

# Oil Condition Monitoring Degradation Mechanisms and Additive Depletion

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**Abstract**—Primarily designed to provide hydrodynamic friction between mechanical parts of a mechanical engine, lubricating oils are hydrocarbon mixtures composed of base oils and chemical enhancers or additives. The degradation of a lubricant should be regarded as a result of depletion in its additives. Through an extensive analysis of various grades of car engine oils, this work intended to elucidate the chemical mechanisms responsible of depletion in additives, thus loss of efficiency. Using both analytical tools and traditional oil condition monitoring techniques, performance enhancers degradation was found to be induced by a complex tribo-chemistry process occurring within the engine. Furthermore, physical conditions existing within were believed to promote oxidation processes that yielded acidic materials causing lubricant performance alteration. Triggered by wear metals, it has been established that conversion of antioxidant additives along with inhibition of antiwears were primary reasons of loss of efficiency. This study has not only highlighted the catalytic and inhibiting strength of wear metals, but also it has discussed, on a chemical point of view, mechanisms leading to additive depletions.

**Keywords**—*lubricating oils; degradation additives; antioxidants; antiwears; infrared spectroscopy*

## I. INTRODUCTION

This Lubricating oils are complex composite of hydrocarbons blended with chemical enhancers known as additives designed to operate under hostile environment. Their prime function is to provide a hydrodynamic lubrication on the surface onto which they are dispersed [1,2]. The type of additive as well as the concentration to be blended in a specific lube oil base is dependent to various factors including engine specifications, the physical property to be upgraded. Thus, degraded lubricating oils should be regarded as a result of depletion of its chemical enhancers that have undergone through chemistry, which is yet to be fully understood [3,4].

Acidic materials, generated during combustion within the engine, are responsible of corrosion of sliding parts [5]. An incomplete, process whereby lubricating oil and air are come in contact, produces carbonaceous particles that further deposit in the oil in

the form of soot. In other hands, metals, usually present in lubricating in trace amount, are believed to be one of the major sources of external contamination [6]. In excess, wear metals are likely to behave as catalysts. Produced as free radicals, they hasten a series of chemical reactions following Jones's oxidation chemistry, which invariably increases acidity within the car engine oil [7].

In that regards, oil condition monitoring has been extensively investigated through various techniques over the last decades. Fast Transform Fourier Infrared (FT-IR), as an analytical tool, has been introduced in the engine oil analysis to identify degraded compounds imputed to depletion in additives [8-10]. By minimizing the spectral variation issue often encountered in oil condition using traditional FTIR, a combined technique known as Attenuated total reflectance (atr-FTIR), was introduced and it was believed to provide a better accuracy in results. Metallic components are introduced in low concentration in lube oils; concentration above which they become poisonous or precursors of wear within the engine [11]. Literature reported Flame Atomic Absorption Spectroscopy (FAAS) as an elemental detection technique with a broad range of detectable metals widely used in oil condition monitoring [12]. The span of detectable elements has been broadened by the introduction of induced Coupled Plasma (ICP-OES) [13-16].

Given the wide range of metals in engine oils, in this paper, only iron (Fe), copper (Cu) and chromium (Cr) were investigated because of their potential as Jones's catalysts [17]. Moreover, we have combined the use of analytical methods to elucidate the mechanisms responsible of additive depletions.

## II. EXPERIMENTAL PROCEDURE

### A. Materials and sampling

Two grades of lubricating oils were selected for this study. Two engine cars, travelling mainly within the city, were selected as models. Prior the experimental investigation, the engines were cleaned and have undergone through a spot-checked to minimize any external poisoning. The samples were collected at a regular interval of 500 kms and were centrifuged to eliminate solid materials present during the sampling. TABLE I outlines the characteristics of lubricating oils used in this research.

TABLE I. LUBRICATING OILS CHARACTERISTICS AND SAMPLING DISTANCE

Type of Lubricating Oil	Lubricating Oil Grade	Sampling Distance, In Kms
Fully synthetic	5W-40	0
		1850
		2320
		2800
		3220
Semi-synthetic	15W-40	0
		2387
		3251
		4522
		5100

**B. Measurement techniques**

**1) Kinematic viscosity**

Kinematic viscosity was determined using viscometer bath apparatus (Model 18V Julabo). 5 ml of the used lubricating oil was introduced in a Cannon-Fenske viscometer (model 200, N48). The efflux time required by a sample to flow through the tube was recorded. Viscosity Index (VI) was further computed using the kinematic viscosities trended at 40°C and 100°C [18].

