corrosion control are supplied by the additives [30]. There are many kinds of additives used

during a typical formulation of an engine oil, which can handle different undesired conditions. Classification of additives based on both of their chemical and physical properties in engine oil are shown in Figure 1.6. In the following section, we will discuss Interfacial Surface Active Additives, Bulk Additives and mostly used engine oil additive - Zinc Dialkyl Dithio Phosphate (ZDDP).

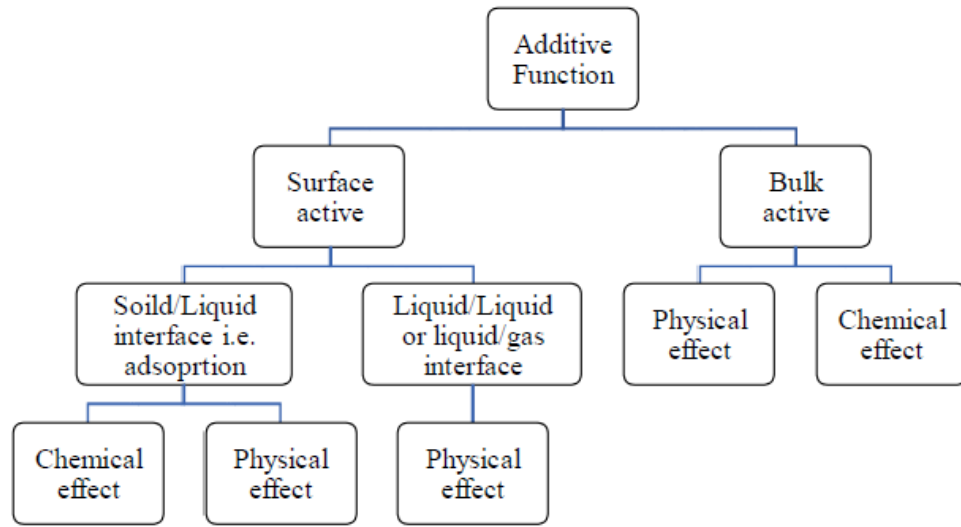


Figure 1.6: Categories of engine oil additives depends on their related functions [16]

1.3.2.1 Interfacial surface active additives

Surface active additives may act on liquid-liquid (emulsifiers, and demulsifiers) or liquid-gas (defoamers) interfaces [29]. Defoamers are surface active additives, which have low solubility in lubricants. As their name implies, they are used for preventing foam formation, foam growth, or cavitation. Defoamers are compatible with almost all kind of lubricants [29]. The chemical structure of defoamers warrants the contact between liquid and air. Mostly, silicone oils or polymethacrylates are the main elements of defoamers, which are added in small percentages to the base oil [16]. In metal-working applications, water is used to keep the overall temperature down. Here, emulsifiers help separate any water that leaks into the lubricant.

Water would contribute to buffering hydrolysis or increased oxidation rate of the lubricant. Emulsifiers can be used in many metal-working products such as rolling fluids [16]. Emulsifiers decrease the surface tension of water and the droplets of water in oil are divided into smaller droplets thereby forming an emulsion. In the chemical structure of emulsifiers there are hydrophilic groups having nitrogen, oxygen, phosphorus or sulfur [16]. Contrary to emulsifiers, demulsifiers facilitate water separation by increasing water's surface tension. Demulsifiers are formed with polymers that molecular weight is up to 100 000 g/mole and they contain 5–50% polyethylene oxide [16].

1.3.2.2 Bulk additives

In the previous part, we have mentioned some additives that act on oil's surface. In this section, we will discuss some additives, which physically and chemically improve oil properties.

Viscosity modifiers (VMs): VMs are one of the bulk additives which changes the viscosity of base oils, which can reduce the fuel consumption. VMs act by steric action and they have a very low reactivity with base oils and other additives. VMs increase the lubricant viscosity at all temperatures. VM should be selected properly by considering several factors such as operating temperature, suitable viscosity grade, the application field of oil, etc. Basically, viscosity modifiers are comprised olefin copolymers (OCP), polyisobutylene (PIB) i.e. olefin polymers or polymethacrylates (PMA) i.e. ester polymers [31].

Pour Point Depressants (PPDs) – In current industry, PPDs are commonly used to decrease pour points in base oils. With proper selection PPDs according to base oil types, pour point may be decreased below to 40 °C. The concentration of base oil is a critical factor affects PPDs function. At low temperatures, the viscosity of lubricant increases, lubricant liquid can even crystallize below a certain temperature. By adding PPDs to the lubricant, this rapid increase in viscosity can be avoided. PPDs can interfere with the crystallization by restraining crystal growth or by increasing the solubleness of the base oil crystals [31].

Antioxidants- Oxidation is a substantial issue in engine oil usage. The antioxidant additives are used to lower the oxidation rate of lubricants, thereby operation life of lubricant oil can be extended. The complex oxidation process (Figure 1.7) of the oil can be summarize into three steps: initiation, propagation, and termination [32].

Besides slowing down the oxidation rate, the use of antioxidants reduces the undesired formation of oxidation debris. Antioxidants also decrease the corrosion rate of soft metal components, which increases by the formation of acids—a common type of oxidation product. Generally used antioxidants are metal deactivators, radical scavengers, and hydroperoxide decomposers [32].

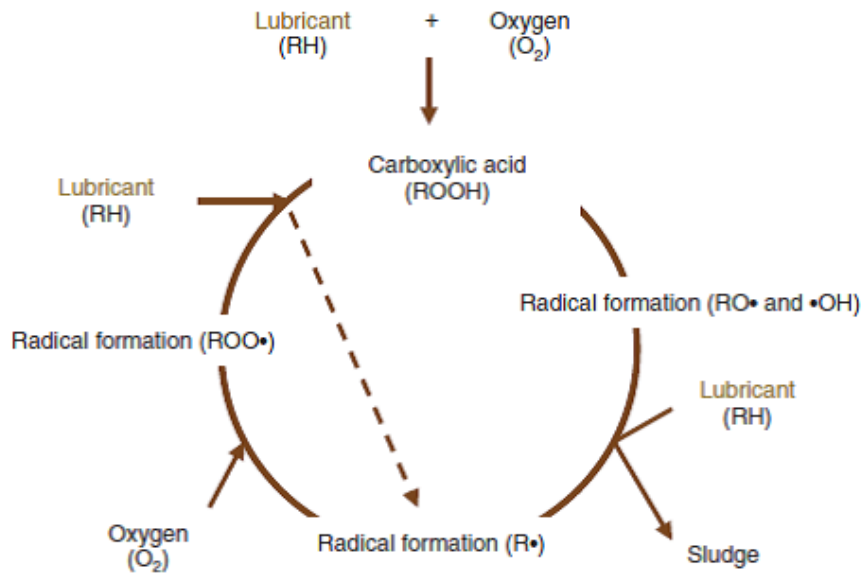


Figure 1.7: The complex chain reaction process of oxidation in a lubricant [16]

1.3.2.3 Zinc dialkyl dithio phosphate (ZDDP)

ZDDP is an antioxidant additive, but in engine oil industry, it is mainly used for its antiwear property. ZDDP is initially produced by the reaction of phosphorus pentasulfide (P₄S₁₀) with one or more alcohols, which provides dialkyldithio-phosphoric acid. Then, zinc oxide is added for removal of the acidic part and the final product is generated as shown in Figure 1.8 [21].

Both acidic (monomeric) and neutral (dimeric) ZDDP can be present in a solution of ZDDP [33], however, basic ZDDP, unlike the acidic and neutral ZDDP, promote the combination of excess zinc oxide into a structure [34]. There is also a polymeric form of ZDDP in solid state [35]. The chemical structure of these four basic forms of ZDDP shown in Figure 1.9.

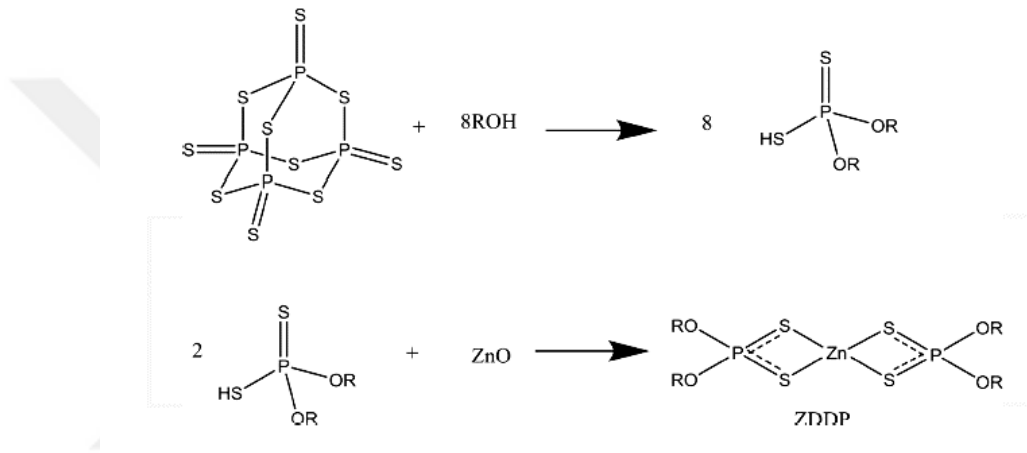


Figure 1.8: Reaction processes of the ZDDP preparation [21]

The antiwear function of ZDDPs is achieved upon creation of a film between the metal surfaces as follows: As temperature increases, ZDDP begins to degrade as a result of decomposition into ZnO and sulfur-containing groups. These sulfur-containing groups are attached onto the iron surface with chemical bondings (the typical surface in common machine parts) as shown in Figure 1.10 [23]. On the iron surface, zinc sulfide and iron sulfide are generated and they form a thin film layer. This ‘tribofilm’ functions as protecting metal parts from the direct friction and prevent scuffing. The detailed process of film formation is shown in Figure 1.11 [8].

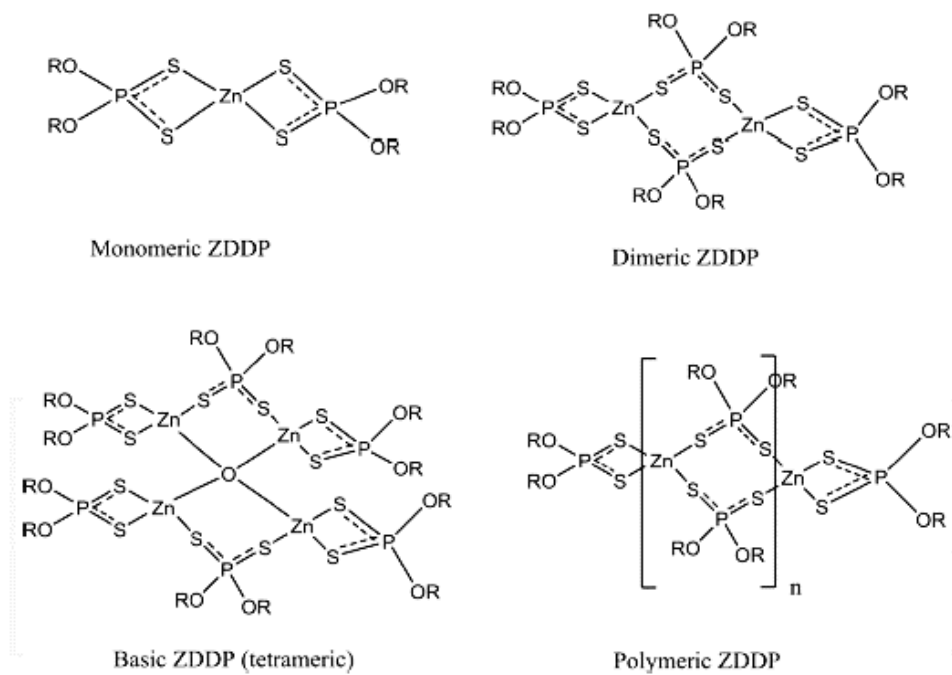


Figure 1.9: Structures of some of the observed forms of ZDDP [22]

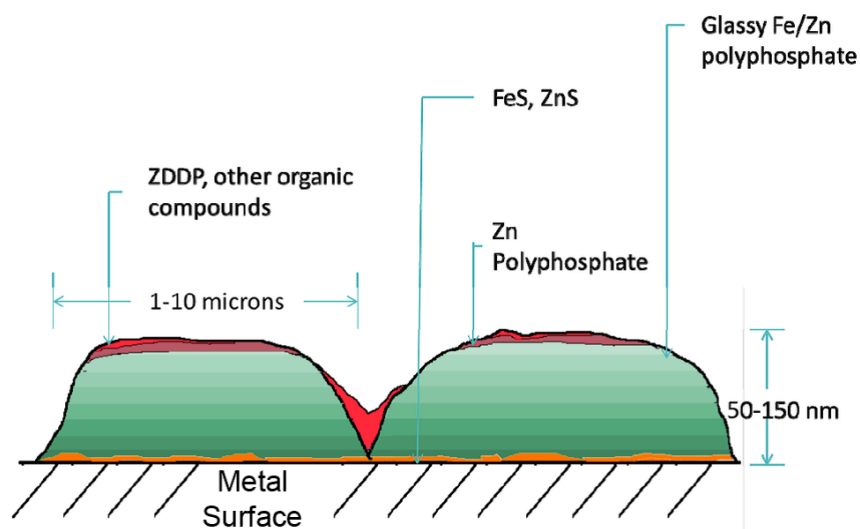


Figure 1.10: The structure of tribofilm formation with ZDDP [23]

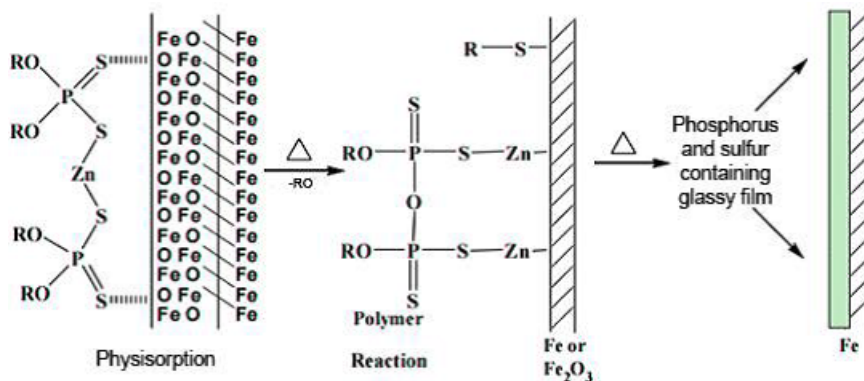


Figure 1.11: The scheme of tribofilm formation on metal surface [8]

1.4 Triboelectric Effect

Triboelectric effect is defined as surface charging of surfaces of materials, when a dielectric material comes into contact with another material [36]. The triboelectric effect has been known for thousands of years. Although triboelectrification is one of the most common phenomena that we inevitably experience every day, the mechanism behind triboelectrification is still being searched, with a debate [36]. It is commonly accepted by scholars that after two materials get to approach and contact, adhesion takes place between parts of two surfaces. Upon separation, chemical bonds on the surfaces break, leading to cations, anions (charged species) and radicals. The unequal distribution of cations and anions at nanodomains and their summations give rise to a net charge accumulation on dielectric surfaces [36].

1.5 Thesis Outline

The remainder of this thesis is organized as follows: Chapter 2 focuses on reviewing the current academic literature regarding different methods of oil degradation monitoring and prediction of remaining useful life of engine oil, such as viscosity sensors, infrared sensor system, electrical technique- dielectric measurement, electrochemical sensor array. Chapter 3 describes the experimental materials, techniques and instruments etc. will be covered in detail Chapter 4. Summarizes

the project results and highlights the major contributions of this dissertation. Chapter 5 Dissertation is completed by concluding remarks and future research suggestions.



Chapter 2

Techniques for investigation and prediction of remaining life of lubrication oil: A review

In this chapter, a comprehensive review of related literature on various methods for monitoring oil degradation and prediction of remaining useful life are presented. These methods include viscosity sensor, the infrared sensor, electrical techniques, dielectric measurement, and electrochemical sensor array.

2.1 Infrared sensor system

Over the past decades, the condition of the engine oil used in automotive applications is basically determined by some parameters such as engine speed, temperature, and performance level. However, these parameters generated by some indirect methods are not able to provide a reliable assessment of the remaining life of the engine oil. For more specific analysis, oil samples are taken for off-line laboratory analysis at a fixed period and this would require high costs and time consumption. Recently, Infrared (IR) Spectroscopy analysis has become a

formidable, feasible analytical technique for engine oil analysis. The degradation of different lubricant oil additives can be directly observed in the IR spectrum, meanwhile, many unwanted contaminants in the oil, such as soot, glycol, water, and unburned fuel can be detected. The oxidation index is one of the most important parameter in IR analysis for oil samples [37]. Figure 2.1 shows the spectrum of the used oil (SAE 10W40 engine oil oxidized artificially with a standard CEC (L-48-A-95) method at 160 °C for 8 days) was normalized at the reference wavenumber at 1970 cm^{-1} to the fresh oil spectra [37]. It is exhibiting the noticeable high absorption value in the oxidation band around the wavenumber 1710 cm^{-1} [37]. However, for online monitoring of the oil condition, the laboratory spectrometer is expensive and bulky for transporting. Therefore, a simple IR detector sensor was put forward by A. Agoston et al. [9]. In the setup, they selected a single reference point at 1970 cm^{-1} , therefore the mean line of the optical filters is adjusted only to the wavenumber 1710 cm^{-1} and 1970 cm^{-1} [37].

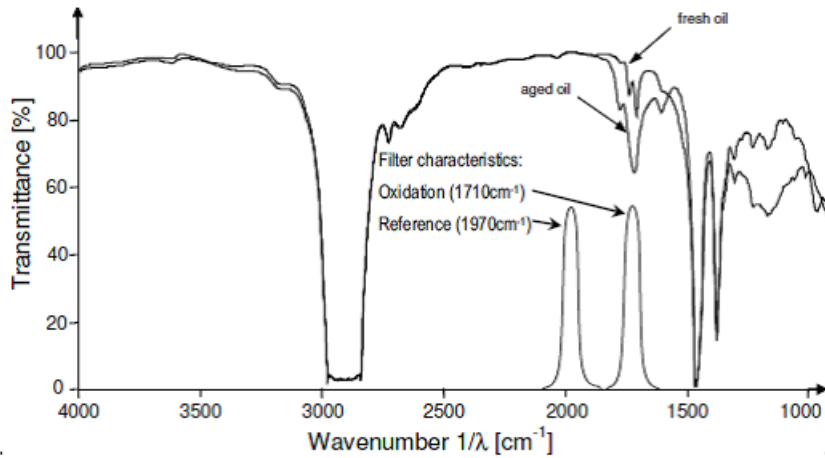
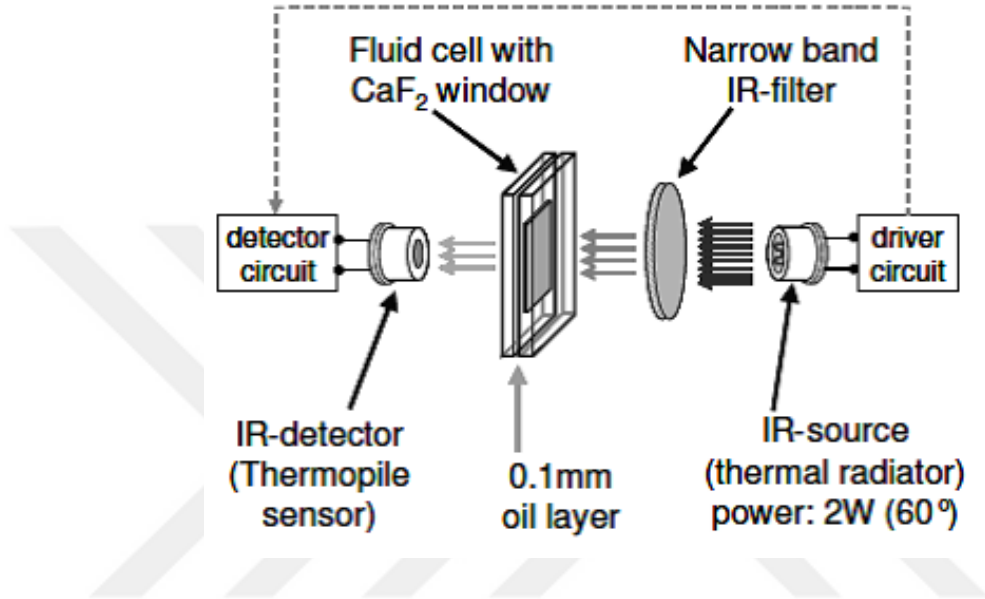


Figure 2.1: FT-IR spectrum of fresh and artificially aged (8 days) SAE 10W40 engine oils [9]

The working principle and structural components of this sensor is shown in Figure 2.2, which include a thermal IR-emitter (Ion-Optics NL8NCC), IR filter (interference filter) for selecting the spectral line of the desired band, fluid cell and a thermopile sensor to detect the intensity of the IR light transmitted through the filter and the oil film [9]. Custom-made electronics (not-shown) modulate the IR source and demodulate the preamplified sensor signal in a synchronized manner in order to eliminate the drift caused, e.g., by changes in the room temperature.

