Physicochemical Characterization of the Synthetic Lubricating Oils Degradation under the Effect of Vehicle Engine Operation

Soukayna Zzeyani [1,2*], Mohammed Mikou [1], Jamal Naja [2]

[1] Laboratory of Systems Analysis and Information Processing, Hassan 1st University Faculty of Science and Technology, Settat, MOROCCO

[2] Laboratory of Applied Chemistry and Environment, Hassan 1st University Faculty of Science and Technology, Settat, MOROCCO

ABSTRACT

The degradation analysis of three categories the synthetic lubricating oils during operation of the vehicle engine was undertaken according the number of kilometers covered, using the evaluation of viscosity, basicity, pour point, flash point, formation of heavy metals from the engine abrasion phenomena, that will detect by inductively coupled plasma optical emission spectrometry (ICP/OES), and the differentiation of the chemical composition of virgin and degraded lubricating oil using gas chromatography associated with mass spectrometry (GC/MS). These analyzes reveal the regular decrease of the viscosity, the basicity, the flash point and the significant evolution of the iron and lead content and the formation of polycyclic aromatic hydrocarbons. Thus, the important degradation of the additives tends to thicken the lubricating oil and consequently the continuous increase in the pour point.

Keywords: degradation analysis, lubricating oil, chemical composition, GC/MS, ICP/OES

INTRODUCTION

Engine and turbine components undergo continual wear under normal operating conditions. This wear is of physical origin (friction between metallic parts, high temperature and pressure) and chemical origin (corrosion) [1]. To minimize the wear, the lubricating oils are used. These latter are composed of paraffinic, naphthenic and, to a lesser extent, aromatic hydrocarbons. Several additives, including metalloorganic ones, are also part of the final composition of commercial lubricating oils. During operation of the engine, the lubricating oil is degraded and these physicochemical properties are modified. Thus used oil is composed of a complex mixture of a considerable number of different compounds derived from the original base oil, its additives, lubricating oil degradation products, wear metals and contaminants.

At elevated temperatures, lubricating oil exposed to oxygen from the air, will oxidize to form a variety of compounds, which can be measured by different spectroscopic techniques [2], this oxidation of the lubricating oil is represented by a series of chemical reactions initiated and propagated by free radicals as a function of the degradation rate of the lubricating oil [3].

It should be noted that the majority of the particulate matter in the lubricating oils comes from the scraping down due to the motion of rings or from the blowby gases [4].

As a result, the operating conditions undergo high thermal stresses and the excess of air required for the diesel combustion lead to a highly oxidizing environment in the lubricating oil sump. For this purpose, we will follow the evolution of viscosity, viscosity index, pour point, flash point under the effect of operation of the vehicle engine of different categories of lubricating oils.

Table 1. Experimental and standard rheological properties of the lubricating oils

properties / Lubricating Oil category	Test method	SAE-5W40 standard	SAE-5W40 measured	SAE-5W30 standard	SAE-5W30 measured	SAE-10W40 standard	SAE-10W40 measured
Kinematic viscosity at 40 °C (cSt)	ASTM D445	90	**89,21**	63,48	**62,73**	90.9	**89,79**
Dynamic viscosity at 100 °C (cP)	ASTM D2983	14,7	**13,42**	10,60	**10,72**	13.9	**12,92**
Viscosity index(°C)	ASTM D2270	172	**171**	157	**158**	156	**153**
Pour point (°C)	ASTM D 97	-39	**-40**	-36	**-37**	-42	**-42,5**
Flash point (°C)	ASTM D93	230	**228**	234	**232**	230	**229**
TBN (mg KOH/g)	ASTM D2896	8,12	**7,98**	7,35	**7,29**	8.25	**8,23**

In addition, the analysis of heavy metals in motor oils aims to detect failures of engine components at an early stage before major damage, because metals such as iron (Fe), chromium (Cr), aluminum (Al), lead (Pd) and cadmium (Cd) may indicate engine wear or any compartment containing lubricating oil [1]. However, for silicon (Si) metals, sodium (Na) and boron (B) can explain a contamination that could lead to system failure, but the degradation of metals from additives such as calcium (Ca), phosphorus (P) and zinc (Zn) causes variation in rheological properties of lubricant [5-6]. The purpose of this study is to determine the evolution of the content metals in the lubricating oil during operation of the vehicle engine.