**2) Refractive Index and Insoluble Content.**

Refractive Index (RI) was determined at room temperature using Abbe Refractometer. A drop of sample was deposited on the holder and the corresponding value was read therefrom. Insoluble Content was determined following a technique as described by Callat (1975) [19]. The used oil was diluted in a benzene solution (Merck, Darmstadt, Germany), vacuum-filtered and dried at constant temperature of 90°C during 3 days. Insoluble Content was obtained by subtracting the weight of the filter before drying from its initial weight.

**3) Acid Number and Spectral analysis.**

Total Acid Number (TAN) was measured through a conventional potentiometric titration. The mixed solution was prepared by mixing toluene (Merck, Darmstadt, Germany), isopropanol (Merck, Darmstadt, Germany) and water at ratio 1:0.99:0.01; (v:v:v). The titrant solution was obtained by diluting potassium hydroxide (Merck, Darmstadt, Germany) in isopropanol. Used lubricating oil was blended with mixed solvent, at a ratio of 1:6 (v:v) and further titrated.

A pH meter was used to monitor the change in acidity throughout the potentiometric titration.

Ultraviolet absorption spectroscopy was performed with a Hitachi U-2900 spectrophotometer (Hitachi, Japan). The spectra were smoothed using Savitsky-Golay method and overlaid from 200 nm to 1000 nm. The scan speed was set at 40nm/ min with a sampling interval of 1.0 nm. The stock solutions used to generate the spectra were prepared by diluting into 0.1 mg of sample into methyl ethyl ketone (Merck, Darmstadt, Germany) at ratio of 0.1% (% w/v).

Wear metal analysis was performed using Perkin Elmer AAnalyst 400 (Perkin-Elmer, Malaysia). Three different lamps, iron, chromium and copper were used. Standard solutions were prepared from a stock of 1000 ppm of respective elements. Further serial of dilutions were performed to obtain the desired standard solutions.

Infrared analysis was conducted using Perkin Elmer atr FT-IR (Perkin-Elmer, Malaysia). A drop of the sample was deposited on the crystal diamond surface. The values obtained were based on transmittance with a wavelength scan ranging from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The equipment was set at 16 scans with a generated spectrum, which has a resolution of 0.4 cm<sup>-1</sup> for 3028 cm<sup>-1</sup> in band in methane.

**III. RESULTS AND DISCUSSION**

**A. Rheological analysis**

Viscosity Improvers are additives designed to stabilize viscosity and to optimize the rheological properties of the oil. Fig. 1 depicts the behavior of VI improvers within the investigated lubricating oils.

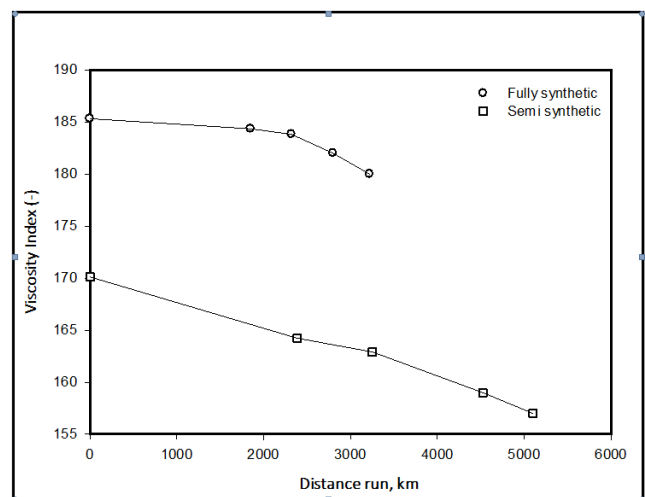


Fig. 1. Viscosity Index monitoring

VI improvers were found to decrease linearly with the increase of the mileage. Also, the fully synthetic model has shown a better resistance towards shear forces comparatively to semi-synthetic model. This observation is thought to be imputed the difference in the base stock of the two car engine oils.