The demodulated signal is amplified again yielding the electric output signal of the setup [9].



In this sensor, the experimental results were compared to the results of the FT-IR analysis of the oil samples that were taken in at regular intervals (250 hours). The samples were also analyzed using the developed sensor, then the oxidation value is calculated in reference to the fresh oil. The correlation of measured oxidation values and oxidation index obtained from the FT-IR spectrum is shown in Figure 2.3. The results indicated that the sensor values were coincident to the laboratory result.

The developed sensor measures and validates an average within a narrow spectral band specified by the filter instead of a single point [9]. Figure 2.4 shows the oxidation values obtained by using the sensor with respect to the increasing operating hours of the stationary engine. As expected, the trend of the oxidation value gives more precise information regarding the current condition and remaining lifetime of the engine oil. Overall, this sensor setup has overcome the unpractical aspect of using an IR spectrometer for online monitoring of oil condition. As mentioned by A. Agoston et al. [9], the developed sensor prototype can be further miniaturized for online monitoring of engine oil and measure other spectroscopic parameters, which are useful on engine oil monitoring.

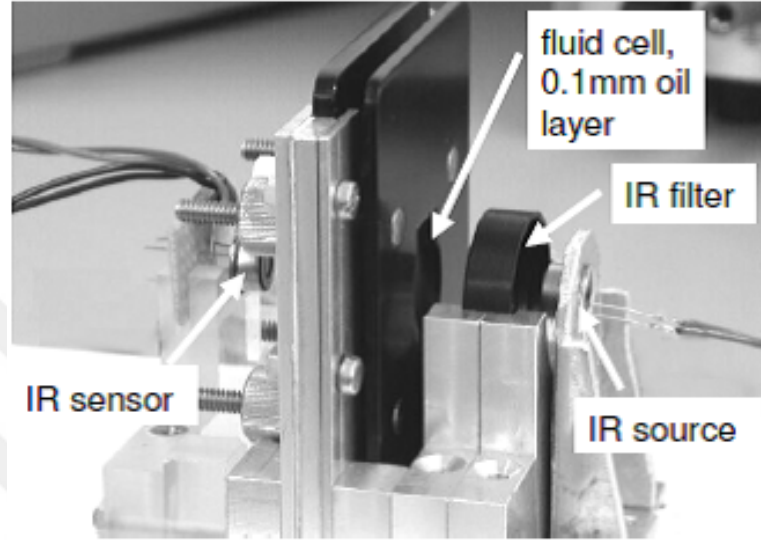


Figure 2.2: Working principle (up) and structural components (down) of IR-sensor prototype setup [9]

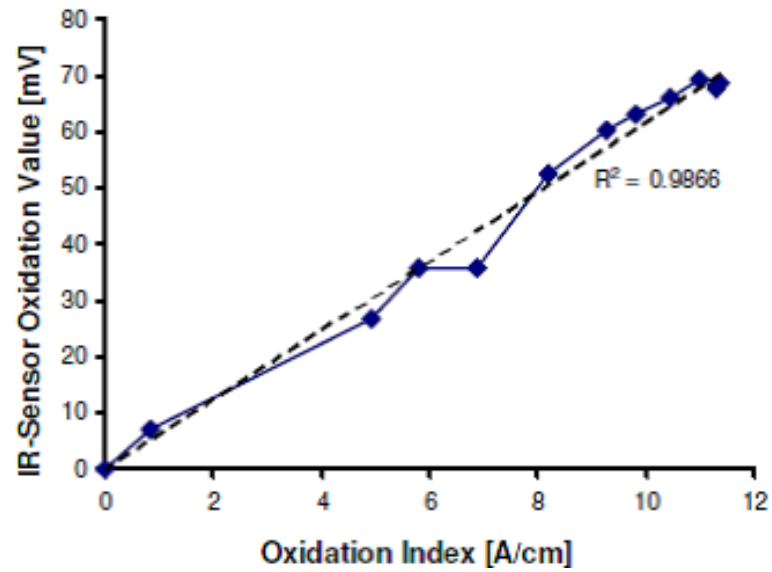


Figure 2.3: Comparison of the oxidation values from the developed sensor setup signals and the oxidation index acquired from the FT-IR-Spectrum [9]

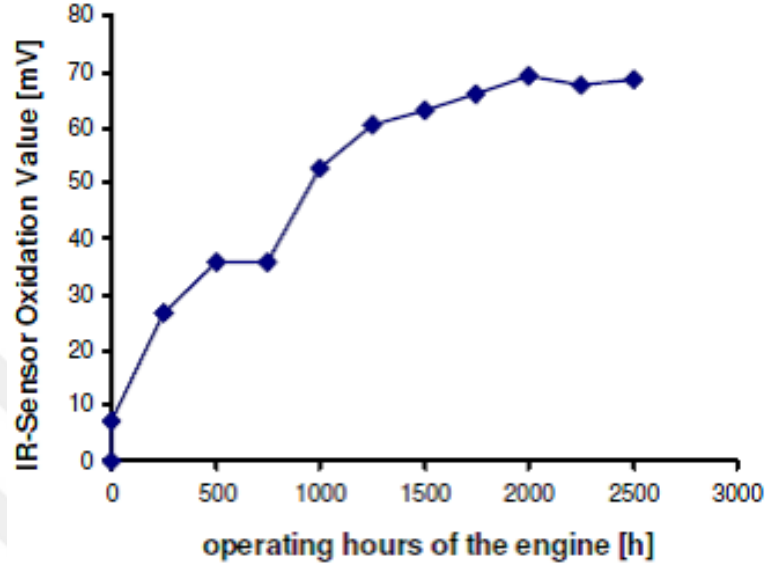


Figure 2.4: Trend of the oxidation measured with the IR sensor prototype [9]

2.2 Viscosity sensor for engine oil condition

Viscosity index is one of the most important index parameters for determination of lubrication effect of engine oils, above all in online monitoring systems as suggested by earlier studies [38]. However, the conventional viscometers do not allow for the on-line monitoring system in terms of reliability and analysis costs. The study by A. Agoston et al. [10] mentioned a new type viscosity sensor called thickness shear mode (TSM) for the detection of engine oil degradation. The functionality of this new type sensor was compared to conventional viscometers in terms of their usability. The described device fundamentally consists of a thin piezoelectric quartz disk, which is electrically energized by the thin conducting electrodes deposited on both sides of the disk [10]. With an ac-voltage, the device displays mechanical resonances at certain frequencies. The thin liquid film is formed at the surface, when the device in contact with a viscous liquid. Meanwhile, the loading issue results in a relative difference in the electrical parameters of the resonator in terms of the viscosity (and density) of the oil. In the study [10], the loss resistance (R) is detected by the sensor. In experiments, a series of artificially deteriorated SAE 15W 40 grade engine oils were used (Table

2.1) [10] and both of the conventional Ubbelohde method and the microacoustic TSM sensor were employed to measure viscosity.

Name	Type of SAE 15W 40 engine oil
A009	Diesel, with additive package 1
A010	Diesel, with additive package 2
A011	LPG, with additive package 3
A012	LPG, with additive package 4

Table 2.1: Four different types of engine oils of the grade SAE 15W 40, which were selected for artificial deterioration [10]

Upon oxidation of the base oil, an increase in oil viscosity is expected. Initially, (Figure 2.5) for the oil samples A010 and A012, a linear increase in viscosity value was displayed for both methods. However, unexpected decrease in viscosity occurred on sample A010 between day 6 and 7 on the conventional Ubbelohde method. Moreover, with the oil samples A009 a continuous decrease in the conventionally measured kinematic viscosity was observed, in contrary to a steady increase in the microacoustic viscosity. These observations proved that conventional viscosity measurement methods are not reliable for indicating the oxidative degree of the oil's deterioration. On the other hand, the viscosity index from the new sensor shows a linear increase in viscosity for all sample series (Figure 2.5). (It is stated in the reference that the decrease in viscosity for samples A009 and A010 is ascribed to the degradation of the viscosity modifier polymers.) The sensor basically measures the viscosity of the base oil, therefore the output signal is not affected by the degradation of the viscosity modifier [37]. For further confirmation, the correlations of the sensor signal with the oxidation value and the total acid number (TAN) were plotted. A steadily increasing signal for both increasing oxidation level and TAN degree for all types of engine oil were observed in these plots.

Above mentioned sensor gives direct information about the age of oil in terms of oxidation. It is much superior to the conventional measurements of "macroscopic" viscosity in providing an approximate estimation on remaining useful life of the engine oil before replacement.

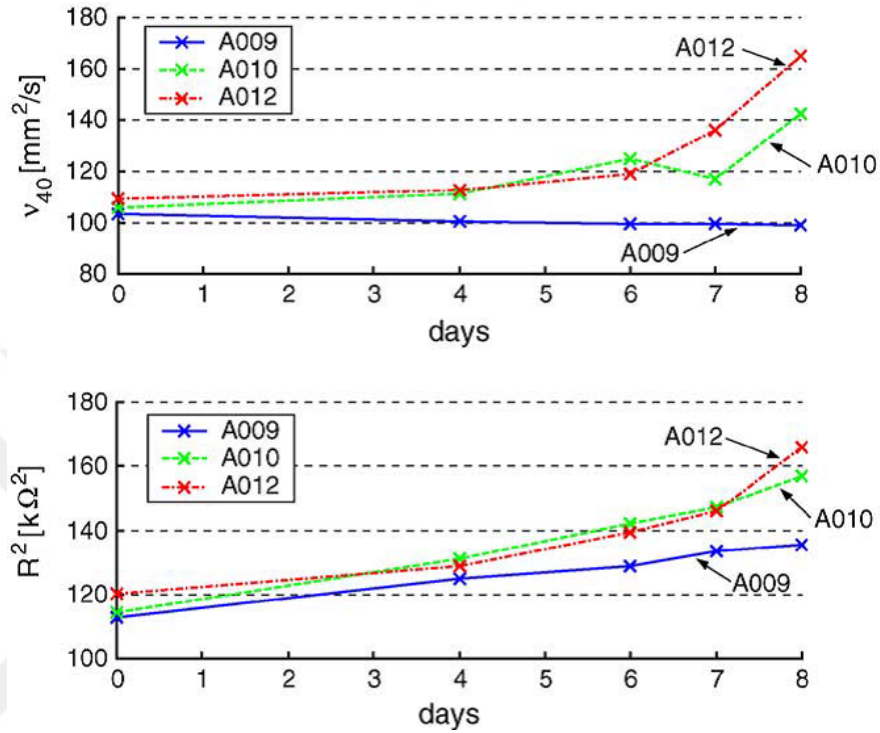


Figure 2.5: Comparison of the changes of viscosity indication of different engine oil series (SAE 15W 40) measured by Ubbelohde (upper plot) and the sensor-viscosity (lower plot) [10]

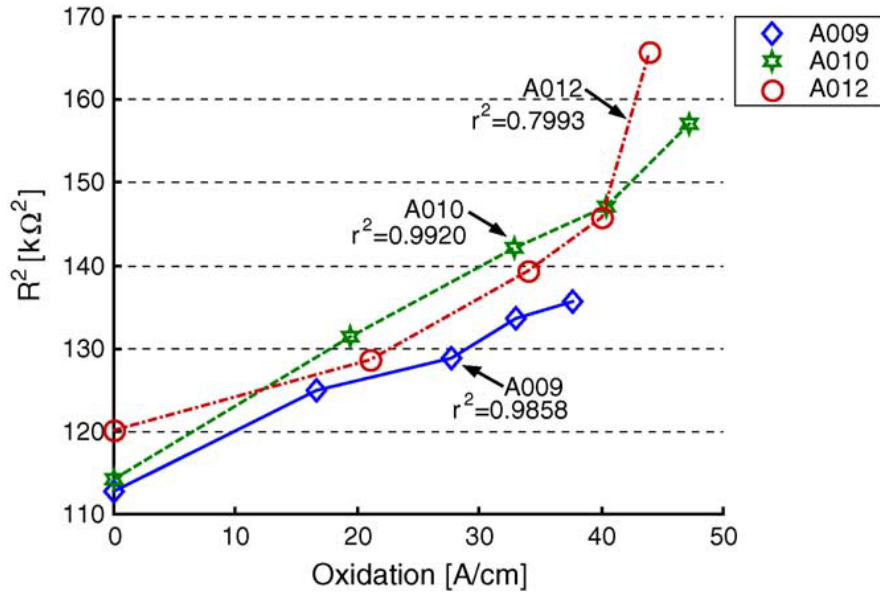


Figure 2.6: Correlation of the sensor signal with the oxidation value (measured with FT-IR spectroscopy) [10]

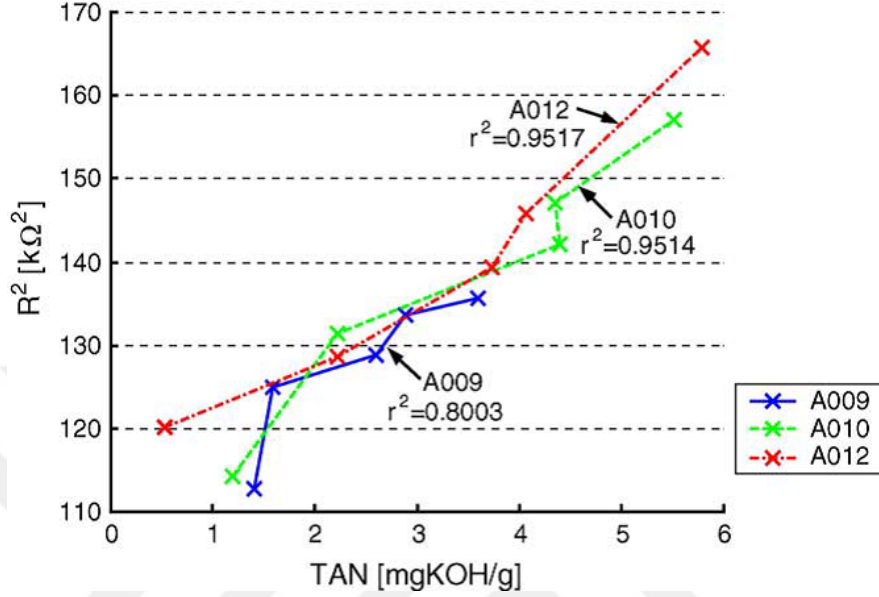


Figure 2.7: Correlation of the sensor signal with the increasing value of TAN for artificially aged engine oils) [10]

2.3 Electrical technique-dielectric measurement- for monitoring engine oil condition

Owing to increased polarity of the oxidized oil, it has been referred that there is a correlation between dielectric constant and oxidation of the oil. The dielectric constant measures the ability of the materials to store electrical energy [39]. However, the lubricating engine oil molecules have long and flexible chains giving rise to a net dipole moment that is hard to estimate at a given time. Nevertheless, for further investigation about the link between the electrical properties (dielectric constant and magnetic susceptibility) of engine oil and its usage, Turner and Austin developed a sensor [11]. In their experiments, a miniaturized electric capacitor which is made of 10 brass discs (50 mm diameter, 1 mm thick with 1 mm separation attached on a nylon core) was constructed as shown in Figure 2.8. The oils samples extracted from different engine types were taken from a local garage. 90 samples were prepared for investigation. The oil samples were poured in a wide-necked jar and the handmade capacitor is slowly drowned. After making sure no air bubbles were left inside of the device, the capacitance was recorded,

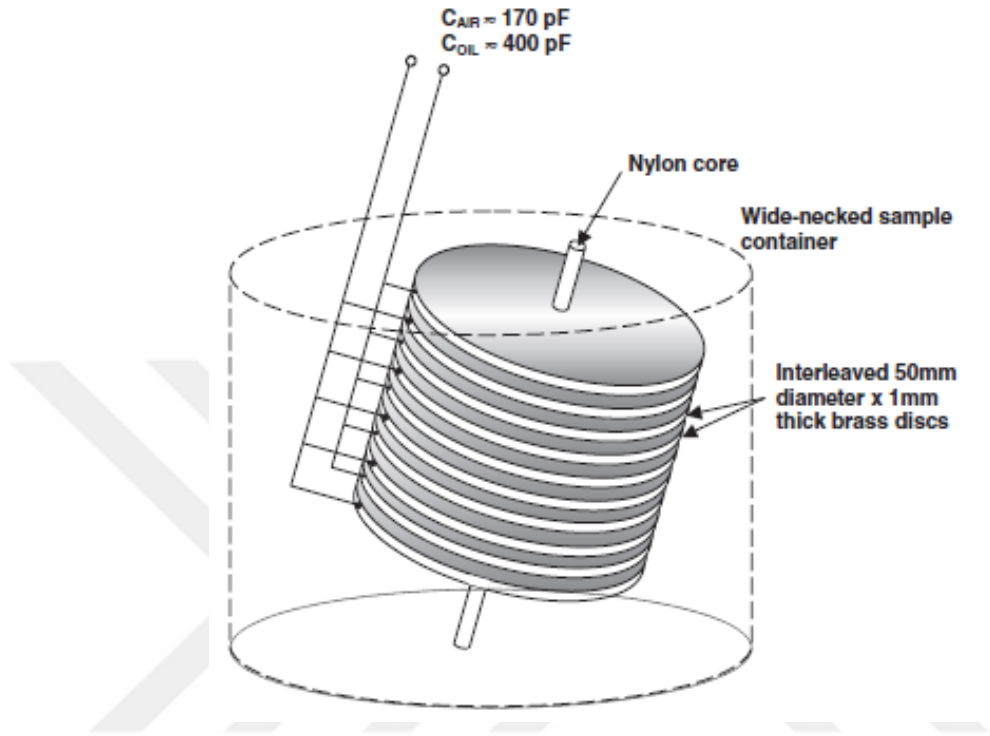


Figure 2.8: The developed capacitor for measuring the dielectric constant [11]

and the dielectric constant was calculated.

The experiment was conducted at room temperature. The results, which are shown in Figure 2.9 indicate the increase in dielectric constant D , with increasing viscosity degree. D is obtained from the relationship:

$$D = C_{oil}/C_{air}$$

The average correlation coefficient was calculated as 0.70. This outcome premises that the device has potential development prospects for a larger scale online monitoring system.

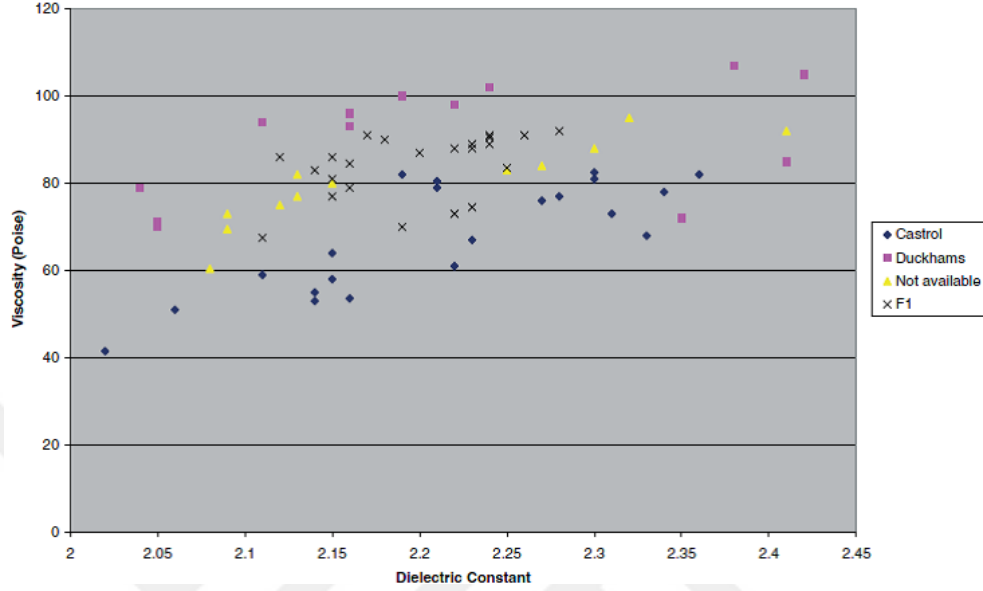


Figure 2.9: Lubricating oil viscosity versus dielectric constant [11]

2.4 The electrochemical sensor array for online lubricant oil condition monitoring

The electrochemical sensors that monitor the changes in lubricant's conductivity and permittivity can be used for probing oil condition. However, conductivity and permittivity are susceptible to the changes in soot content, oxidation, fuel dilution, water/moisture content, metal wear debris, and generated ions, etc. Changes in these factors make the output signal from such a sensor monitoring conductivity or permittivity to fluctuate and the sensitivity or the sensor decreases [40]. In order to address this problem, Zhu et al. [12] developed a new microsensor array that makes use of an artificial neural network. One prominent feature of this microsensor is that the four variables - water content, total acidic number (TAN), soot content, and sulfur content- are measured separately. The microsensor indeed consists of four different sensors and each sensor has unique sensitivity and selectivity according to these variables mentioned. As shown in Figure 2.10, Sensor 1 is responsible for sensing water content in oil. It has interdigital transducers/electrodes (IDT) (Figure 2.10(b)) and a polyimide coating (see Figure 2.10(a)). Polyimide has strong selectivity on absorption, which does

not absorb lubricant oil but effective in absorbing humidity [41]. Sensor 2 is composed of IDTs with a Teflon AF layer as the sensing material (see Figure 2.10(a)). Teflon AF has relatively high hydrophobic and oilphobic property [42]. The sensor 2 responds to all lubricant properties (water, acid, soot, and sulfur) while each response is different from that of sensor 1. Sensor 3 is in charge of measuring soot content in lubricant. It consists of gold IDTs without any coating layer on electrodes, the amorphous carbon particles that are bases of soot in lubricant oil, are apt to adhere to the gold electrodes easily [43]. This will cause the capacitance change of the sensor. Finally, Sensor 4 response for the acidity (acidic number) of lubricant oil. It is made of a single copper electrode without a coating layer. Due to the reaction between acidic components in the lubricant and copper electrode, the resistance changes. This change of the IDT electrodes primarily responds to acid and sulfate.