Moreover, the identification of the chemical elements responsible for the degradation of lubricating oils was undertaken using GC/MS, this identification is essential to understand the aging mechanism of lubricating oils [7-8]. Several extraction techniques exist, but extraction by GC/MS remains the most relevant for isolating organic species from a fluid sample. This technique has main advantages the efficiency of the extraction of the analytes from a complex matrix and the absence of filtration steps [9].

MATERIALS AND METHODS

The synthetic oil samples analyzed in this study collected from a Diesel engine include:

o A synthetic lubricating oil SAE-5W40 multigrade Ester was an ACEA A3/A4 and API SN/CF reference oil collected from April until June 2015 in Morocco.

o A synthetic lubricating oil SAE-5W30 multigrade PolyAlphaOléfine was a ACEA C2 and API SL/CF reference oil containing about 800 ppm Phosphorus Rate, and 0.25% Sulfur Rate collected from February until April 2014 in Morocco.

o A synthetic lubricating oil SAE-10W40 multigrade Ester was an ACEA A3 and API SL/CF reference oil collected from February until March 2014 in Morocco.

Samples of the oils were withdrawn from the engine gauge for analysis at intervals, usually after the cars had travelled a distance of 1000 km. The experiment was terminated after the cars had travelled a distance of 10000 km, Thereafter, they are filtered to remove insoluble particles.

The operation is characterized an average speed of 100 Km/h, this corresponds to a duration of 10 hours of operation. The time spent between each withdrawal depends on the rate of use of the vehicle.

The engine oil was at a very high temperature during operation (of the order 200°C), and the relative humidity of lubricant that does not exceed 0.2% over the entire distance traveled by the engine of the vehicle [10].

Exposure to extreme atmospheric conditions (heavy snowfall, storm, hail) and excessive amounts of dust should be avoided. Before the test start, the vehicle and equipment shall be checked for damages and the absence of warning signals, suggesting malfunctioning.

In order to complete the previous work [3], we have analyzed three categories of lubricating oils SAE-5W40, SAE-10W40 and SAE-5W30 by different spectroscopic and conventional analyzes.

All presented analyzes below are carried out at national laboratory of hydrocarbons and mines "ONHYM" (Rabat - Morocco), and the results obtained for each technique will be compared with the standard values in the results part.

The experimental results of the rheological properties of the different categories of lubricating oils and the standard values shown in **Table 1**.

The measurement methods used give results comparable to the standard values provided by the supplier.

Viscosity Measurements

Kinematic viscosity measurements

The kinematic viscosity of lubricating oils samples was measured by a capillary kinematic viscometer (Autoubbelohde). The method consists in introducing a sufficient quantity (12 ml) of the sample into a capillary tube and immersing it in a thermostatic bath to heat the sample to the desired temperature 40°C and 100°C. At this temperature, the sample must pumped so that it can flow gravity between two points marked on the capillary and thus time the passage of the sample between these two points.

The measurement of the kinematic viscosity done by the following relation

$$\nu = k.t$$

with:

k: a capillary constant periodically set at each calibration

t: the flow time in seconds

Dynamic viscosity measurements

The dynamic viscosity of lubricating oils samples was measured by a dynamic viscometer of the type (Brookfield viscometer USA) DV II with spindle SC 4-21.

In order to determine the dynamic viscosity, we placed 8 ml of lubricating oil in the sample chamber (empty cylinder), after which we placed the spindle along the axis of the cylinder. The desired temperature (40°C or 100°C) is set on the temperature programmer.

Viscosity index measurements

The viscosity index of the different oil samples was determined according to ASTM D 2270 using the ASTM tables. These tables directly fix the viscosity index as the cross-section of the kinematic viscosity values at 40°C and 100°C.