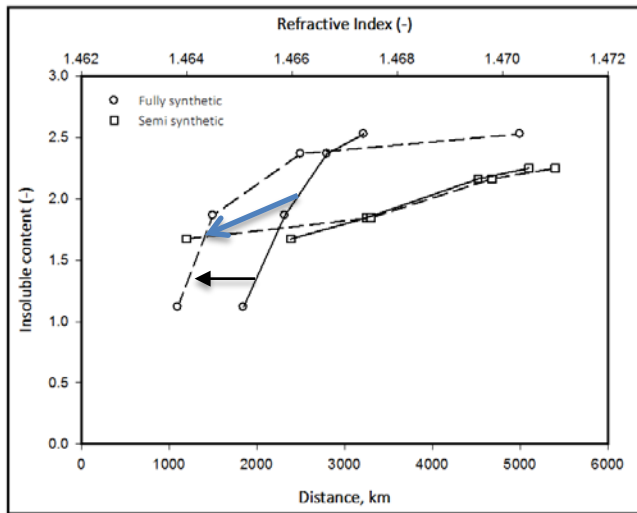


Fig. 2 Oil thickening analysis

Throughout its working life, car engine oil is contaminated by external factors including dirt, wear and/or incomplete products from fuel combustion. As illustrated in Fig. 2, the build-up in foreign particles was found to increase steadily with the mileage. Both fully synthetic and semi synthetic models exhibited a rapid increment the first 2000 kms followed by a constancy for the first model while the latter kept increasing. The difference in blend of dispersant and detergent additives between both is believed to explain such pattern. Also, from Fig. 2, it could be seen that above a certain mileage, insoluble content has reached a concentration sufficient enough to promote chemical reactions within the lubricating oil that invariably alter the performance.

### B. Chemical and elemental analyses

Total Acid Number showed several equivalence points characteristic of polyacidic materials. Polyprotic compounds are formed during oxidation processes of lubricating oils triggered by foreign materials e.g. wear metals. In order to have account the extent to which concentration of wear impacts oxidation processes, elemental analysis has been conducted as outlined in TABLE II.

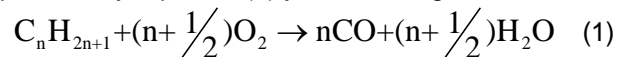
TABLE II. RESULTS OF ELEMENTAL ANALYSIS OF FE, CR AND CU

Distance, in kms	Fully Synthetic Oil		
	Fe <sup>3+</sup> /Fe <sup>2+</sup> in ppm	Cu <sup>2+</sup> in ppm	Cr <sup>3+</sup> in ppm
0	83.95	<1	<1
1850	119.7	<1	<1
2320	124.5	<1	<1
2800	126.5	<1	<1
3220	129.3	<1	<1
Semi Synthetic Oil			
0	129.4	<1	<1
2387	145.2	<1	<1
3251	159.1	<1	<1
4522	162.8	<1	<1
5100	164.2	<1	<1

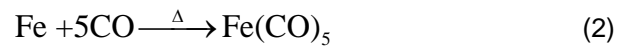
Therefore, the acidity number was evaluated in respect of the iron content whose concentration was found significant as illustrated in Fig. 3. Being a transition metal, iron has various oxidations states, which enables this metal to yield easily free radicals

Acidity within fully synthetic model remained constant regardless build-up in iron concentration while semi synthetic model was found to be strongly iron-dependent. Given operating conditions within the engine, our work believes the combined effect of both foreign particles and iron concentration was sufficient enough to promote free radicals, which subsequently induced oxidation processes.

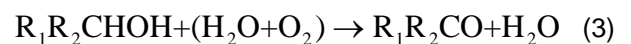
Incomplete combustion of alkyl radical as expressed by equation (1) yields starting materials.



Iron from the wear further combined with carbon monoxide to produce iron carbonyl compounds following a chemistry as expressed by equation (2) [7, 17, 20].



Furthermore, under specific conditions, hydroxyls may be converted into alkyl carbonyls according to equation (3) [21, 22].



where R<sub>1</sub> and R<sub>2</sub> are alkyl or aryl radicals that form the base stock of the lubricant.