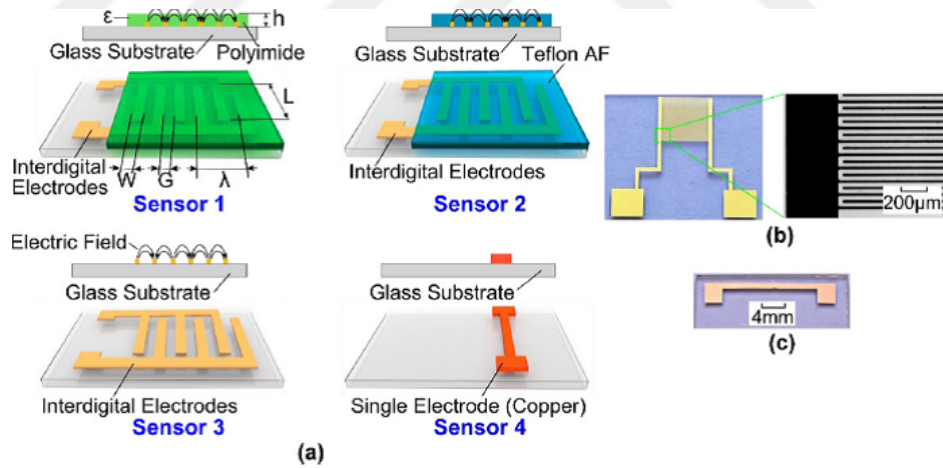


Figure 2.10: (a) Schematics of the microsensor array, (b) a microscope picture of the fabricated gold interdigital electrodes for sensor 1–3, and (c) a single copper electrode for sensor 4 [12]

Total 36 samples were used in the experiment. For each test, a volume of 3 mL sample was used, and the voltage output from each sensor were recorded. Figure 2.11 shows the results from each microsensor array response to six selected samples different time slot. The responses from sensors 1, 2, and 3 show that the soot content in samples is the primary factor that causes differences in sensitivity. Meanwhile, sensor 1 responds to water and acidic content (H_2SO_4). Additionally, sensor 4 response mainly is caused by the changes in concentration of H^+ , in

the meantime water and soot content can also affect the results. It is noteworthy that, in sensor 4, the chemical reaction between the electrode and acidic content causes abrasion of the copper, which results in increased resistance of the sensor. This would increase the output voltage of the microsensor [12].

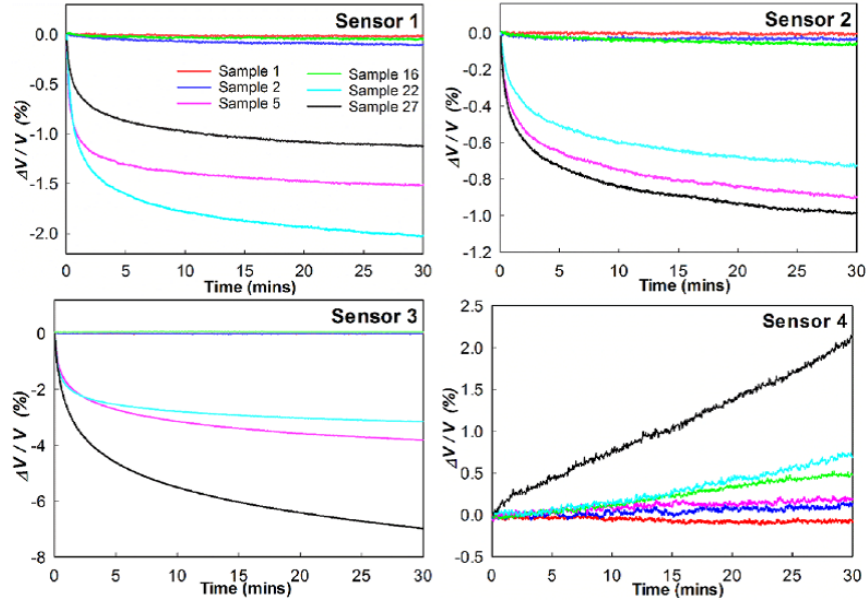


Figure 2.11: Output from six selected samples in four sensors. Sample 1, pure engine oil; sample 2 contains only 500 ppm water; sample 5 contains only 2wt% soot; sample 16 contains 1000 ppm water and 1000 ppm sulfuric acid; sample 22 contains 500 ppm water, 1wt% soot, and 2000 ppm sulfuric acid; sample 27 contains 500 ppm water, 3wt% soot, and 3000 ppm sulfuric acid [12]

As suggested by the authors [12], based on the current electrochemical microsensor array, auxiliary parts which can measure some other properties of lubricant oil, such as fuel or air content. Since it has such a high precision and relatively low cost, with miniaturization of the developed sensor, it can be implemented in online monitoring of lubricant oil condition.

In this section, several sensors which were developed for online diagnosing the oil condition and its remaining lifetime were introduced. Also, their potential development and tendencies regarding the shortcomings and challenges were presented. In the following section, the experimental materials, techniques, and instruments which were used in our project will be present.

Chapter 3

Materials & Mehods

The presented work describes a method that utilizes the changes in triboelectric behavior of used oil to make an online sensor that can monitor the deterioration of the used oil. Initially, in order to prove our hypothesis, we prepared oil samples which are oxidized by chemical means for different periods of time. We firstly used a SN 150 base oil in our experiments. In a typical experiment, 50 mL of the base oil was oxidized at 200 °C in the heating mantles for 32 hours in total. For each sample, triboelectric behavior of the samples were probed with a homemade tapping device. We investigated the triboelectric behavior of the base oil and Castrol Power 1 4T 10w-40 motorcycle oil with different polymer types (10 different polymers were used) at the untreated state and oxidized state. In parallel to these electric potential measurements, the changes in the chemical structure of the base oil was monitored by Attenuated Total Reflectance (ATR) IR spectroscopy; specifically the changes in the carbonyl absorption peak were reported, since the increase in this peak shows the production of the oxidized species (ketones, aldehydes and acids). Secondly, we used a Castrol Power 14T 10w-40 motorcycle oil in our experiments, to show the applicability of our system to a commercial product. The oil samples (50 mL) were oxidized at 150 °C, 175 °C, and 200 °C for 62 hours, 10 hours, and 80 hours respectively. Same procedures were conducted for Castrol Power 1 4T 10W-40 motorcycle oil as the base oil used in the first part. For the commercial product we have additionally

monitored the ZDDP peak in addition the carbonyl (oxidation) absorption. In the third part of our project, we used another common commercial product Shell Helix HX7 10W-40 synthetic engine oil, which was oxidized at 150 °C in the reactor for 30 hours in total. In all three parts, we have also probed the changes in the viscosity of oxidized oils, which is a vital factor for oil performance as we have mentioned above. Dynamic viscosity of samples from each type of oil was measured by Physica MCR 301 Rheometer.

3.1 Oils used

There are three different lubricant oils were used in our experiment, SN 150 base oil, Castrol Power 1 4T 10W-40 motorcycle oil and Shell Helix HX7 10W-40 Synthetic motor oil. The information and experimental procedure applied for each lubricant oil is given in detail.

3.1.1 SN 150 base oil

The lubricant oils are divided into several groups by API as mentioned in the previous chapter. The name of the base oil is given according to the group they belong and to their physical properties. The Group I base oil are called as SN, (S stands for solvent because of the solvent extraction step and N means neutral because of neutralization after acid washing step) [44]. We used the group I base oil SN 150 in our experiment. Detailed physical and chemical properties are given in table 3.1 [44]. The product was offered by Özçınarlar A.Ş. Oil Manufacturing Company in Kutahya/Turkey.

Oil property	SN 150 specification
Kinematic viscosity, mm^2/sec (cSt) at: 100 °F 100 °C	27 – 31, 4.5 – 5.5
Viscosity index	90
Acid index, mg KOH/1g oil	Not normalized
Ash %	0.005
Water content, ppm	100
Flash point, °C	195
Pour point, °C 1.09 – 1.04 1.04 – 1.09	Minus 15 Minus 10
Sulfur content %	0.3
Polycyclic aromatic hydrocarbons (PAH) %	3
Appearance	Homogeneous clear fluid
Specific gravity at 15 °C, kg/m ³	0.87

Table 3.1: Physical and chemical properties of Group I SN 150 Base oil [44]

3.1.2 Castrol 10W-40 motorcycle oil

Castrol Power 1 4T 10W-40 motorcycle oil consists of synthetic base oil and is designed for 4-stroke motorcycle engines that increases engine acceleration and power right up to maximum rpm. It has been approved by API and JASO [45]. The general lubrication properties are given in table 3.2 [45]. It is worldwide and very commonly used by motorcycle users all around the world. It contains a polymethacrylate based viscosity modifier and ZDDP additive [45]. The product was offered by BP Petrolleri A.Ş. Oil Manufacturing Company in Bursa/Turkey.

3.1.3 Shell Helix Hx7 10W-40 Synthetic motor oil

Shell Helix HX7 10W-40 is a semi-synthetic engine oil and makes use of both synthetic and mineral base stocks to achieve higher performance levels. The

Name	Method	Units	POWER1 Racing 4T 10W-40
Density @ 15C, Relative	ASTM D4052	g/mL	Report
Appearance	Visual	-	Clear & Bright
Viscosity, Kinematic 100C	ASTM D445	mm ² /s	13.0
Viscosity, Kinematic 40C	ASTM D445	mm ² /s	83
Viscosity Index	ASTM D2270	None	160
Viscosity, CCS -25C (10W)	ASTM D5293	mPa.s (cP)	5000
Total Base Number, TBN	ASTM D2896	mg KOH/g	9.8

Table 3.2: Typical characteristics of Castrol Power 1 4T 10W-40 motorcycle oil [45]

typical physical characteristics are given in table 3.3 [15]. It was offered by Shell & Turcas Petrol A.Ş. Oil Manufacturing Company in Kocaeli/Turkey.

Properties	Method	Helix HX7 AV
Viscosity Grade		10W-40
Kinematic Viscosity 40C cSt	IP 71	92.1
Kinematic Viscosity 100C cSt	IP 71	14.4
Density 15C kg/I	IP 365	0.88
Flash Point (PMCC) °C	IP 34	220
Pour Point °C	IP 15	-39

Table 3.3: Typical characteristics of Shell Helix HX7 10W-40 Synthetic motorcycle oil [15]

3.2 Procedures

Here I describe the main procedures used in oxidation of oils (SN 150 base oil, Castrol 10W-40 motor oil and Shell Helix HX7 10W-40 Synthetic motor oil), characterization by IR spectroscopy, and the triboelectrification tests on oxidized oil samples.

3.2.1 Oxidation of SN 150 base oil

The oil samples were oxidized on MS-DMS stirring heating mantles (Figure 3.1). 50mL SN 150 base oil was placed in a 250 mL round-bottomed flask and was oxidized at 200 °C in air (under atmospheric pressure) for 32 hours in total. After 32 hours the viscosity of the samples increased and the oxidized base oil turned into a semi-solid. The temperature was controlled by the temperature probe and temperature-setting dial. At the beginning of the oxidation, the samples for analyses were drawn at every 30 minutes. After four hours of oxidation, the time interval was extended to 1 hour. The oxidation process was continued overnight and samples were taken at 2 hours intervals after 24 hours oxidation. The color of the oil gets darker and the oil gets sticky with the passage of time (shown in Figure 3.2).



Figure 3.1: MS-DMS Stirring Heating Mantles applied during oxidation of SN 150 base oil

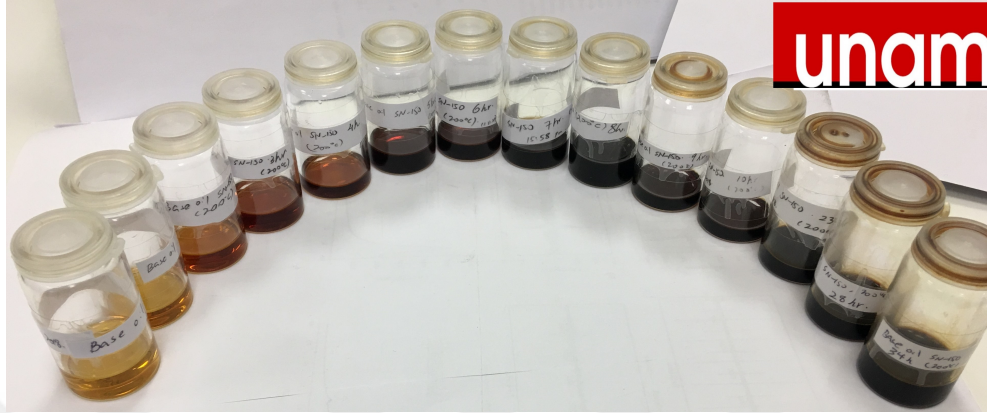


Figure 3.2: Color and viscosity changes on SN 150 Base oil during oxidation process

3.2.2 Oxidation of Castrol 10W-40 motorcycle oil

50 mL samples of oil were oxidized at 200 °C, 175 °C, and 150 °C separately for better observation of different ZDDP degradation rate under different temperature. The oxidation which is at 175 °C and 150 °C was proceeded in the cylindrical reactor. The schematic of this oxidation process is shown in Figure 3.3. The temperature was sensed by the thermocouple, adjusted by the control panel (Figure 3.4). To ensure the efficiency and homogeneity of the oxidation in the samples, air was bubbled during the heating process. The oxidation at 200 °C was continued 62 hours in total and samples were taken in 3 different time intervals (30 minutes, 1 hours, and 3 hours). At 175 °C, the oxidation was carried for 10 hours until which time the ZDDP additive depleted. Similarly, at 150 °C, the oxidation was carried for 80 hours.

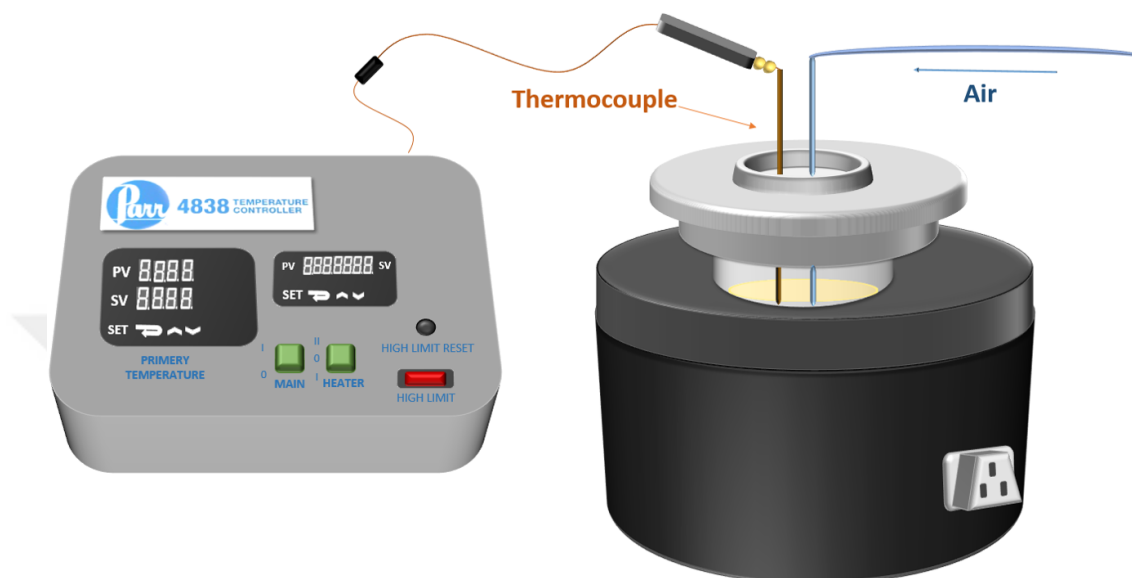


Figure 3.3: Schematic of engine oil oxidation process in reactor



Figure 3.4: Reactor (left) and reactor control panel (right)

3.2.3 Oxidation of Shell Helix Hx7 10W-40 Synthetic motor oil

The oxidation process for Shell Helix HX7 10W-40 Synthetic motor oil was similar to the process of Castrol 10w-40 motor oil oxidation. The 50 mL oil samples were oxidized at 150 °C for 42 hours. Samples for analyses were drawn every 30 minutes until 3 hours of oxidation, and then every 1 hour until the 8th hours of oxidation. After the 8th hour, samples were taken within in periods of 4 hours. The oil samples were then analyzed with the IR spectrometer for monitoring of the chemical changes, and also for understanding of the ZDDP additive consumption during oxidation.

3.2.4 Infrared spectroscopy

The IR absorption peak changes corresponding to different chemicals in oils during the oxidation process are given in Figure 3.5 [46]. We used the Bruker ALPHA ATR Spectrometer for the IR characterization of the oil samples. It is a benchtop style small size diamond based single reflection instrument. It comprised several flexible modules depending upon applications. The image of IR spectrometer and simple working scheme are represented in Figure 3.6.

Molecular Functionality	Specific Structure ^a	Functional Group	Frequency (cm ⁻¹)
Carboxylic acid	R-(C=O)-OH	C=O	1,710 (dimer) 1,760 (monomer)
		C=O	1,690 (dimer)
	Ar-(C=O)-OH	OH	3,000–2,500 (dimer)
			3,530 (monomer)
Ketone	R-(C=O)-R	C=O	1,715
	Ar-(C=O)-R	C=O	1,685
	Ar-(C=O)-AR	C=O	1,665
Aldehyde	R-(C=O)-H	C=O	1,735
	Ar-(C=O)-H	C=O	1,705
		(C=O)-H	2,900–2,700
Ester	R-(C=O)-OR	C=O	1,740
	Ar-(C=O)-OR	C=O	1,725
	R-(C=O)-OAr	C=O	1,770
		C-O	1,300–1,100

^a R = aliphatic group, Ar = aromatic group

Figure 3.5: Typical IR absorption peaks of different carbonyl moieties

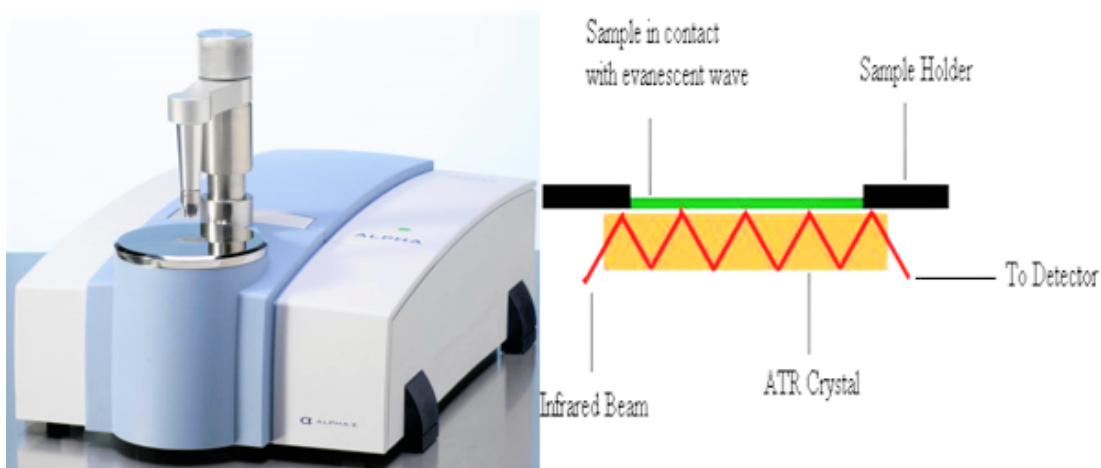


Figure 3.6: Bruker ALPHA ATR Spectrometer and simple working schematic diagram [13,14]

3.2.5 Triboelectrification

We developed a tapping device so-called triboelectric sensor (TES) for probing the changes in the triboelectric behavior of the oil upon oxidation. The schematic representation of TES based prediction system for the remaining life of engine oil is shown in Figure 3.7. Two aluminum disks are chosen as substrate material due to its good impact strength, lightweight, and easy handling. On the right plate, a thin 0.37 mm ($\varnothing$ 12.3 mm) polyvinyl chloride (PVC) film was adhered by carbon tape as a back electrode. On the left plate, an oil absorbed cellulose paper ($\varnothing$ 14.5 mm, 0.17mm thick) was stuck to the aluminum substrate by a plastic holder. The cellulose paper was selected as the absorbent material due to its high oil absorption efficiency and stability of the structural form during the tapping. (Chemical structure and the corresponding SEM image of the cellulose paper surface are shown in Figure 3.8.) The fabrication process of the TES system is sketched in Figure 3.9. The working mechanism of the TES system can be illustrated by the coupling between the triboelectric effect and electrostatic effect [47]. Before switching on the electromagnet device, the two plates are at their initial, separated states and there is no contact between the two plates. When the electromagnet device is turned on, it forces the left plate to approach the plate side and two plates are brought into contact and this results – very basically - in electron transfer from one material to the other [47]. As the pulling force is away, the two surfaces are separated, again the electrons are transferred. The overall effect of the tribocharging was measured by monitoring the open-circuit voltages of the circuit that is constructed by attaching these plates as the electrodes of an oscilloscope (OWON SD57072).