Basicity Index (TBN) Measurements

The Total Base Number (TBN) was measured by means on titration of KOH of the lubricating oils samples by perchloric acid.

The titration manipulation consists in carrying out the determination of the potassium hydroxide (KOH) which exists in the oil by perchloric acid diluted in acetic acid of 1 mol/l concentration.

The solution to be titrated contains a mass m of the sample dissolved in a suitable solvent (30% acetic acid + 70% benzol) and a few tastes of p-naphtholbenzein.

Flash Point Measurements

The flash point of the different lubricating oil samples are measured using the Controlab flash point meter B0094M-Method Pensky Martens.

The manipulation consists of filling a sample container, heating it with a resistance and passing a test flame over the sample at specified time intervals.

Depending on the volatility of the product from which is desired to measure the flash point, the heating rate must be set from a thermostat to the control panel.

Pour Point Measurements

Pour point may be defined as the lowest temperature at which the oil will stop to flow. Lubricating oil having low pour point shows its good quality.The pour point of the samples was analyzed by a pour point apparatus according to ASTM D97 method on a pour point tester Model WIL-471.

The pour point was measured by introducing 20 ml of lubricating oil sample into a container, the samples are cooled to a specific speed, where some hydrocarbon paraffins (wax form) start to solidify and separate into a crystalline form. The temperature at which this occurs is known as cloud point cooling, which continues until the oil stops flowing.

ICP-OES Measurements

The quantitative determination of wear metals in used lubricating oils is an important application for engine and turbine diagnostic purposes, allowing preventive maintenance (oil changes, equipment overhauls and replacement of components) to be made before the collapse of equipment.

Instrumental and experimental parameters

The inductively coupled plasma optical emission spectrometer employed in this study was a Perkin Elmer Model Plasma P1000 (Perkin-Elmer, Canada) equipped an Ebert-Type monochromator with a holographic grating (2400 grooves mm-1) and an Rf generator of 27.12 MHz.

Process of extraction induced by emulsion breaking

The metals was extracted from lubricating oils through the application of the extraction induced by emulsion breaking, which was based on the formation of stable emulsions between the samples and an acid solution of TritonX-114 [11].

GC/MS Measurements

All GC / MS analyzes were performed on the Varian CP3800 chromatograph coupled with the Saturn 2000 ion trap. The flow rate of the carrier gas was adjusted to 1.4 mL.min-1 at the outlet of the column and the temperature programming of the column heating furnace was as follows: after a one minute plateau at 50°C, Column is heated to 280°C at a rate of 7°C.min-1 and then maintained at this temperature for 24 minutes before applying a new heating to 315°C, with temperature ramp of 5°C.min-1.

The mass spectrometer was set in full scan mode between 50 and 600 atomic mass units at a scanning speed of 0.5 scan.s-1. Two ionization modes have been applied: Electronic impact (EI) and chemical ionization (IC). In EI mode, the ionization energy of the electrons was 70 eV with an emission current of 10 µA. Chemical ionization carried out with methanol as an ionization reagent, which had a proton affinity value compatible with that of the compounds expected during the analysis. The emission current was set to 20 µA in this case.

The identification of the products carried out using the mass spectrum database present in the National Institute of Standards and Technology (NIST) library, the mass spectra obtained in chemical ionization for the determination of molecular masses by comparing retention times with those of commercial products in case of uncertainties over allocations.