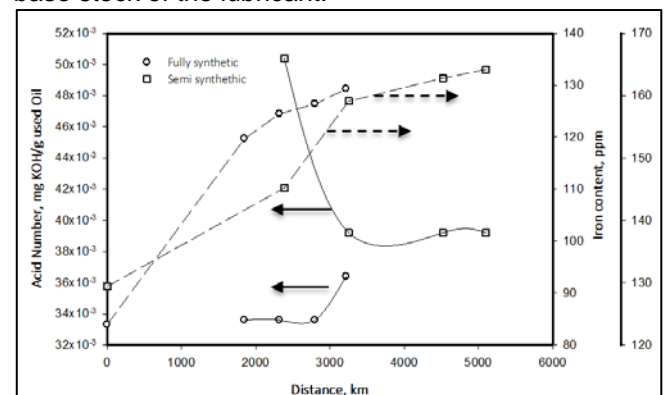


Fig. 3 Acidity monitoring in function of wear metal apparition in used lubricating oils

### A. Lubricating degradation and spectral analysis

In this research, Ultraviolet visible spectroscopy has been telltale of unsaturated materials present in the car engine oils. At different mileage, the samples have shown three strong absorptions around 325 nm, 900 nm, and 950 nm as it is shown on Fig. 4.

Strong peaks suggested the presence of highly conjugated materials such as polyenes or conjugated carbonyl compounds whose radical might be a polyphenyl and/or olefin yielded during lube oil oxidation. Also, the presence of heteroatoms, either from wear metals or degraded additives or both, strengthen peaks of absorption as electronic transitions ( $\sigma \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$ ) require high energy. Such unsaturated materials are highly undesirable, as they tend to polymerize and to form gum or sludge.