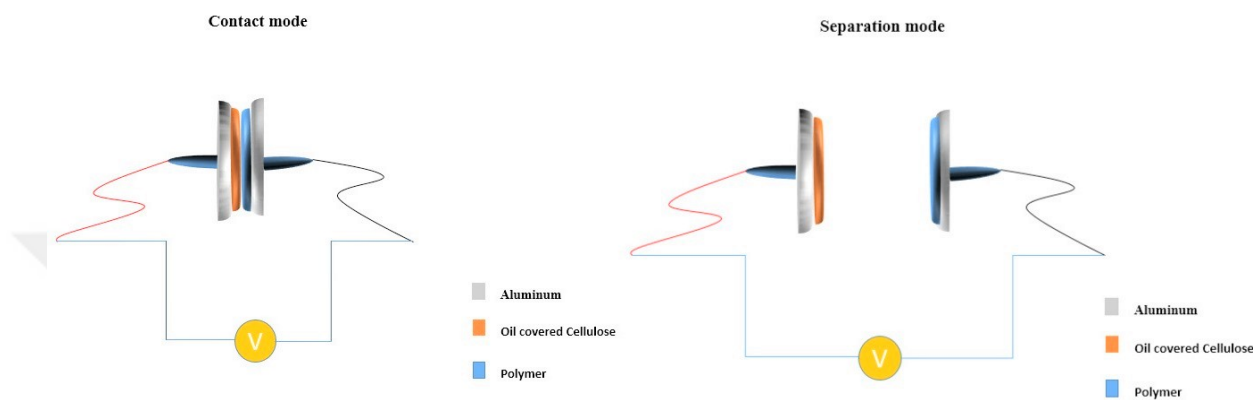


Figure 3.7: (a) Separation mode of triboelectric (b) contact mode of triboelectric

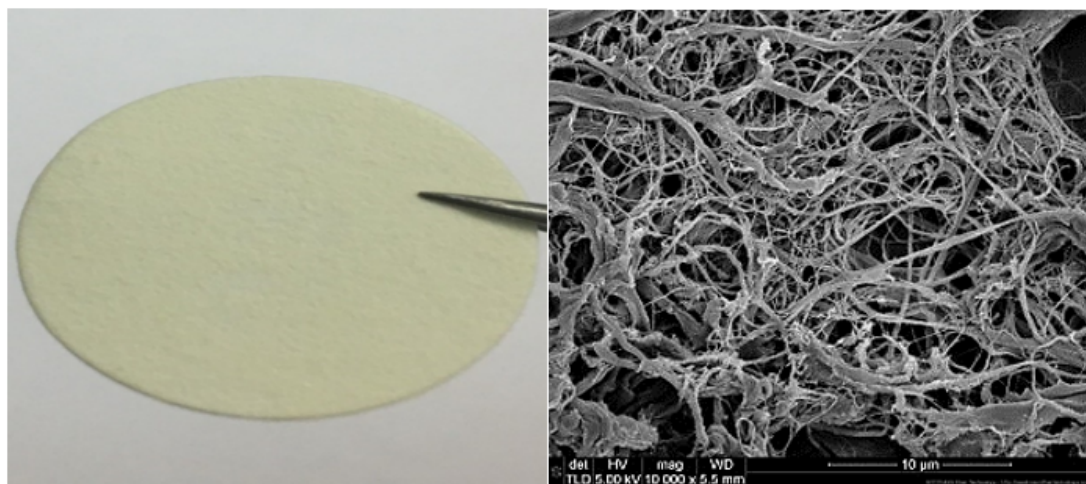


Figure 3.8: (a) 100% cellulose paper (left) (b) Corresponding SEM image of the cellulose paper surface (right)

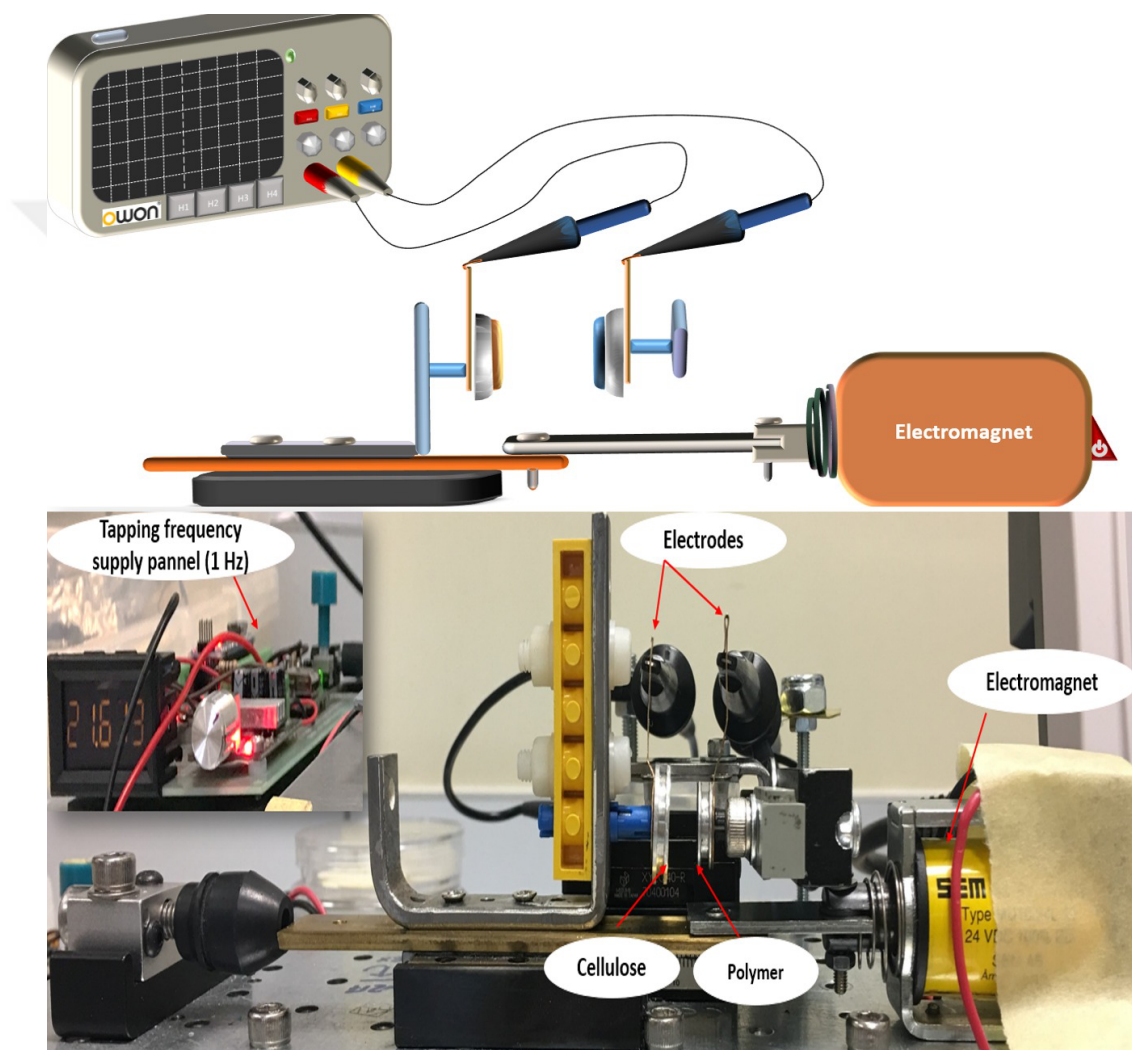


Figure 3.9: Schematic of easy operation and slimline outlook TES system and TES device used during experiment

3.2.6 Dynamic viscosity

Rheometry determines the rheological properties of materials; rheology describes the interrelation between force, deformation and time. Viscosity is a measure of the resistance to flow [48]. The viscosity of a lubricant has a strong relationship with the ability to reduce friction in surface contacts. It is considered one of the most important parameters for the oil's lubrication properties [48]. It has been used as an indicator parameter of the oil condition monitoring system as foregoing in the previous chapter. In our thesis project, we have conducted the dynamic viscosity change of different oils as mentioned versus oxidation time. The measurement proceeded by using Physica MCR 301 Rheometer [48].

3.2.6.1 Physica MCR 301 Rheometer

MCR Rheometer 301 is a compact system with air bearings and high-performance synchronous motor with direct EC control rotor motion and 100% control of the rotor field with continuous torque available, without thermal heating, which allows rheological measurements at high-quality levels [49]. Possible in testing with oscillating or regulation, adjustment of shearing even in samples with low viscosity, survey measurement at low torques $0.01 \mu\text{Nm}$ and divergence sensor or $0.1 \mu\text{rad}$. Fast and automatic identification of measuring geometries (measurement systems) and tempering, and immediate wireless transmission of technical parameters of the electronic Rheometers [49]. The image of MCR Rheometer 301 and simple working scheme are shown in Figure 3.10.

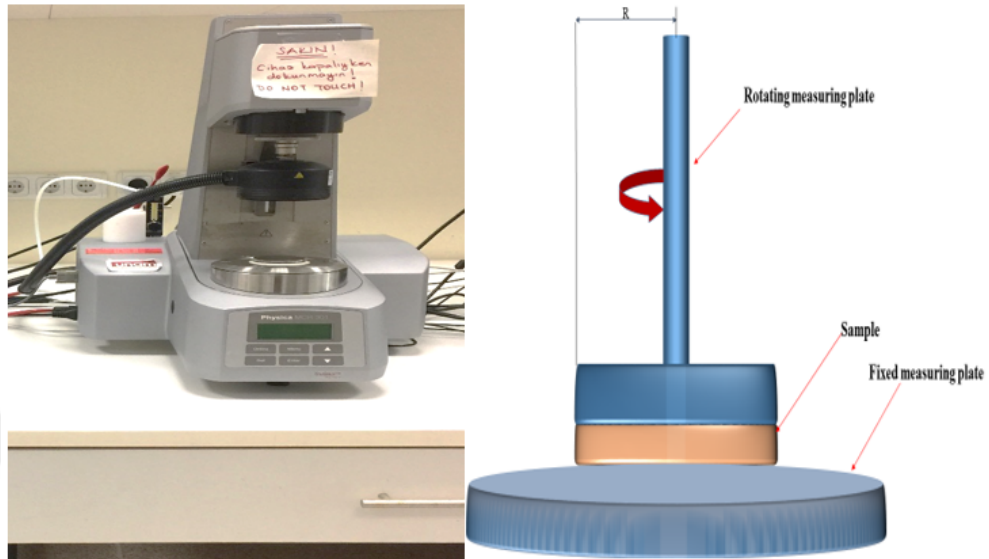


Figure 3.10: MCR Rheometer 301 and simple working scheme

Up to here, I illustrated the materials, devices, and equipment were used during the experiment. Moreover, the three main procedures of our experiments (oxidation of the oil, characterization, and monitoring the triboelectric behavior of oxidized oil) were presented. Next chapter, I will discuss the experimental results regarding the correlation of triboelectrification and oil oxidation.

Chapter 4

Results & Discussion

4.1 SN 150 Base oil Results

4.1.1 Triboelectrification

For triboelectric measurements, we used the above-mentioned homemade tapping device. Firstly, we used base oil and dipped the cellulose paper in the oil sample for soaking the oil, dried off the paper for a while, and then set it on the device for tapping. Due to its high viscosity, the oxidized oil could not be homogeneously absorbed by cellulose paper, thus, the most oxidized sample that can be used in our TES detection with high reliability was the one that was oxidized for 26 hours at 200 °C. On the other plate, to serve as the triboelectric pair, we selected and mounted a PVC disk, specifications of which are described in the above section. Upon tapping of the two materials on the plates, the oil/cellulose and PVC, open-circuit voltages (Voc) were recorded, which result from the contact/separation electrification of the two materials. Each oil sample has been measured at least five times to obtain a standart deviation of the results. (Figure 4.1).

As seen from the electrical output (Voc) change between untreated base oil and oxidized oil is a good parameter to detect the oxidation level of the oil. From

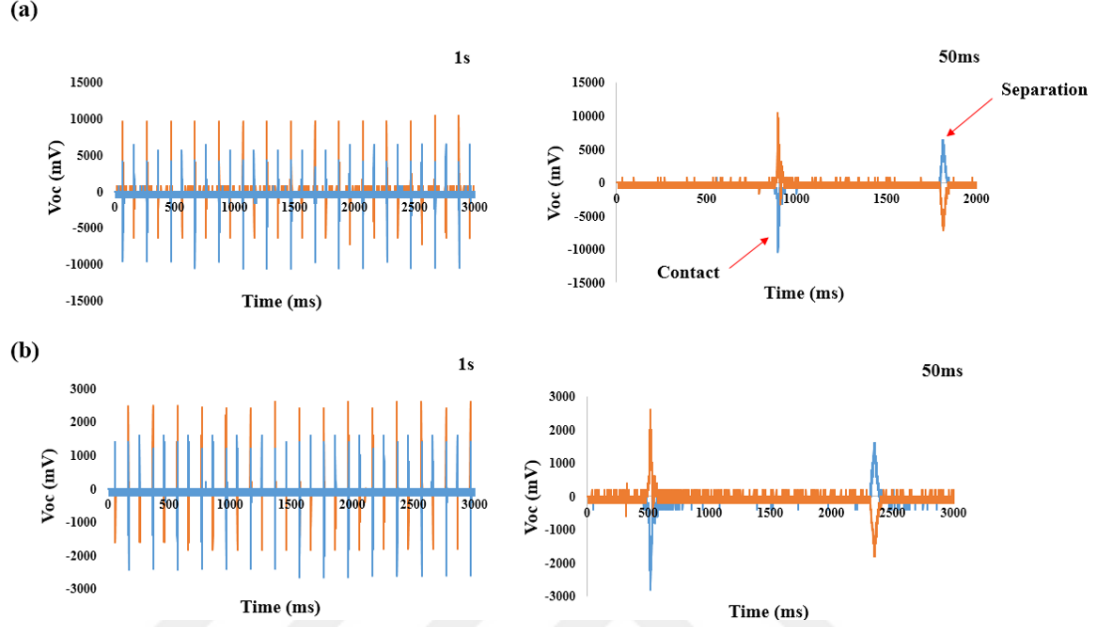


Figure 4.1: The generated Voc of (a) untreated base oil and (b) 26 hours oxidized base oil under 200 °C presented with 1s and 50ms time scale (Orange for PVC, blue for oil absorbed cellulose)

Figure 4.1 (a) and (b), it is evident that the Voc output (absolute value) of the base oil $|-10.4 \text{ V}|$ decreased approximately 5 times in comparison to that of Voc of untreated oil $|-2.6 \text{ V}|$ after 26 hours oxidizing. In Figure 4.2, we plotted the continuous decrease of Voc obtained by the cellulose/PVC contact/separation electrification of oil samples oxidized for different times and then soaked on cellulose paper.

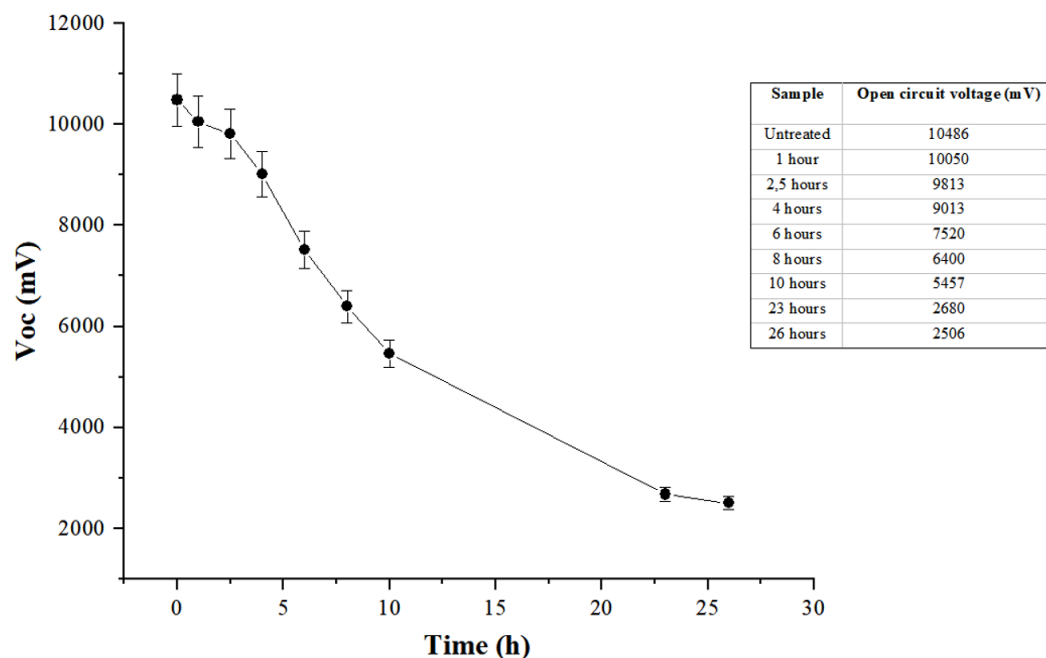


Figure 4.2: Triboelectrification (Voc) trend of SN 150 base oil oxidized in total 26 hours

These results give us preliminary confirmation of our hypothesis, which was the idea that a correlation between oxidation time and triboelectric generation from base oil may exist. To further understanding of the chemical changes in the oil itself along with increasing of oxidation time, we conducted IR spectrum analysis with Bruker ALPHA ATR Spectrometer. (The resolution of FTIR spectrometer is 2 cm^{-1} , number of scans is 128).

4.1.2 IR spectrum for SN 150 Base oil

We monitored the changes in IR spectrum of the SN 150 base oil samples drawn from the oxidation described in the previous section throughout their oxidation, by ATR spectroscopy. Figure 4.3 shows the intensity changes observed in the ‘oxidation peaks’ over the 32 hours of oxidation.