RESULTS AND DISCUSSION

Viscosity Results

Kinematic viscosity

Figure 1 shows the evolution of the kinematic viscosity at 40°C and 100°C respectively of the SAE-10w40, SAE-5W40 and SAE-5W30 lubricating oils according the distance covered by the vehicle engine.
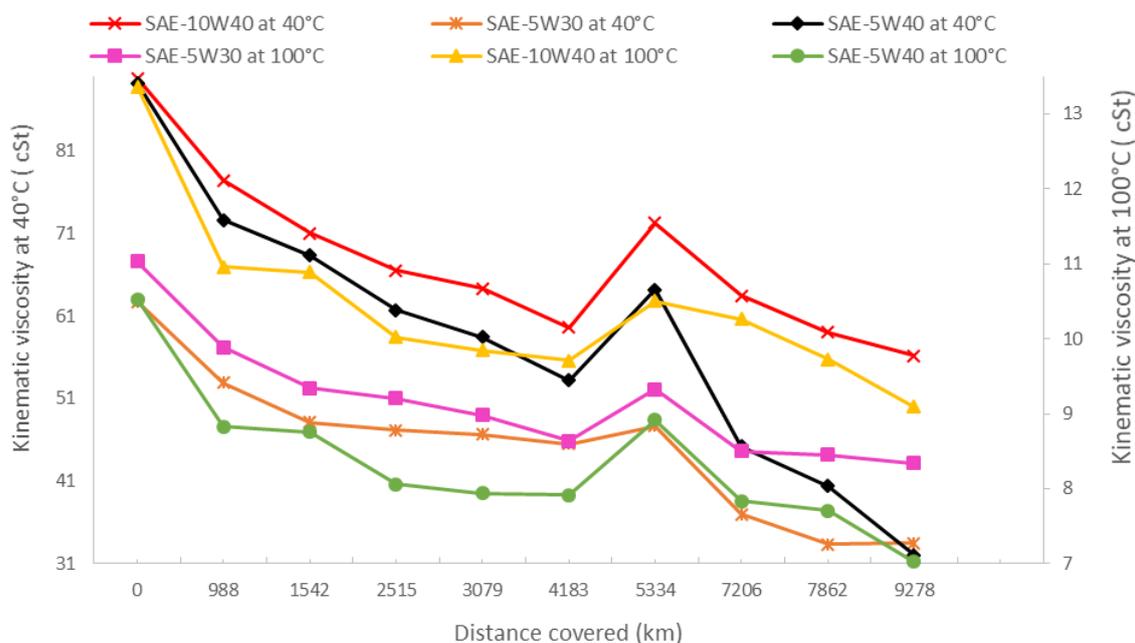
Figure 1. Evolution of the kinematic viscosity at 40°C and 100°C of the lubricating oils versus the distance covered by the vehicle engine
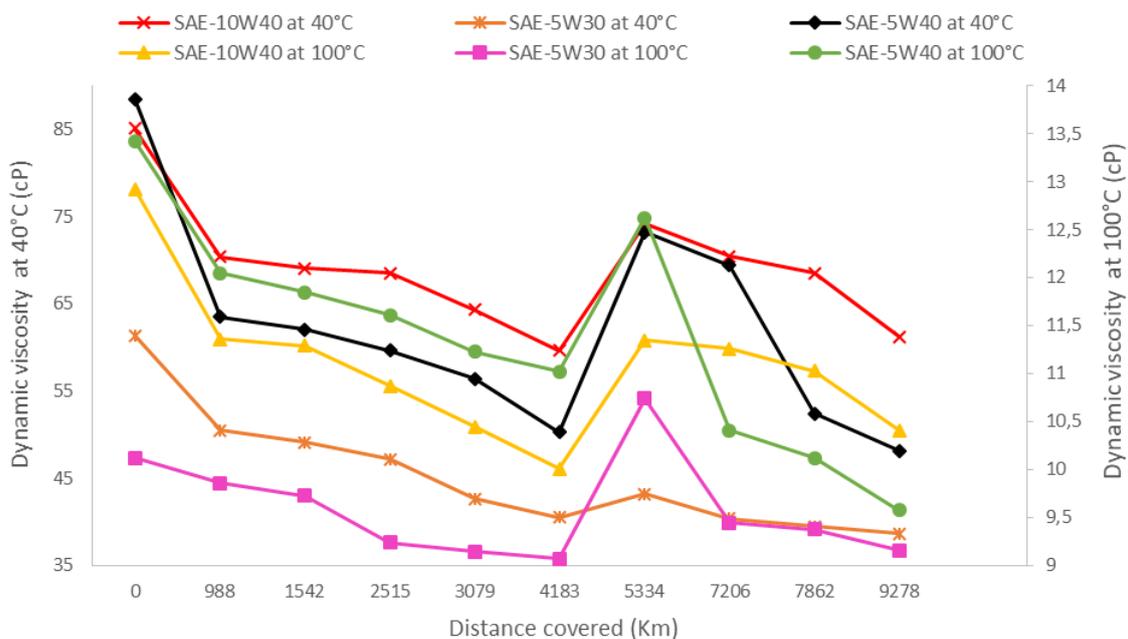