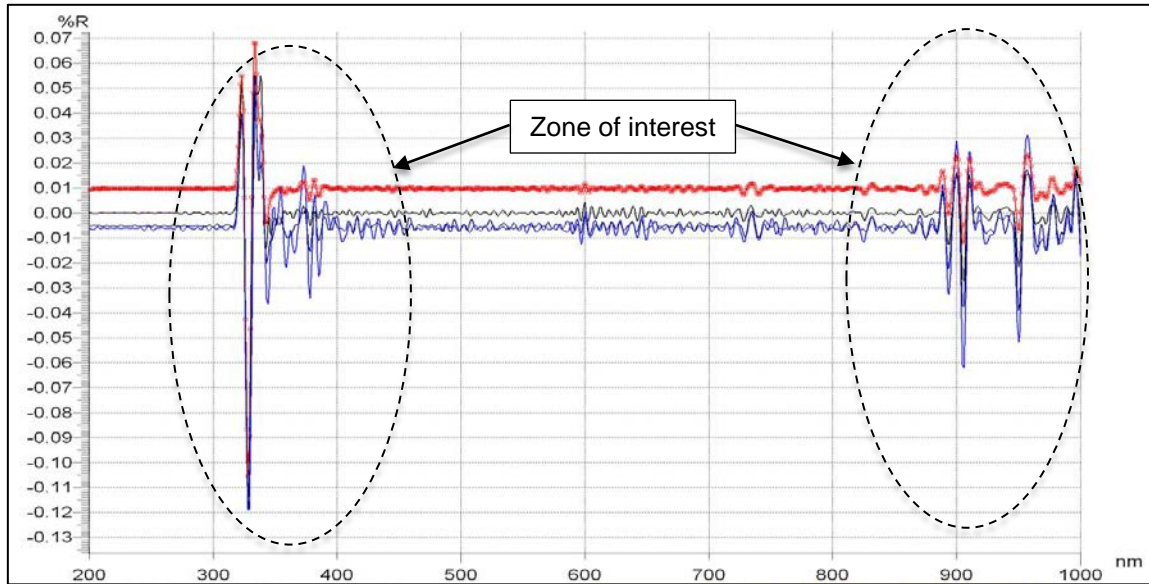


Fig.4 UV Spectra of used semi synthetic oil at various mileage

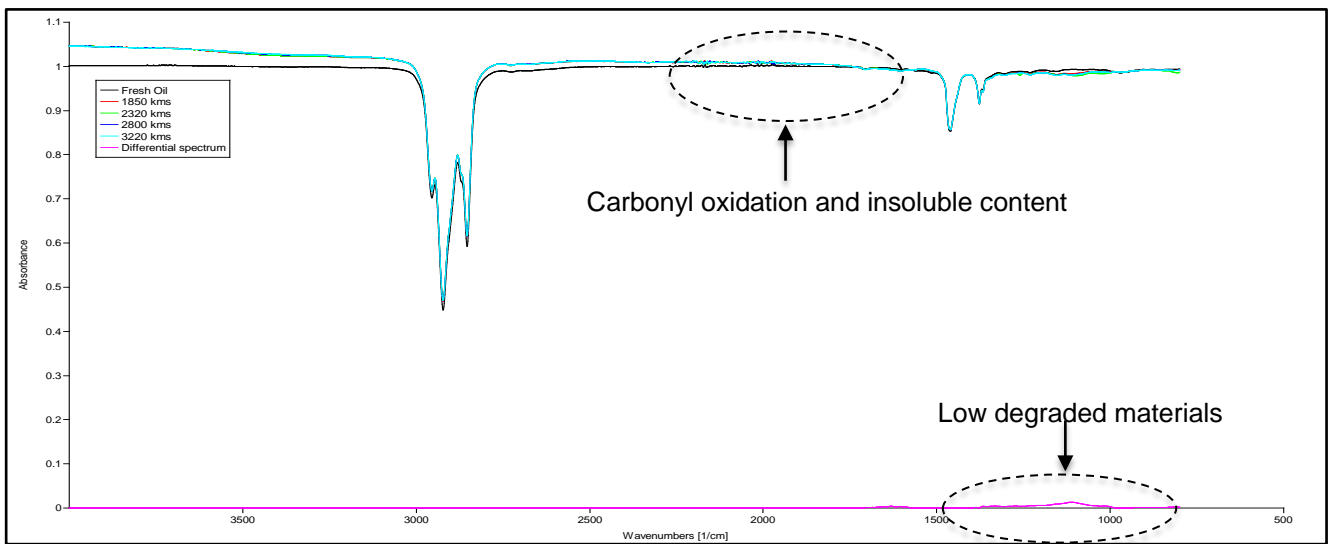


Fig. 5a Infrared spectra of fully synthetic at different mileages

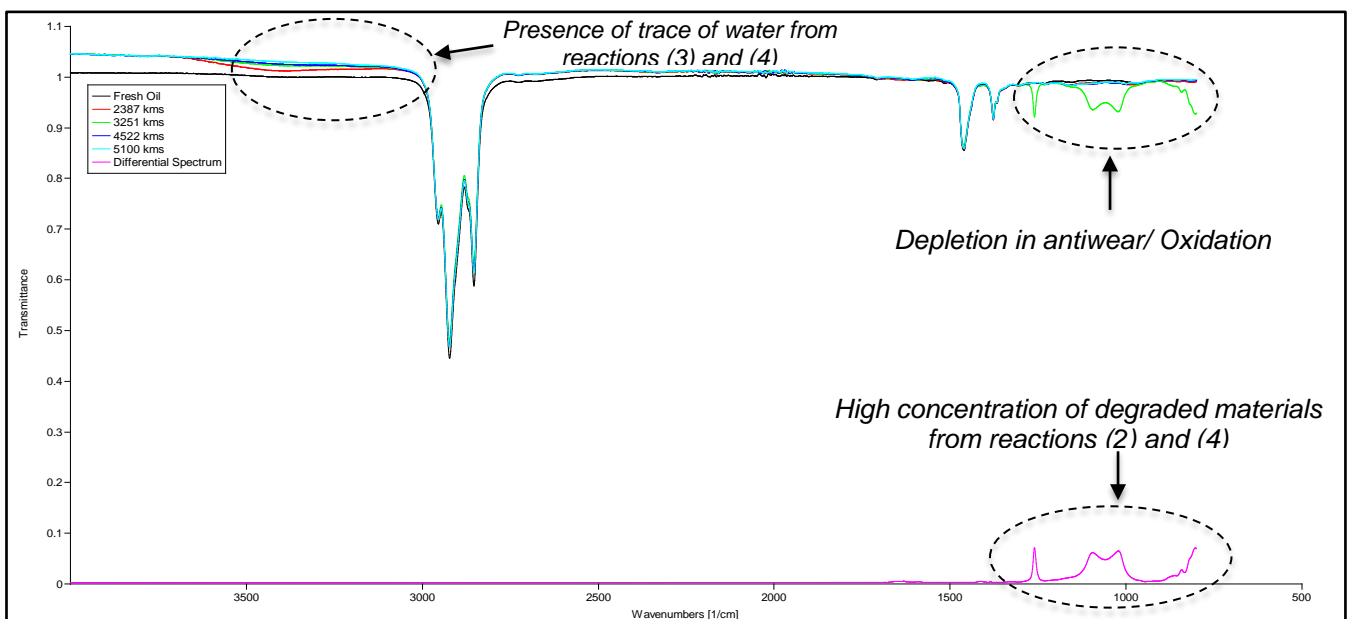


Fig. 5b Infrared spectra of semi synthetic at different mileages



Infrared analysis of used lubricants was performed for both fully and semi synthetic oils and the spectra obtained are shown in *Fig. 5a* and *Fig. 5b* respectively. The differential spectra sought to determine the regions of the spectrum characteristic of depletion in additives or regions subjected to major changes in chemical composition of the lubricating oil.

A peak of a fair intensity was observed around  $1000\text{ cm}^{-1}$ . The vibration is associated to an asymmetric motion P-O-C, found in zinc dithiophosphate (ZDDP) an anti-wear additive [23]. With the usage, metals poisoned the lubricating oil. Elemental analysis has revealed that iron (Fe) was believed to induced a chemical reaction (1) into which ZDDP is inhibited. As the wear within the engine builds-up, depletion in antiwears was enhanced.

Around  $1100\text{ cm}^{-1}$ - $1200\text{ cm}^{-1}$ , an absorption peak associated to an asymmetric motion of  $-\text{SO}_3$ , suggested the presence of sulfur oxides, which are likely to be yielded during oxidation process. At elevated temperatures, oil reacts with sulfured materials to form as sulfur oxides ( $\text{SO}_3$  or  $\text{SO}_2$ ) that combine with free water to yield acidic materials. The broadness of the peak observed at  $3000\text{ cm}^{-1}$ , implied a broad variety of acidic compounds formed including carbonyl materials. While at  $1630\text{ cm}^{-1}$ , a weak peak, associated stretch of  $-\text{N}=\text{O}$ , was observed. Produced