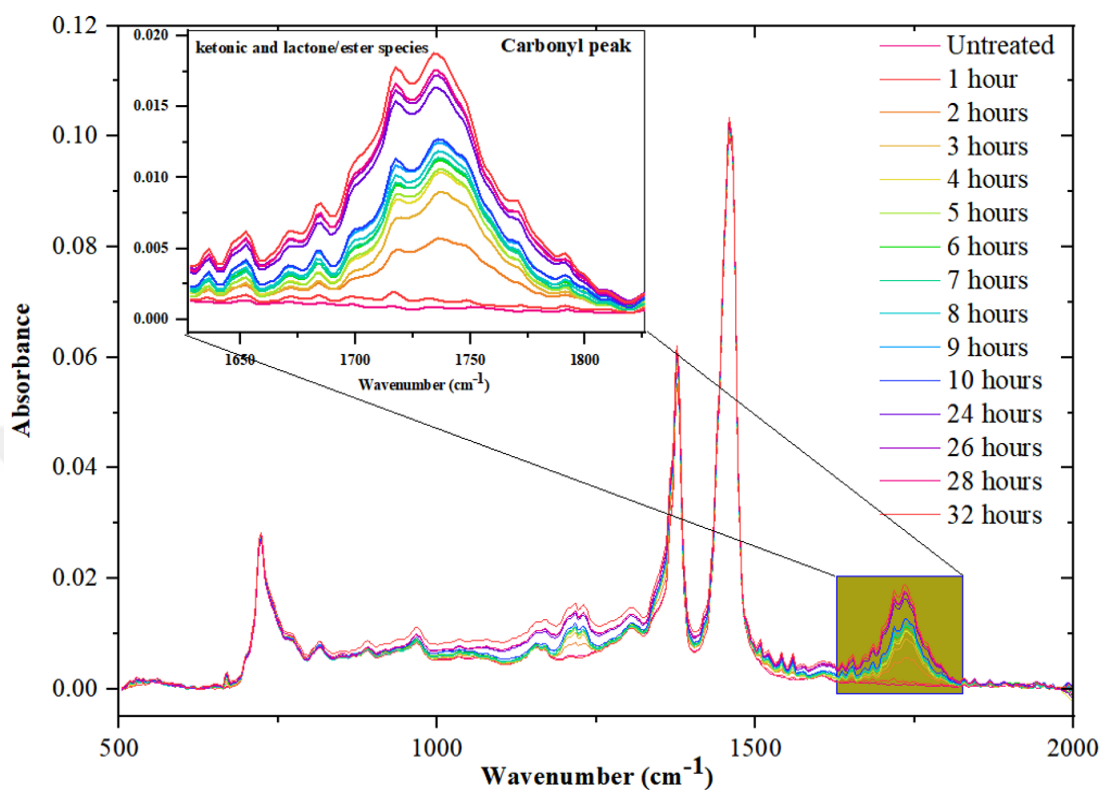


Figure 4.3: The changes of oxidation peaks (carbonyl region) of base oil on ATR spectroscopy

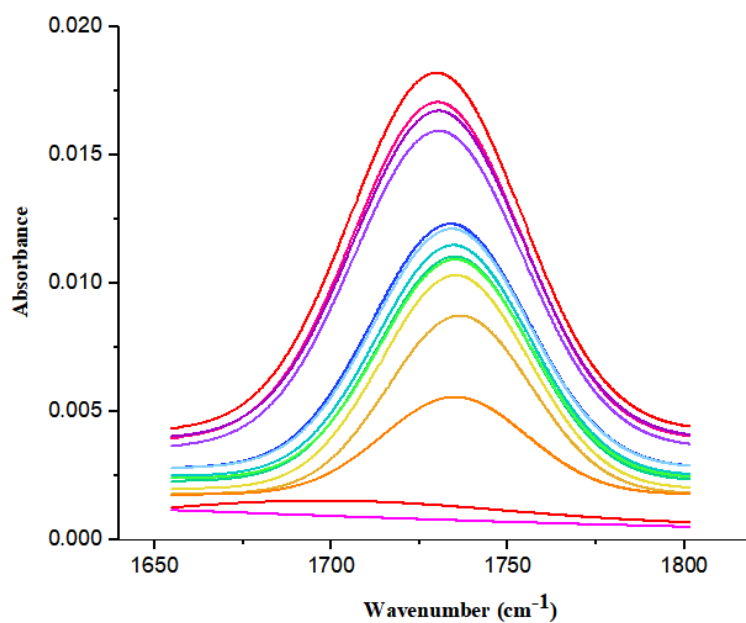


Figure 4.4: The fitted IR absorbance peaks at oxidation region (carbonyl region) of base oil heated at 200 °C

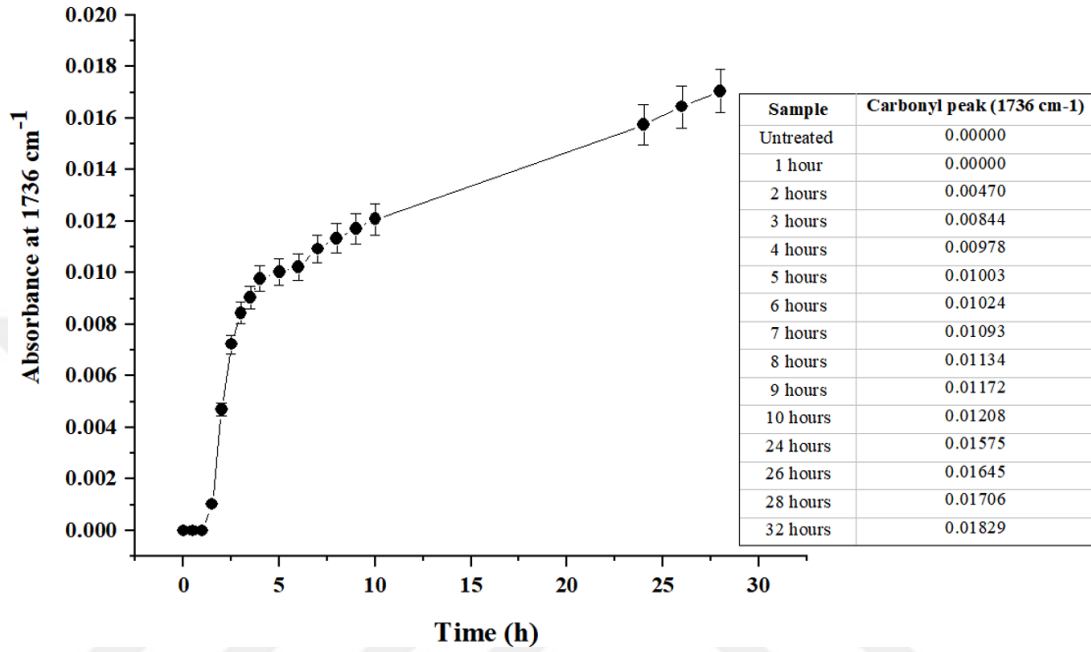


Figure 4.5: Absorbance trend over the 32 hours oxidation under 200 °C

As shown in Figure 4.3 and 4.4 a significant increase in the intensity of ‘oxidation peaks’ of base oil began to appear after 2 hours of oxidation at 200 °C, the absorbance increases quickly between 2 and 5 hours of oxidation and continues to increase at a slower rate after that. At 32 hours, the absorbance reaches a value of 0.018, 45 times higher than of the untreated state of base oil. The experimental data indicate that the electrical output of TES is depended on the oxidation time of the base oil at a given temperature.

4.2 Castrol 10W-40 motorcycle oil results

Now I will present the results that we get from Castrol Power 1 4T 10W-40 motorcycle oil. As mentioned in the previous chapter, the oxidation process for Castrol Power 1 4T 10W-40 motorcycle oil was carried out at three different temperature. The triboelectrification results and related characterization results for each condition are given below.

4.2.1 Oxidation at the temperature of 200 °C

The same process that was applied for the SN 150 base oil measurement in the previous section was carried out for the Castrol Power 1 4T 10W-40 motorcycle oil. The oil was oxidized at 200 °C oil for 62 hours in total, however, because of the high viscosity of oil after 56 hours of oxidation, the samples were drawn only up to the 56th hour.

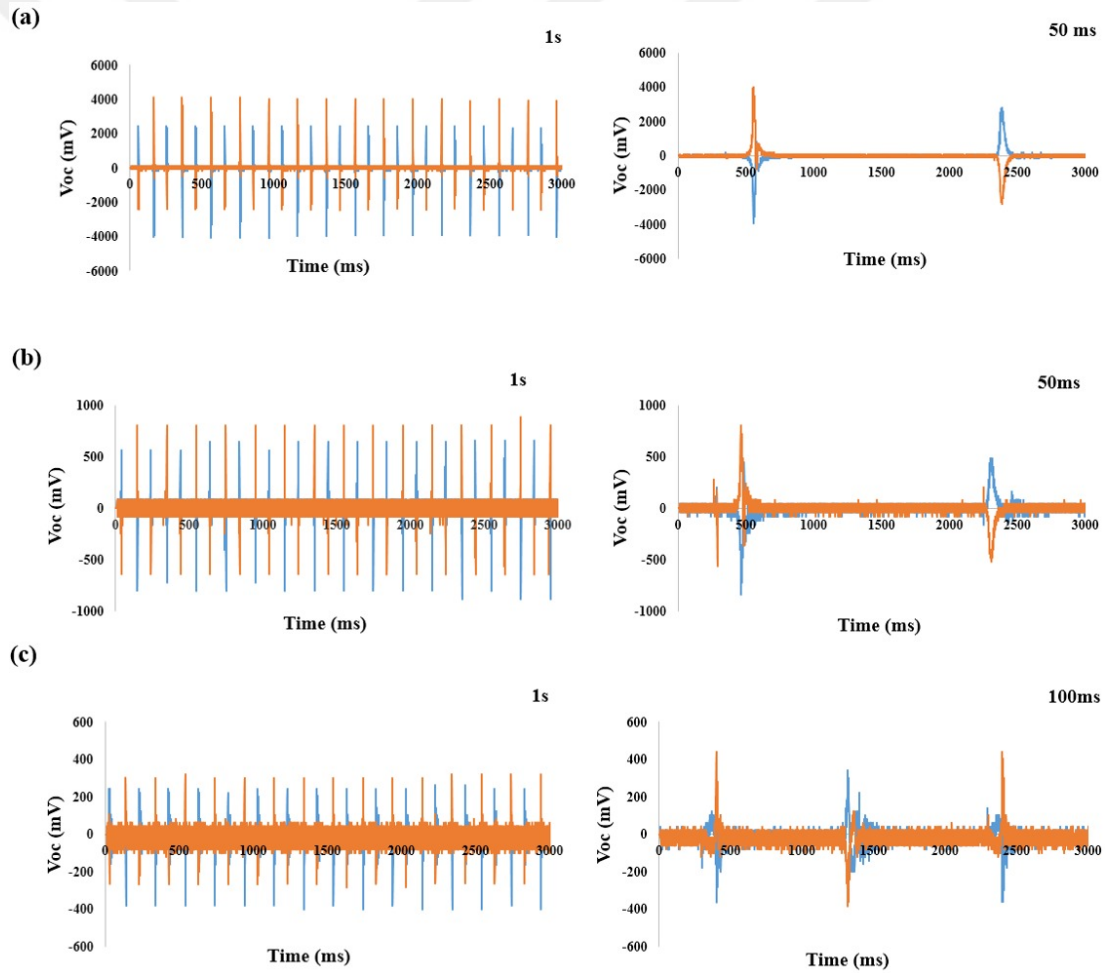


Figure 4.6: The generated Voc of (a) untreated (b) 10 hours oxidized and (c) 56 hours oxidized Castrol Power 1 4T 10W-40 motorcycle oil at 200 °C presented with 1 s and 50 ms time scale (Orange for PVC, blue for oil absorbed cellulose)

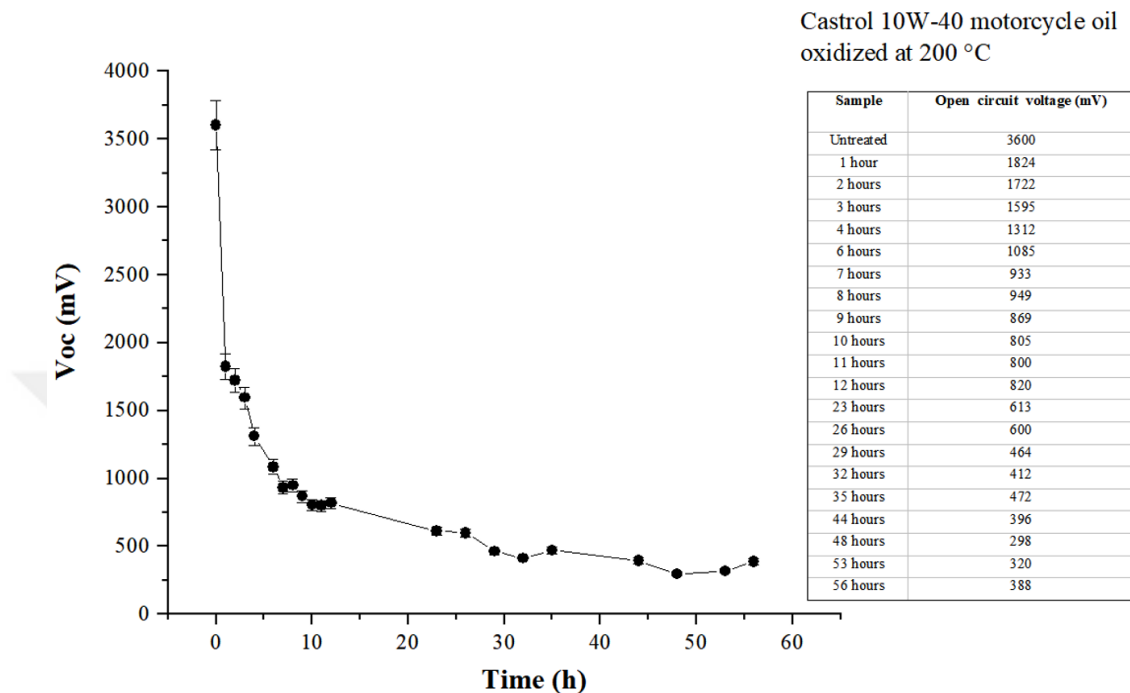


Figure 4.7: The electrification trend of Castrol Power 1 4T 10W-40 motorcycle oil oxidized at 200 °C in total 56 hours

The electrical output (Voc) change between untreated and oxidized oil is similar to the results of base oil. From Figure 4.6 (a) and (c), the Voc output of the Castrol Power 1 4T 10W-40 motorcycle oil shows approximately 12 times decrease in comparison to the untreated oil, after 56 hours oxidation (the Voc is decreased from $|-4.04|$ V to $|-0.34|$ V). The decrease trend is maintained along the increase in oxidation time as shown in Figure 4.7. The graph shows that even after 1 hour of oxidation, the Voc value immediately dropped almost half of that of the untreated, non-oxidized state. Afterward, the decrease slowed down and reached a saturation after 32 hours.

Figure 4.8 shows the IR spectral changes in the carbonyl region and ZDDP additive peak over the time. As shown, in the carbonyl region peaks start to appear, for which the increase in the intensity was plotted as shown in Figure 4.11. (Note that: In the carbonyl region, untreated sample also have peaks that belong to PMA based viscosity index improver additive.) Furthermore, the absorption

peak that is assigned to ZDDP additive at 975 cm^{-1} disappeared even after 1-hour oxidation. Based on these results, we assume that the triboelectrification ability of Castrol Power 1 4T 10W-40 motorcycle oil is related to the PMA based viscosity index improver additive and ZDDP additive. For a deeper understanding of the oxidation process, we have conducted the oxidation process at $175\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$.

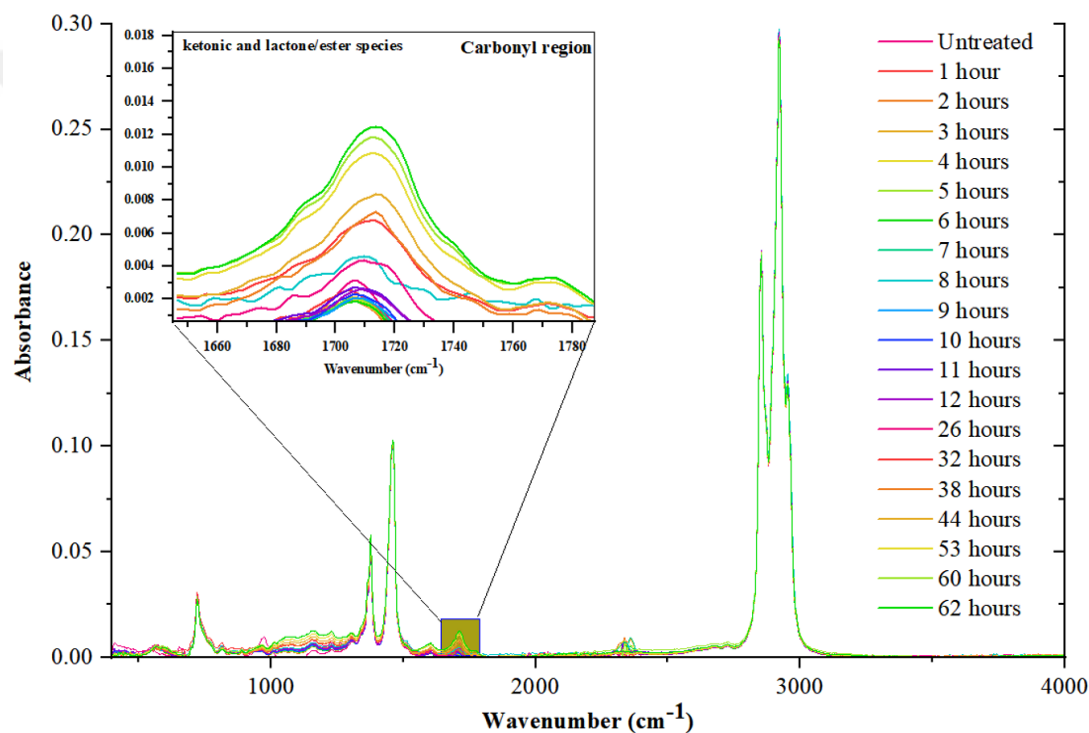


Figure 4.8: IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at $200\text{ }^{\circ}\text{C}$ for 62 hours in total. Carbonyl peaks begin to appear and arise throughout the oxidation

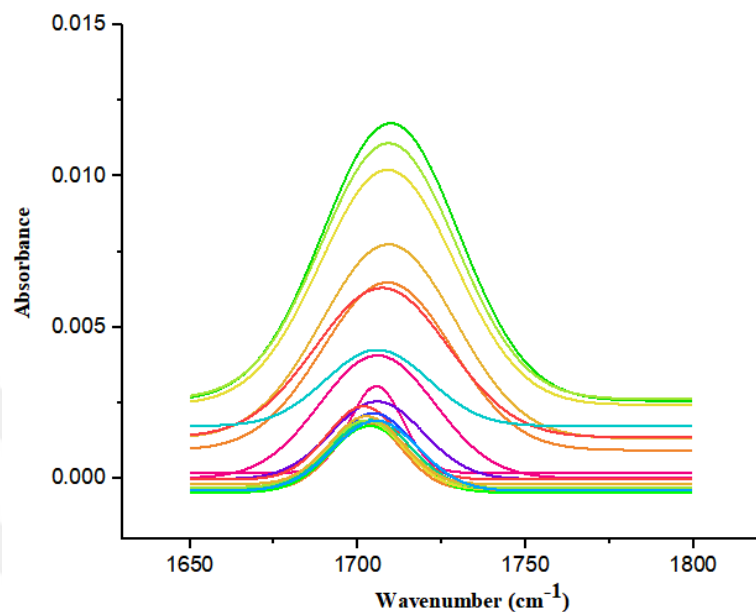


Figure 4.9: The fitted IR absorbance peaks of oxidation (carbonyl region) of Castrol Power 1 4T 10w-40 engine oil heated at 200 °C for 62 hours in total

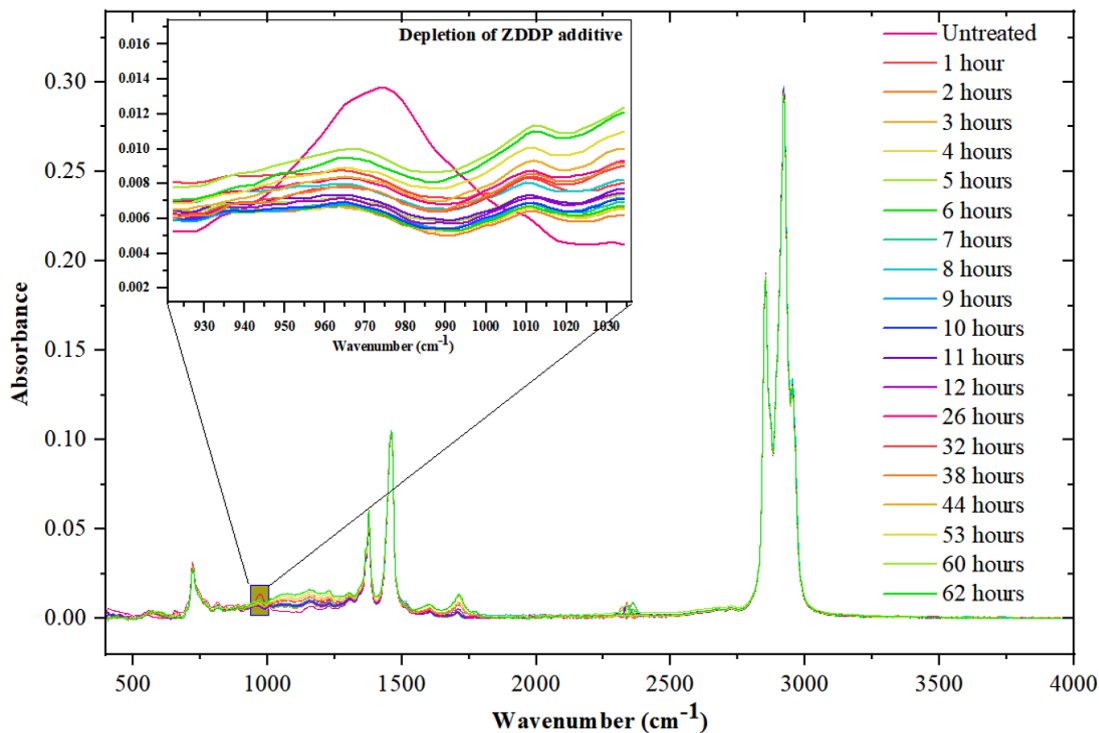


Figure 4.10: IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at 200 °C for 62 hours in total. ZDDP additive peak has vanished immediately after 1 hour oxidation

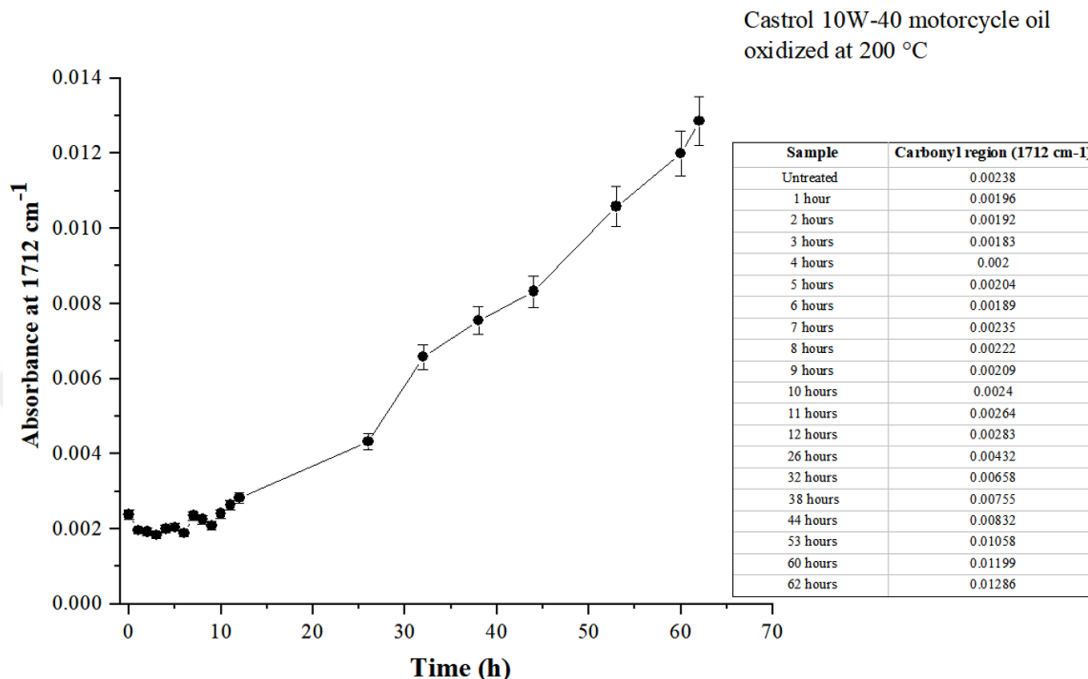


Figure 4.11: The trend of absorbance arising at 1712 cm^{-1} over 62 hours oxidation

4.2.2 Oxidation at the temperature of 175 °C

In the IR spectra of samples drawn during the oxidation at 175 °C (figure 4.12), the absorbance of carbonyl peak did not change significantly with increasing oxidation durations. The absorbance of the ZDDP additive at 975 cm^{-1} decreased much slower in comparison to the oxidation at 200 °C disappeared only after 10 hours of oxidation. This is due to the different decomposition rate of ZDDP additive under different thermal condition. In higher temperature it is decomposed into sulphuric group much faster than in lower temperature.

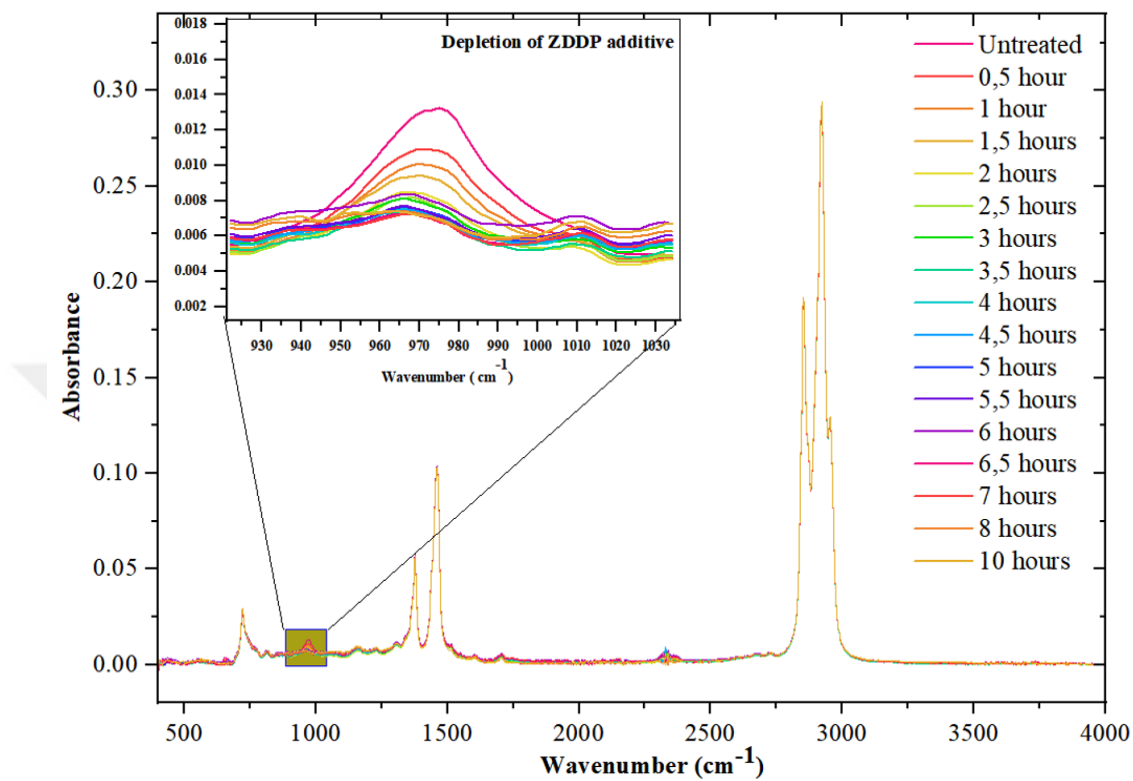


Figure 4.12: IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at 175 °C for 10 hours in total. Magnified IR region of ZDDP additive

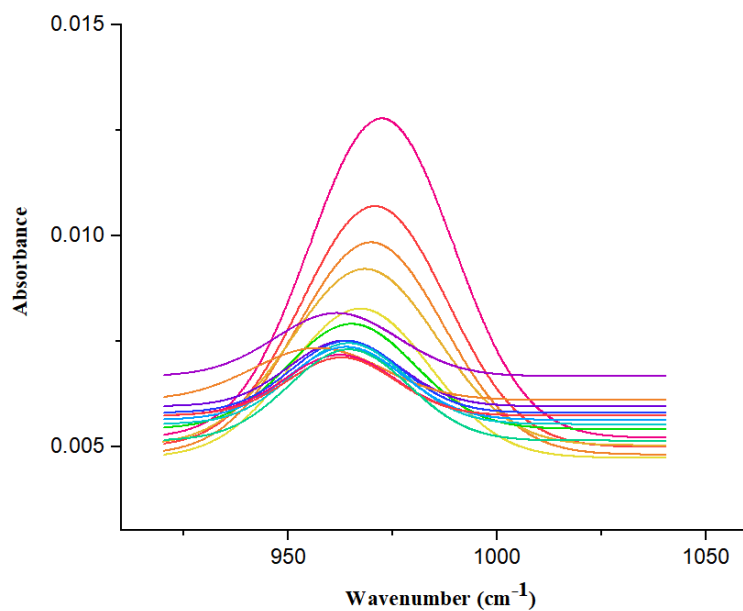


Figure 4.13: The fitted IR absorbance peaks of ZDDP additive in Castrol Power 1 4T 10w-40 engine oil heated at 175 °C for 10 hours in total

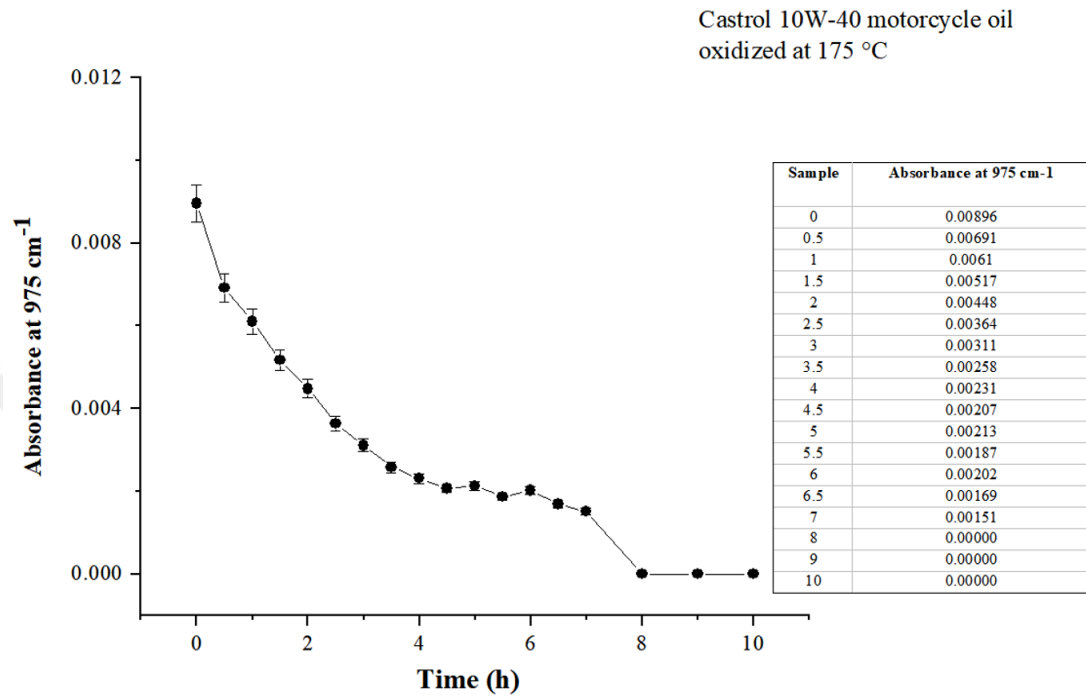


Figure 4.14: ZDDP additive degradation trend over 10 hours oxidation

The TES measurements show that Voc decreased sharply right after 1 hour oxidation with an approximately 6 times decrease ($|-3|$ V to $|-0.5|$ V) alone within this time. Figure 4.15 shows the different triboelectric signals between untreated and 2.5 hours oxidized samples. The saturation was reached after 2.5 hours of oxidation as shown in Figure 4.16. Due to the relatively low and noisy Voc output, the measurement was carried out up to 6 hours.

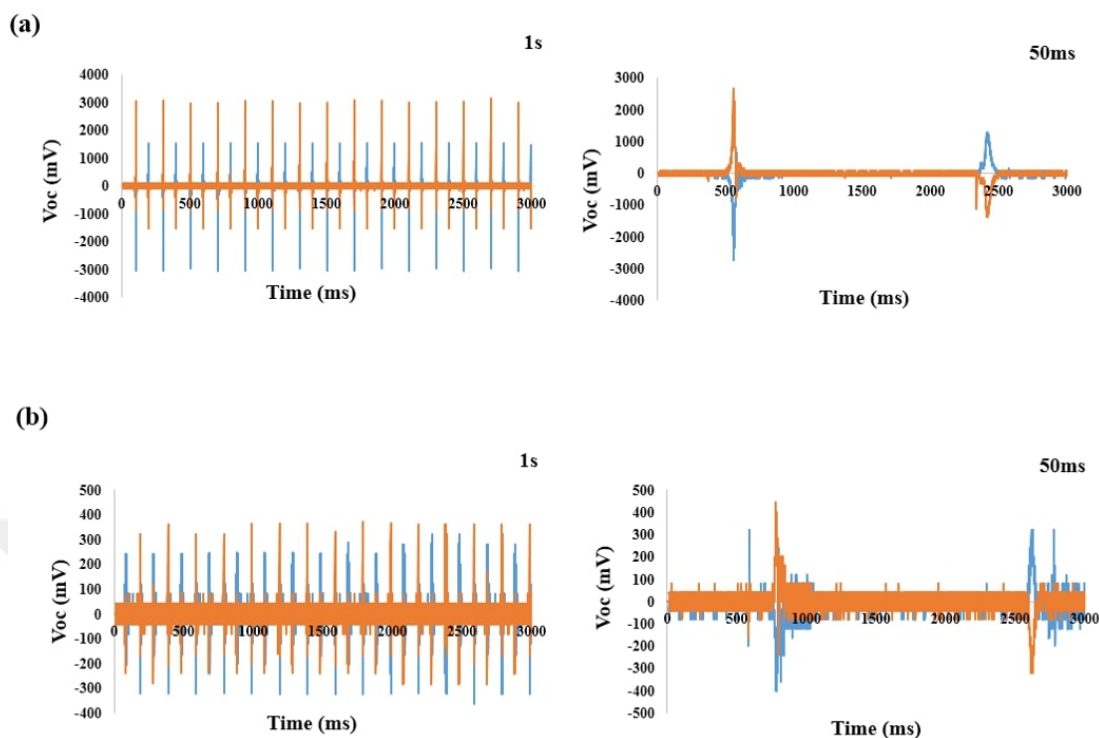


Figure 4.15: The generated Voc of (a) untreated (b) 2.5 hours oxidized Castrol Power 1 4T 10W-40 motorcycle oil at 175 °C presented with 1s and 50 ms time scale (Orange for PVC, blue for oil absorbed cellulose)

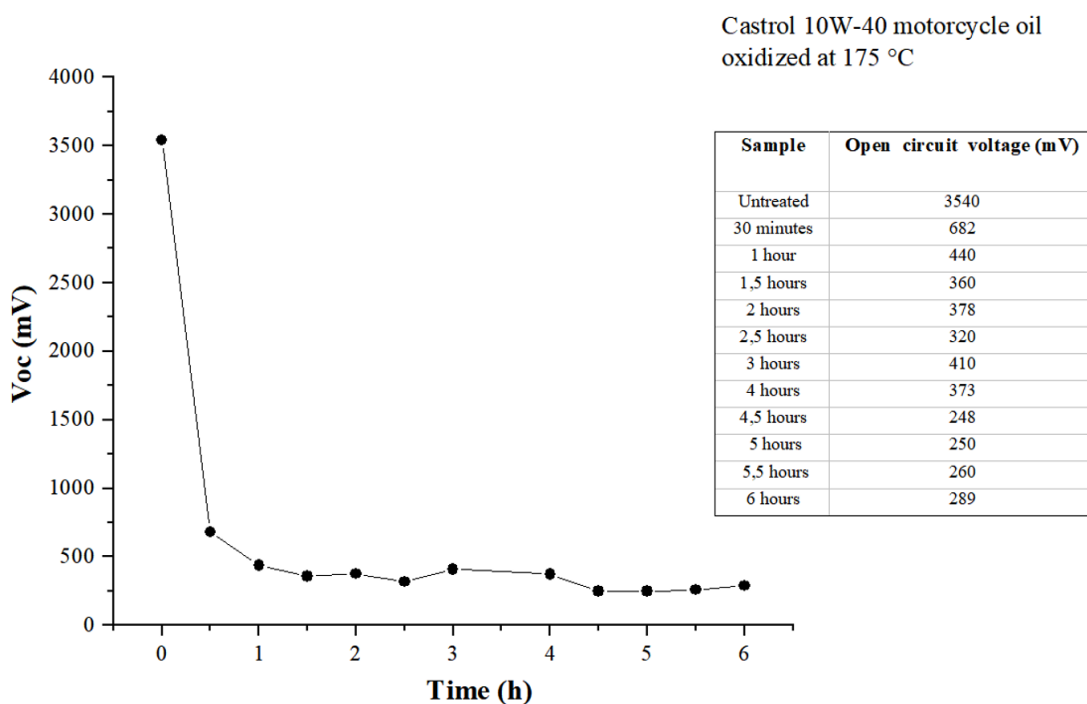


Figure 4.16: The electrification trend of Castrol Power 1 4T 10W-40 motorcycle oil at 175 °C

4.2.3 Oxidation at the temperature of 150 °C

In the IR Spectrum of the oil oxidized at 150 °C (Figure 4.17), it is shown that ZDDP peak did not disappear promptly but its intensity declined in a relatively low rate and the peak can be said to disappear after 80 hours oxidation. Moreover, there was no emergence of new peaks around carbonyl region.

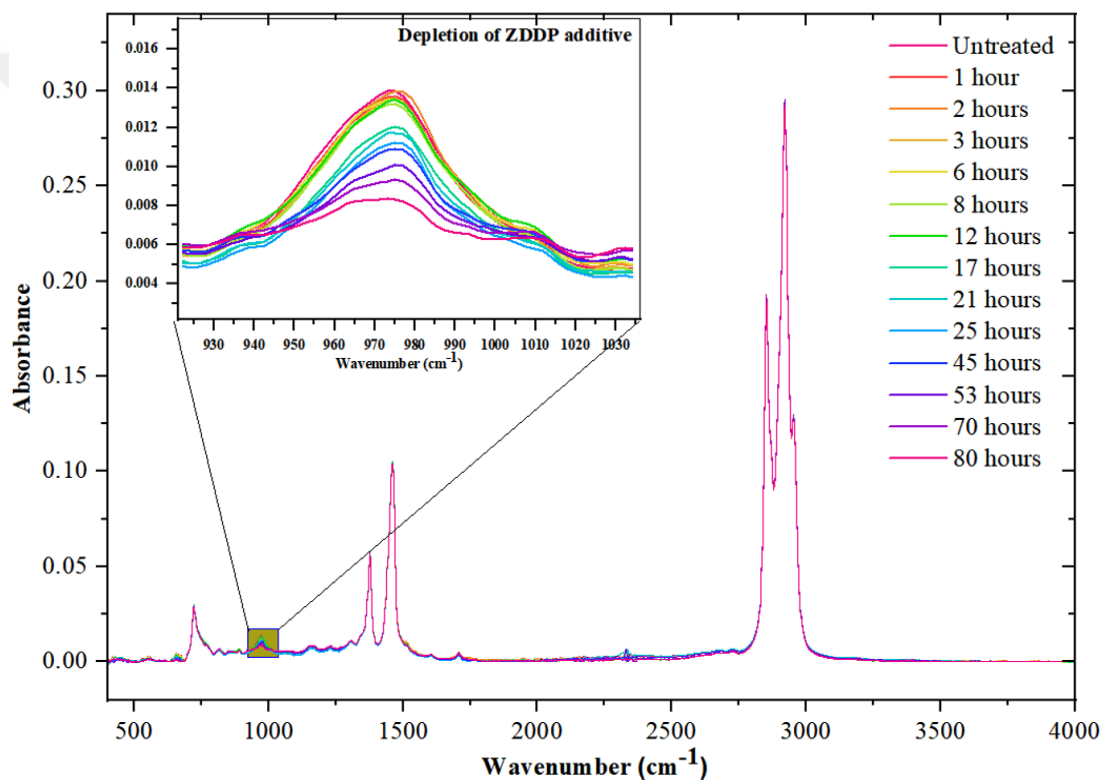


Figure 4.17: IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at 150 °C for 80 hours in total. (Magnified IR region of ZDDP additive)

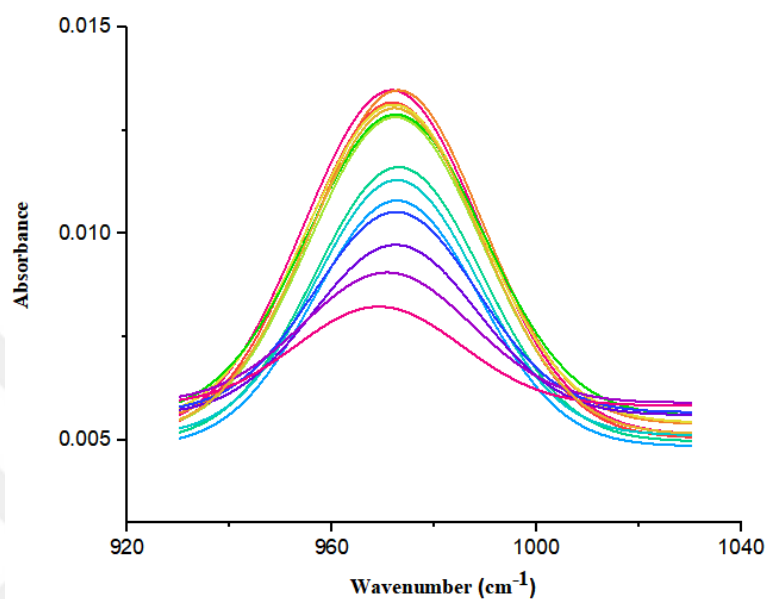


Figure 4.18: The fitted IR absorbance peaks of ZDDP additive in Castrol Power 1 4T 10w-40 engine oil heated at 150 °C for 80 hours in total

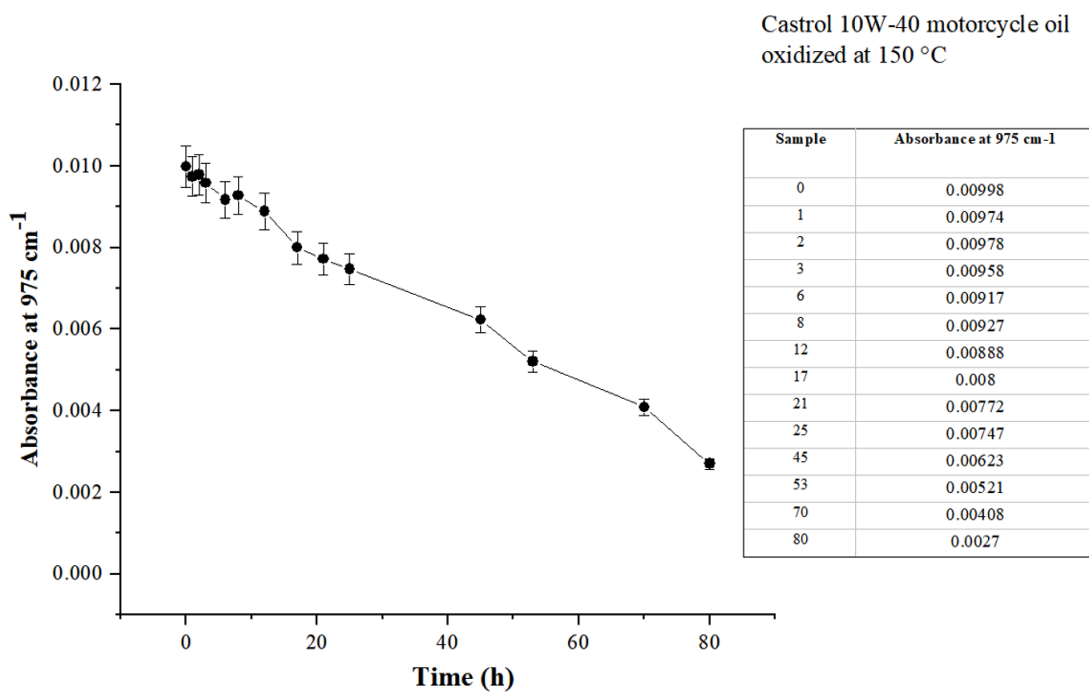


Figure 4.19: ZDDP additive degradation trend over 80 hours oxidation

In the TES probing of Castrol Power 1 4T 10W-40 motorcycle oil degradation at 150 °C, Voc signal decreased approximately 22 times after 80 hours oxidation (the Voc decreased from $|-3.5|$ V to $|-0.164|$ V). The detailed result is shown below in Figures 4.20 and 4.21.