during nitration of oil, nitrated compounds tend to hasten the process of oxidation of oil. Also, this peak asserted the presence of unsaturated materials as observed in UV-Vis spectra. Absorption credited to the presence of carbonyl compounds, was observed around  $1700\text{ cm}^{-1}$ - $1750\text{ cm}^{-1}$ . It was found to be a result of  $\text{C}=\text{O}$  stretching motion. Carbonyls are produced via a tribochemistry involving engine oils, oxygen, and wear metals. Under specific conditions, lubricating oil oxidizes and yields acidic materials. Moreover, this region is known to interfere with VI improvers, which explains the decrease observed in *Fig. 1*.

Hydroxyl group ( $-\text{OH}$ ) of water, detected at  $3200\text{ cm}^{-1}$ , revealed the presence of water. Water detected on the spectra was believed to be a by-product of dehydration of hydroxyl materials or their conversion into carbonyl compounds following chemistry as expressed by equation (4),



where  $\text{R}_1$ ,  $\text{R}_2$ , are either alkyl or aryl or both radicals of the lubricating oil base stock.

#### IV. CONCLUSIONS

The performance of an engine depends of the condition monitoring of its lubricating oils. This paper has extensively discussed on the degradation of car engine oils and the mechanism incriminated by means of analytical methods supported by traditional techniques. The loss of performance of a typical lubricating oil, rather to be exclusive to a single mechanism, is results of several processes resulting

from a complex chemistry. Also, additives depleted in lubricant following oxidation processes triggered by wear metals. Furthermore, the use of analytical tools including UV-Visible, elemental spectroscopy and infrared was revealed as excellent screening tool in engine oils analysis.