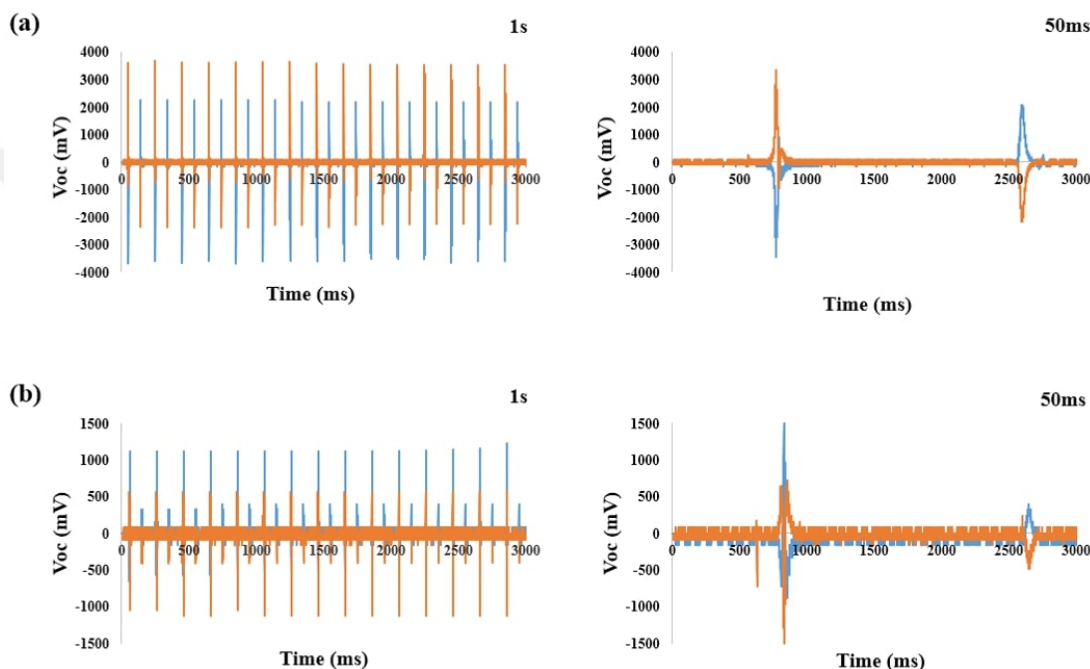


Figure 4.20: The generated Voc of (a) untreated (b) 45 hours oxidized Castrol Power 1 4T 10W-40 motorcycle oil at 150 °C presented with 1 s and 50 ms time scale (Orange for PVC, blue for oil absorbed cellulose)

We have combined the results for both electrification (open circuit voltage) and IR absorbance data (absorbance at wavenumber of 975 cm^{-1}) from the 3 different thermal conditions (150 °C, 175 °C, 200 °C). We defined the concentration (percentage) of ZDDP additive by IR absorbance of 975 cm^{-1} (which is representing ZDDP additive), e.g. for untreated oil the absorbance at 975 cm^{-1} is 0.0099, then this value is defined as 100%. (Figure 4.22)

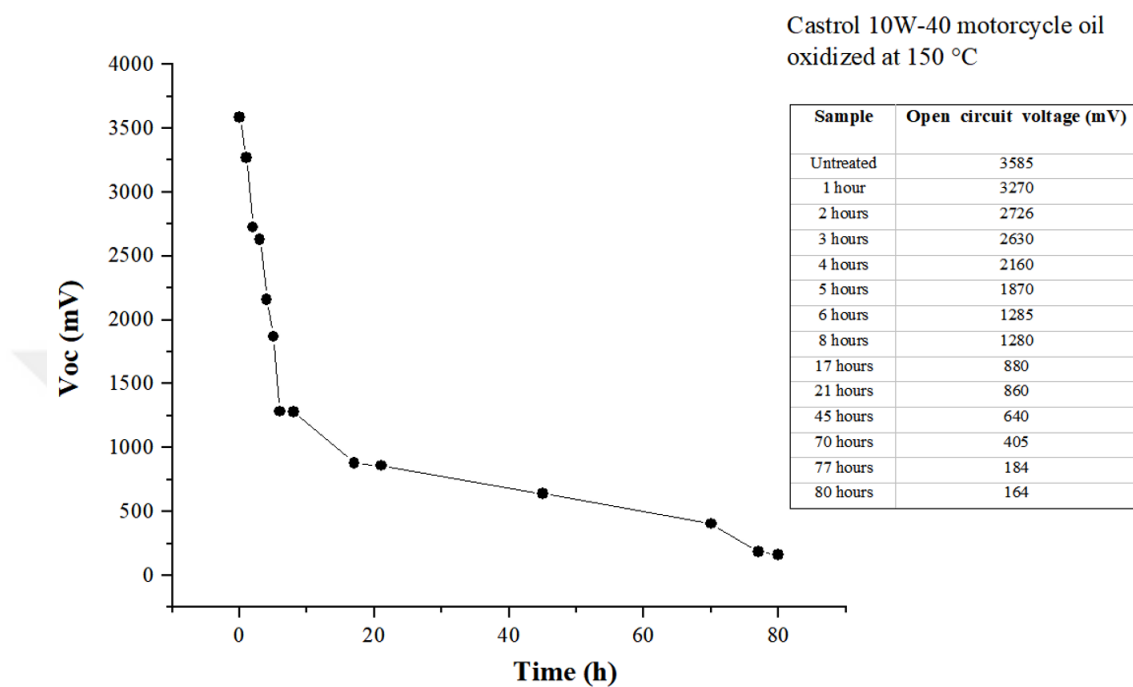


Figure 4.21: The electrification trend of Castrol Power 1 4T 10W-40 motorcycle oil oxidized at 150 °C

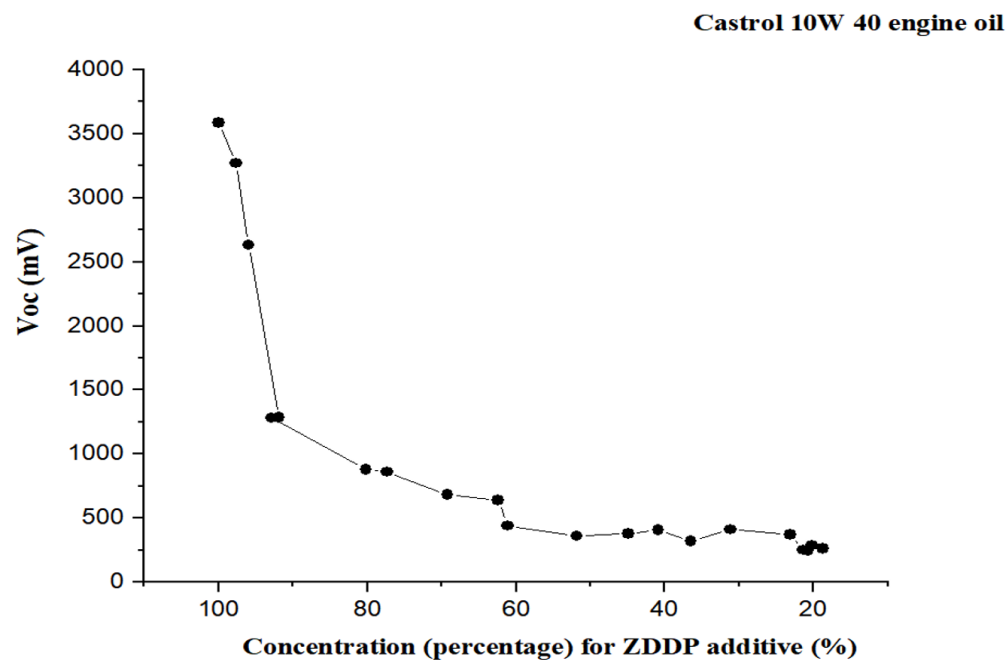


Figure 4.22: Electrification vs. concentration (percentage) of ZDDP additive in Castrol Power 1 4T 10W-40 motorcycle oil

4.3 Shell Helix Hx7 10W-40 Synthetic motor oil results

As the third part of our work, we performed and monitored the oxidation of Shell Helix Hx7 10W-40 Synthetic motor oil, which took place at 150 in the reactor for 30 hours in total. The oxidation process was monitored with the ATR spectroscopy, of which the results are shown below. The intensity of the ZDDP additive peak at 975 cm^{-1} dropped drastically after 8 hours oxidation and completely nullified after 30 hours.

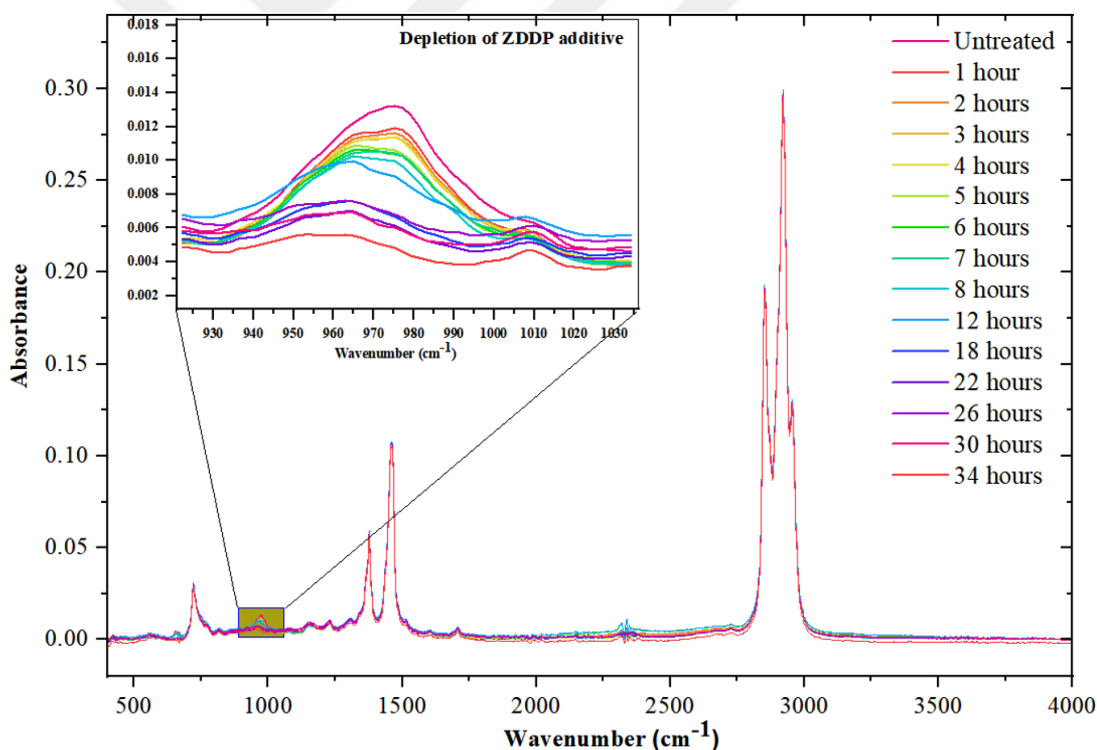


Figure 4.23: IR spectra of Shell Helix Hx7 10W-40 Synthetic motor oil heated at 150 °C for 30 hours in total. (Magnified IR region of ZDDP additive)

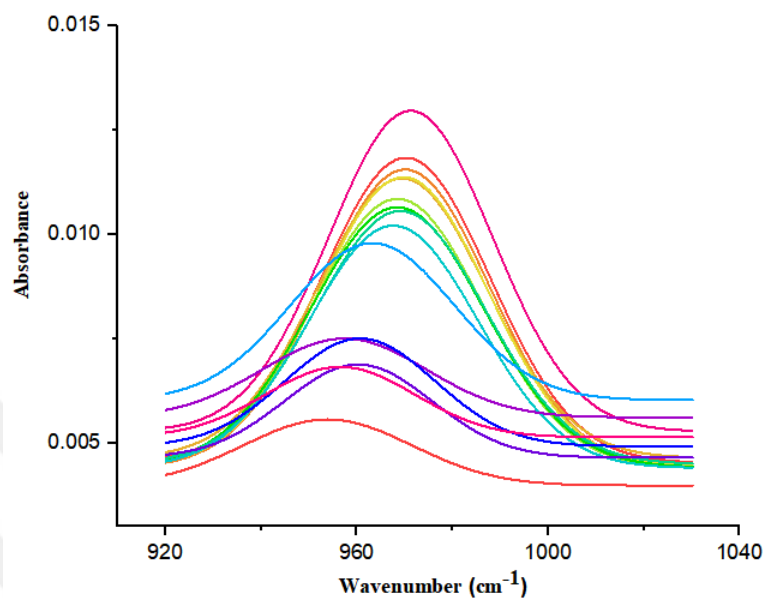


Figure 4.24: The fitted IR absorbance peaks of ZDDP additive in Shell Helix Hx7 10W-40 Synthetic motor oil heated at 150 °C for 30 hours in total

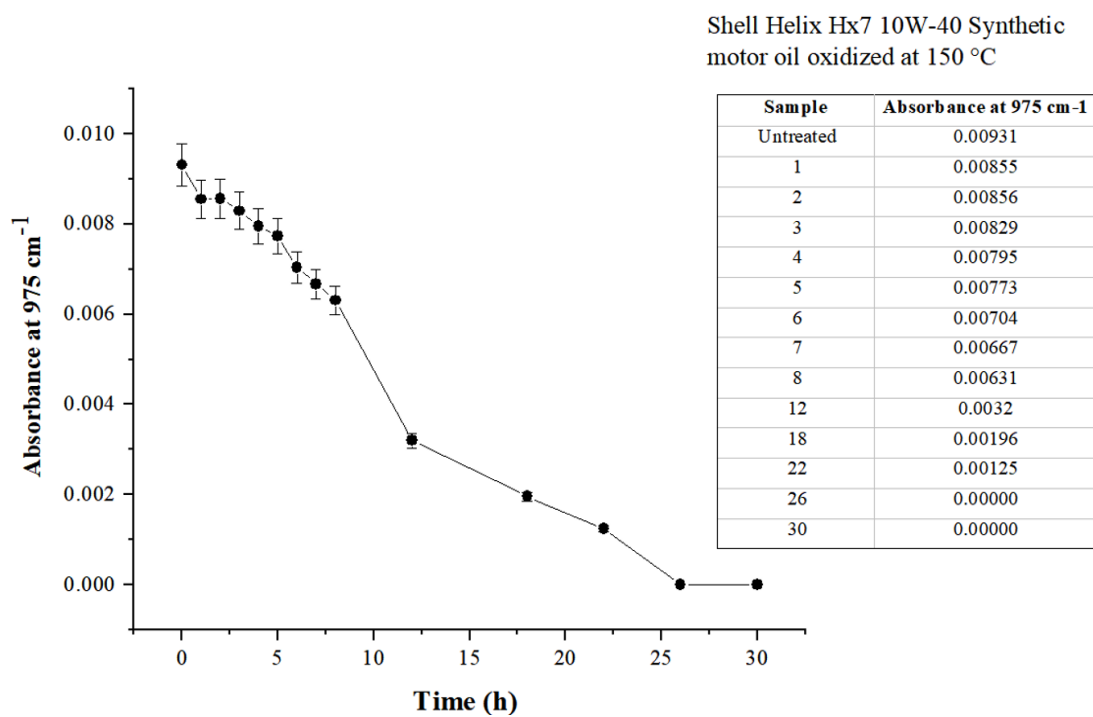


Figure 4.25: ZDDP additive degradation trend over 80 hours oxidation

As shown in Figure 4.23 and 4.24, ZDDP peak absorbance intensity degraded in slowly first eight hours, sharply dropped after 12 hours oxidation and approached to zero level after 30 hours oxidation. For Shell Helix Hx7 10W-40 Synthetic motor oil TES measurements, we soaked the oil samples to cellulose as also carried out in the previous sections for base oil and Castrol oil, but this time we tapped the cellulose on a Teflon disk (12.3 mm diameter, 0.07 mm thickness). As expected, the triboelectrification results show a decreasing trend, the generated Voc (absolute value) reduced to almost 20 times after 12 hours oxidation ($|-9.4|$ V (untreated oil) to $|-0.48|$ V) and reached to a saturation after 18 hours (the results fluctuated

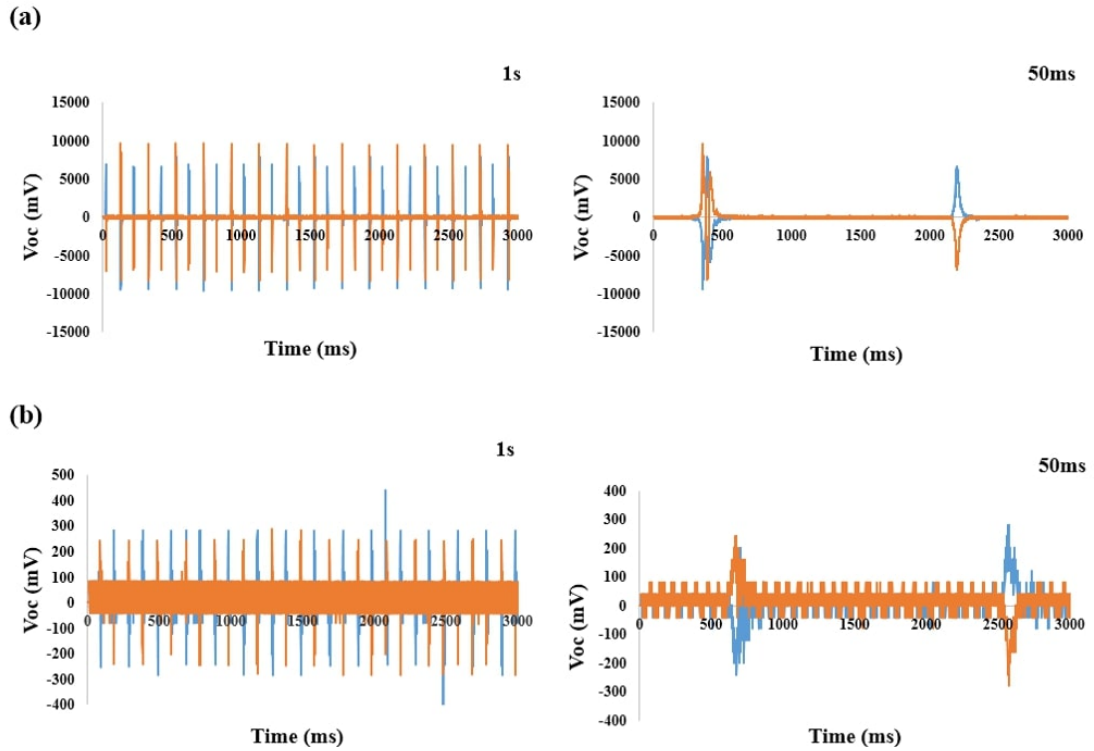


Figure 4.26: The generated Voc of (a) untreated (b) 34 hours oxidized Shell Helix Hx7 10W-40 Synthetic motor oil at 150 °C presented with 1 s and 50 ms time scale (Orange for PVC, blue for oil absorbed Teflon)

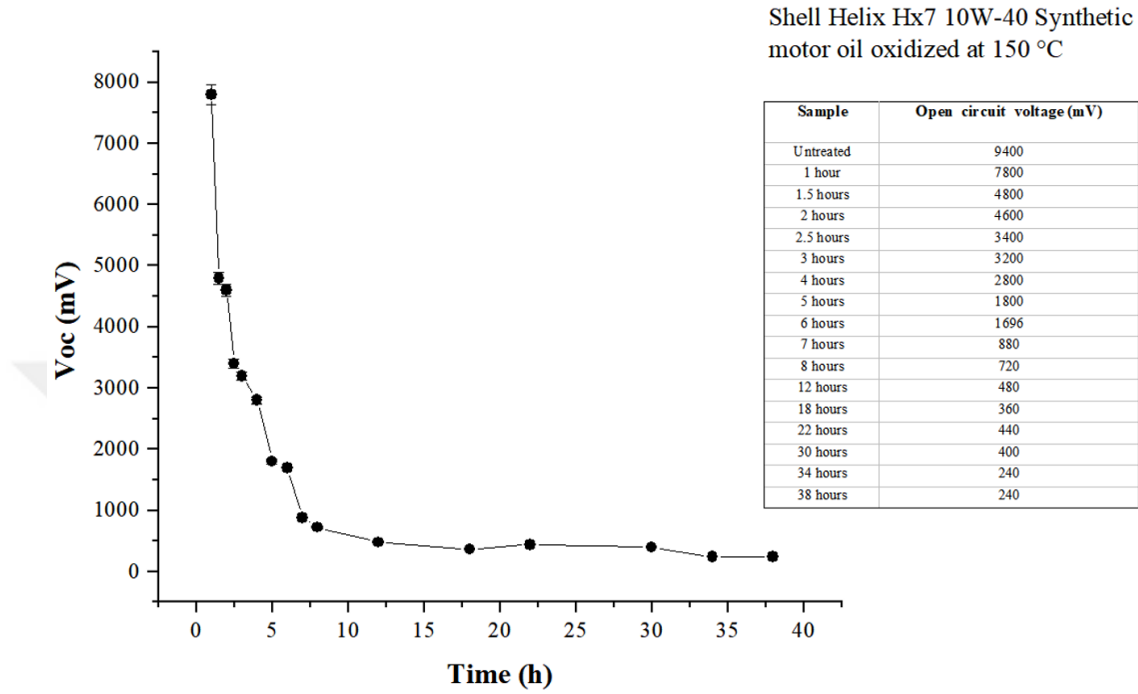


Figure 4.27: The electrification trend of Shell Helix Hx7 10W-40 Synthetic motor oil at 150 °C

4.4 Viscosity measurement results

The dynamic viscosity of the oxidized oil samples were performed on a Physica MCR 301 Rheometer as stated in detail in the previous chapter. Results show that the viscosity of the base oil slightly decreased until 3 hours of oxidation under 200 °C heating temperature. After that, the viscosity increased with increasing oxidation time. For the Castrol power 10W-40 motor oil, the viscosity did not change significantly for samples oxidized at 175 °C and 150 °C; for 200 °C it also remained unchanged up to 30 hours oxidation. For the Shell Helix HX7 10W-40 Synthetic motor oil, viscosity remained constant even when the oxidation time reached 40 hours under 150 °C heating temperature. The detailed results are shown in Figure 4.28.

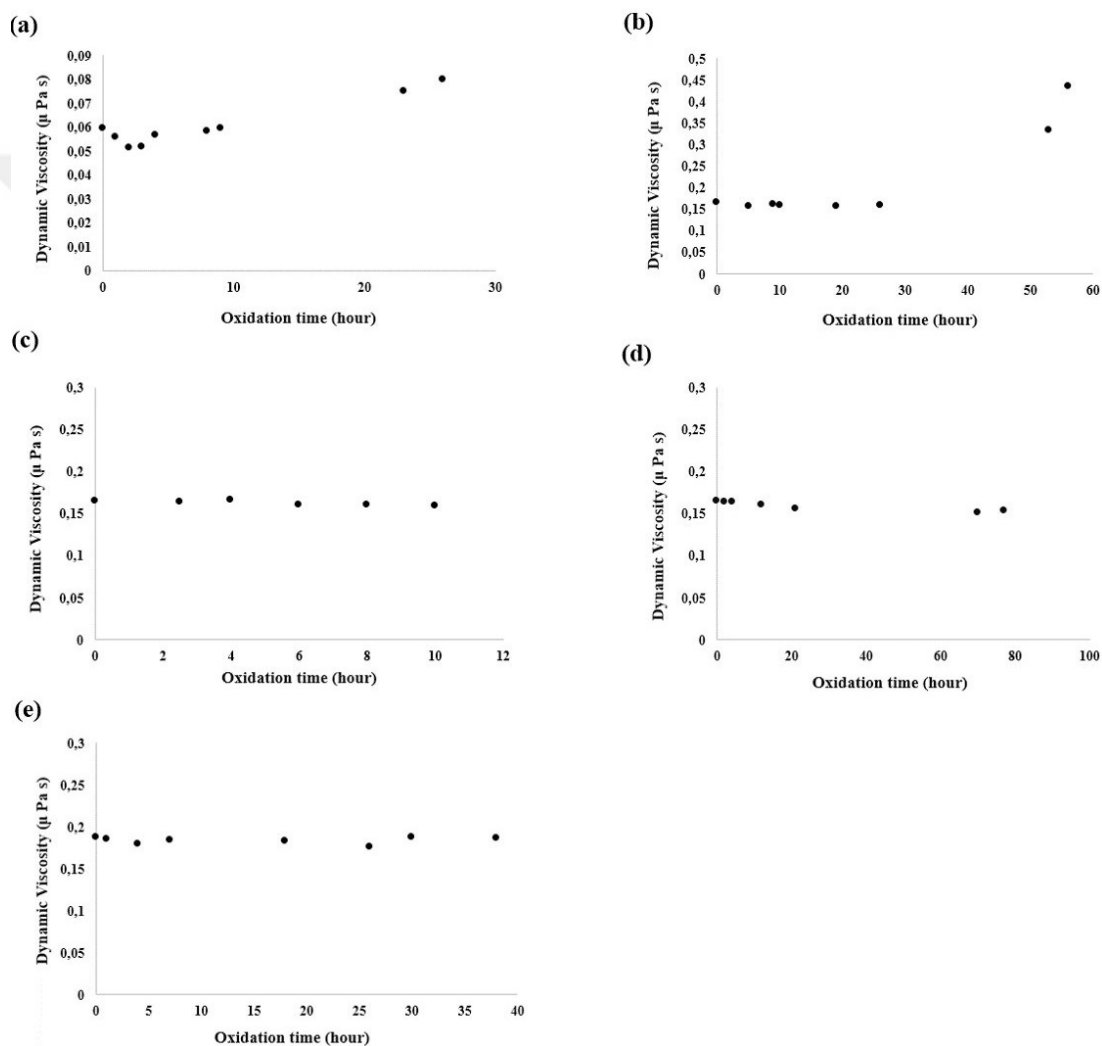


Figure 4.28: Dynamic viscosity changes versus oxidation time (a) SN 150 Base oil lubricant oxidation under 200 °C (b) Castrol Power 10W-40 motor oil oxidation under 200 °C (c) under 175 °C (d) under 150 °C (e) Shell Helix HX7 10W-40 motor oil oxidation under 150 °C

To interpret the results on viscosity, we can think about the following mechanisms of oxidation: One of the most important chemical reaction of a hydrocarbon is oxidation. This reaction is generally referred to as "combustion" or "burning" [50]. Combustion is divided into complete combustion and incomplete combustion. Incomplete combustion of the hydrocarbon chain of a lubricant can produce the carboxylic acid and other impurities [50]. This can be seen from Figure 4.28. In the earlier hours of oxidation, the viscosity of lubricant does not change significantly. However, a change can be observed when this oxidation reaction is prolonged and a large percentage of the molecules in the reservoir has been oxidized. The increases in viscosity as a result of oxidation can be explained by pointing to the polymerization of products making a sludge. Also, the new compounds created from oxidation are chemically quite different than the nonpolar oil molecules and introduce new forces of interaction between the molecules. For instance, carboxylic acid compounds can bound to each other via hydrogen bonding, causing them to behave as a larger molecule, ultimately, this would largely contribute to the increase in the viscosity of oxidized lubricant oil [50].

4.5 Triboelectrification results of untreated and oxidized oils with various polymers

In order to show the universality of the triboelectrification process of oils and its possible applications using in a large variety of polymers - in addition to the PVC and Teflon used as the contact material on the second electrode - we used different commodity polymers in the TES for the triboelectrification measurement for untreated and oxidized lubricant oil samples with different polymers. We also ranked these polymers in order of their electrification ability according to their signals obtained by tapping on untreated and oxidized lubricant oil. In our experiments, we selected 24 hours oxidized SN 150 base oil sample (oxidized at 200 °C) and 80 hours oxidized Castrol Power 10W-40 motor oil (oxidized at 150 °C) for the experiment. The Figure 4.29 shows the diagram displaying the values for untreated and oxidized oil.

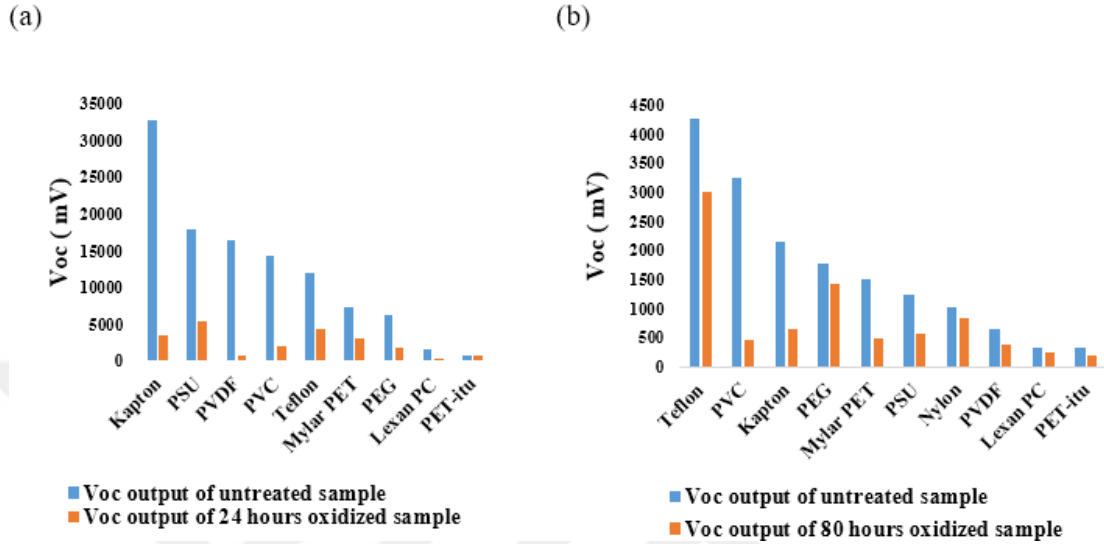


Figure 4.29: Comparison of the electrical output of (a) Clean and 24 hours oxidized base oil (b) Clean and 80 hours oxidized Castrol power 10W-40 motor oil on TES with different polymers

As shown in Figure 4.29 (a), Kapton is performing the highest Voc difference between oxidized and non-oxidized base oil; (b) the highest difference of Voc output between oxidized and non-oxidized Castrol engine oil is performed by PVC.

Finally, we took one used motor oil sample from the car which was driven 20000 km and carried out the triboelectrification measurement. The result was compared with the oxidized Castrol Power 10W 40 motor oil which was oxidized 70 hours under 150 °C. Figure 4.30 shows the two electrification results are very similar, used oil is showing Voc = 320 mV and the oxidized Castrol Power 10W 40 motor oil is showing Voc = 400 mV. IR absorbance peaks shown that the ZDDP additive is totally depleted in used motor oil. (Figure 4.31)

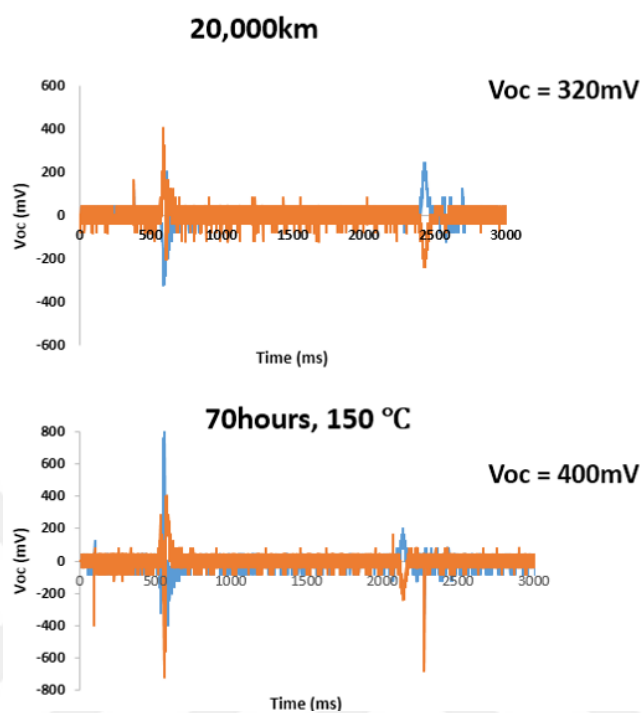


Figure 4.30: Comparison of the electrical output for used oil and 70 hours oxidized Castrol power 10W-40 motor oil under 150 °C

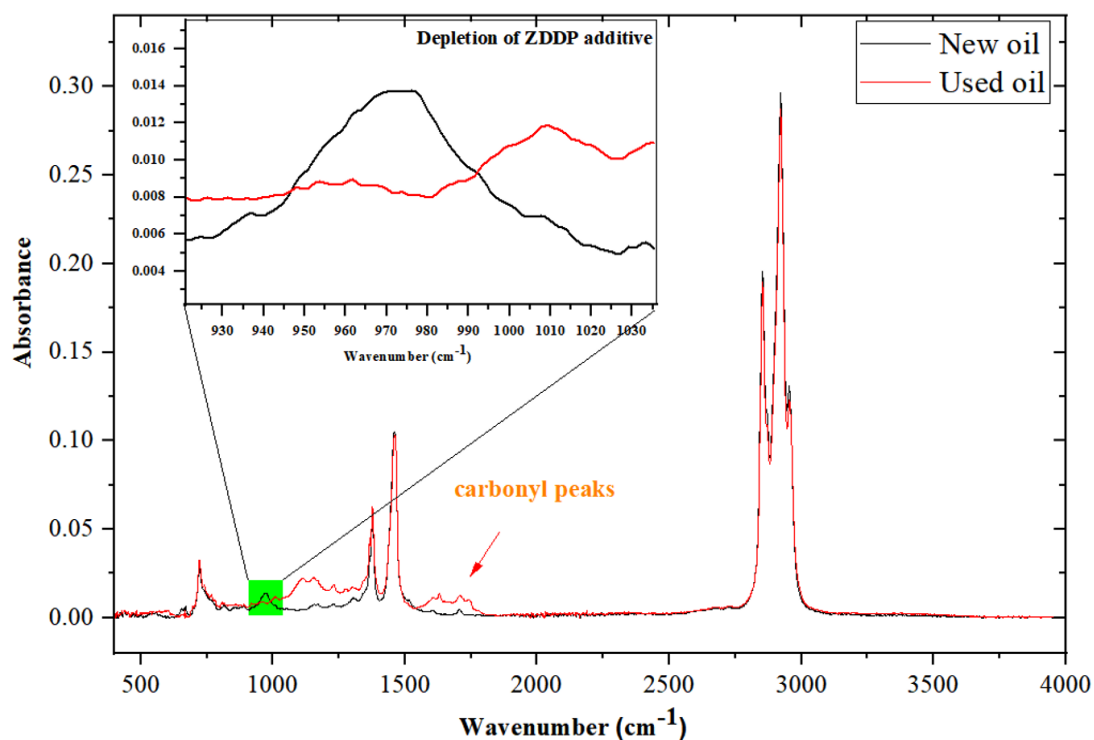


Figure 4.31: Comparison of the ZDDP peak for used oil and 70 hours oxidized Castrol power 10W-40 motor oil under 150 °C

4.6 Summary of this work

In this chapter, we have completed three main procedures for monitoring oil oxidation, which include oxidation of the oil, monitoring sample with ATR spectrometer and measuring its triboelectrification with TES device. Three types of oil were used in the experiments. For SN 150 base oil, the oxidation can be followed directly by the increase in the intensity of the carbonyl peak, which was observed **around** the wave number of 1710 cm^{-1} . For the motor oil, oxidation can be followed by this increase in the carbonyl absorption and also by the decrease in the absorption of the ZDDP additive. The additives, PMA and ZDDP found in Castrol Power 1 4T 10W-40 motorcycle oil were also found to affect the electrification ability. Additionally, we conducted the triboelectrification experiment with different contact polymer materials such as Kapton, Polysulfone, Polyvinylidene fluoride etc. for determining which of the material give the highest Voc difference between oxidized and non-oxidized oil. Moreover, we have investigated the correlation between viscosity changes and the oxidation time of all types of oil which were mentioned. We found that for all oils, if the oxidation temperature is lower than $200\text{ }^{\circ}\text{C}$, the viscosity of lubricant oil does not show any major changes in 50-80 hours of oxidation period, which indicates that the differences in the triboelectric signals arise from the chemical changes in the sample, and are not related to any viscosity change.

Chapter 5

Conclusion

As referred in our literature study, research in practical, simple and intuitive methodologies for monitoring oil condition and prediction remaining useful life to optimize oil change intervals hitherto have been yielded different sensor devices and mentionable achievements in the field of engine lubrication. Moreover, these special designs bring valuable insights to engineers and help them to come up with many innovative methodologies. However, current methods for detecting the degradation level of usability in lubricant oil are not satisfied for several reasons:

- . Developed devices or sensors are not practical enough due to some essential instruments;
- . Are not viable for online monitoring in some case of need;
- . From economic and time-consuming aspects, there are still not have prevailing distinction;
- . Are not able to give direct and precise data some time;
- . Not suitable for long-term and large-scale application;
- . In the case of sustainability and environmental problem, there are still in the phase of improving.

These shortages lead us to generate a sensor which can provide more cost-effective, highly usable, high performance and firsthand method with simplified

operations. In this chapter, we will conclude the works we have done and summarize the overall advantages of our method. Furthermore, based on our studies, some future improvements and recommendations are presented.

5.1 Specialty of our method

In this thesis study, it was shown that a simple sensor setup which is based on triboelectrification principle, featuring a low-cost oil condition detector and capable of giving direct analytical information of additive degradation with sufficient sensitivity by measuring the electrical output signal (Voc). The presented contact materials (PVC, PTFE etc.) in the sensor device are proved reusable after being refurbished with ethyl alcohol. This feature has supplemented the sustainability of our method and device. In addition, at a fixed impact force and frequency of contact separation (1 Hz), the generated power itself is capable of indicating the oxidation state of base oil and residual availability of engine oil (by the indication of remaining ZDDP additive which is most important in general). This property has the potential to get it close to green energy usage. Moreover, the system could be designed to harvest kinetic impact energy in a self-powered manner without supplying an external power. From the aspect of economy and time consumption, the triboelectric sensor device is quite handy and practical. It gives the desired result directly and no need for a laboratory or computational analysis, therefore the sensing process is not long-drawn. Besides, no need for taking a lot of huge testers or equipment, hence it is quite portable and economical.

The justified concept of the triboelectric sensor is environment friendly compared to traditional methods, which would be to draw more people from the fields of ecological sanitation, wastewater and waste oil treatment, environmental degradation, monitoring, assessment and sustainability [47]. Next, I will present some future improvements based on the current developed device and recommendations.

5.2 Future works

Based on our thesis study, we have generalized some potential development which comprises feature, performance, and veracity enhancement on the TES device.

The sensor setup which is utilized in experiment potentially allows a miniaturization, which makes this concept utilizable directly inside of the oil chamber of the engine or online monitoring depends on a compact and robust triboelectric sensor system. This improvement would reduce the material usage, e.g., the measurement process no longer needs for cellulose paper. This time the contact materials can be metal and polymers, but the polymer selection should be considered as high thermal stability and resisting property. Furthermore, it can be developed as a stationary structure for online monitoring of oil condition in some factory line where the engine lubricant should be replaced constantly. This idea would make an enormous contribution to the fabrication line in terms of saving oil cost, expenses of labor, and most importantly it will help to less downtime by correctly estimating the exact time of oil replacement. Considering its high sensitivity, flexibility, and simplicity, we believe the innovative mechanism of TES will become a point of inspiration for related TES studies and contribute to the future development of self-powered triboelectric sensors.

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