#### REFERENCES

- [1] D. Mann, "Motor oils and engine lubrication," *Motor Oil. Eng.*, pp. 5-1, 2008.
- [2] R. M. Mortier, M. F. Fox, and S. T. Orszulik, "Chemistry and Technology of Lubricants," Springer, 2010, pp. 107-152, 2010.
- [3] A. Geach, "Infrared analysis as a tool for assessing degradation in used engine lubricants," *Wearcheck Afr.*, WZA-002 1996.
- [4] J. S. Evans, *Oil Analysis Handbook*. Oxfordshire, United Kingdom, 2008.
- [5] T. McKenzie, "Atomic absorption spectrophotometry for the analysis of wear metals in oil samples," *Varian At. Absorpt.*, vol. AA-10, pp. 1-3, 1981.
- [6] P. K. Tamrakar and K. S. Pitre, "Electroanalysis of trace metals in lubricating oils," *Bull. Electrochem.*, vol. 18, 2002, pp. 35-40.
- [7] R. F. Daley and Sa. J. Daley, *Organic Chemistry handbook*, 998-1031, 2008.
- [8] A. M. Toms, J. R. Powell and J. Dixon, "The Utilization of FT-IR for Army Oil Condition Monitoring," *Proceeding. 1998 JOAP [International Condition Monitoring Conference*, p. 170-176, 1998].
- [9] . M. C. Garry and J. Bowman, "FT-IR Analysis of Used Lubricating Oils –General Considerations," *Thermo Fisher Scientific*, 2007
- [10] R. Nguete, H. S. Al-Salim and K. Mohammad, "Modeling and Forecasting of Depletion of Additives in Car Engine Oils Using Attenuated Total Reflectance Fast Transform Infrared Spectroscopy," *Lubricants*, vol. 2, pp. 206-222, 2014.
- [11] J. A. Burrows, J. C. Heerdt and J. B. WILLIS, "Determination of Wear Metals in Used Lubricating Oils by Atomic Absorption Spectrometry," *Anal. Chem.*, vol. 37, pp. 579-582, 1965.
- [12] . E. O. Ojeka, "Application of mixed solvent system in the determination of metals in lubricating oils using atomic absorption spectrometry," *Bull. Chem. Soc. Ethiop.*, pp. 149-153, 2006.
- [13] V. A. Fassel, C. A. Peterson, F. N. Abercrombie and R. N. Kniseley,

- "Simultaneous Determination of Wear Metals in Lubricating Oils by Inductively-Coupled Plasma Atomic Emission Spectrometry," *Anal.Chem.*, vol. 48, pp. 516-519, 1976.
- [14] J. Mora, J. L. Todolí, F. J. Sempere, A. Canals and V. Hernandis, "Determination of metals in lubricating oils by flame atomic absorption spectrometry using a single-bore high-pressure pneumatic nebulizer," *R. Soc. Chem.*, pp. 244-2349, 2000.
- [15] B. Rahimi, A. Semnani, A. Nezamzade Ejhieh, H. S. Langeroodi, and M. H. Davood, "Application of ICP-OES in the Comparative Analysis of a Used and Fresh Gasoline Motor Oil," *Glo. J. Sci. Front. Res. Chem.*, vol.12, pp. 9-11, 2012.
- [16] D. Hilligoss, "Analysis of wear metals and additive package elements in new and used oil using the optima 8300 ICP-OES with flat plate plasma technology," Perkin Elmer. Inc, 2012.
- [17] P. Patnaik, "Handbook of Inorganic Book Chemistry," Mc Graw Hill, New-York, 2002.
- [18] G. Denis, H. Briant, and B. Hipeaux, "Lubricant Properties Analysis and Testing," Technip, 2000
- [19] R Callat, "Rapid methods for the analysis of used oils," *Sci. Publ.*, 1973.
- [20] R. J. Anderson, D. J. Bendell and P. W. Groundwater, "Organic spectroscopic analysis," *R. Soc. Chem.*, pp 7-19, 2004.
- [21] S. E. Martin and A. Garrone, "Efficient solvent-free iron (III) catalyzed oxidation of alcohols by hydrogen peroxide." *Tetrahedron Lett.*, vol. 44, pp. 549 – 552, 2003.
- [22] F. Rajabi, A. Pineda, S. Naserian, A. M. Balu, R. Luque and A. A. Romero, "Aqueous oxidation of alcohols catalysed by recoverable iron oxide
- [23] T. J. Cardwell, R. Colton, N. Lambropoulos, J. C. Traeger, and P. J. Marriott, "Electrospray mass spectrometry of zinc dithiophosphate derivatives and its application to the analysis of engine oil antiwear additives," *Anal. Chim. Acta*, vol. 280, pp. 239-244, 1993..