Figure 2. Evolution of the dynamic viscosity at 40°C and 100°C of the lubricating oil versus the distance traveled by the vehicle engine

This result shows that the lubricating oils progressively lose its initial lubricating quality according to the number of kilometers on operation of the engine. For a motor operation of less than 4000 km, the kinematic viscosity decreases remarkably, but about 5500 Km, it undergoes a slight increase, and after continues to decrease. This is probably due to the phenomenon of thickening caused by soot [12].

Dynamic viscosity results

Figure 2 shows the evolution of the dynamic viscosity at 40°C and 100°C respectively of the SAE-10W40, SAE-5W40 and SAE-5W30 lubricating oils versus the distance covered by the vehicle engine.
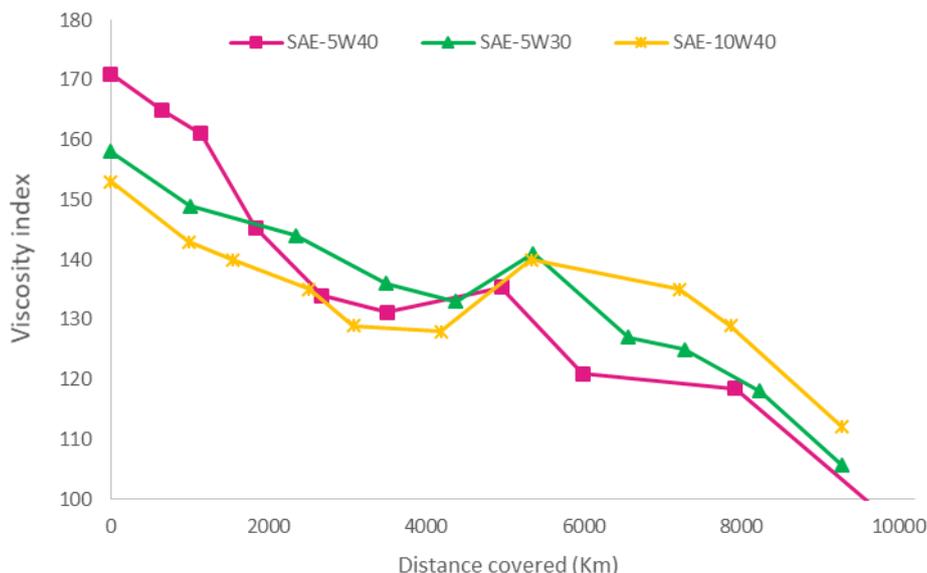
Figure 3. Evolution of the viscosity index of the lubricating oil versus the distance traveled by the vehicle engine

The evolution of the dynamic viscosity measured at 40°C and 100°C is the same as that of the kinematic viscosity, the curves obtained hold the same pace. This result shows that the lubricating oil gradually loses its initial lubricating quality according the kilometers covered by the vehicle engine.

The operation of the engine less than 4000 km of the distance covered, the dynamic viscosity decreases. Nevertheless, it undergoes a slight increase at 5500 Km, this result, probably due to the formation of heavy polymerized products, which pose problems during lubrication. Indeed, when the oil reaches the hot parts of the engine, it polymerizes more and more and thus forms deposits. In addition, the lubricating oil is more loaded with the wear elements, which leads to an amplification on the process of lubricating oil degradation [3, 12].

This result is in correspondence with that obtained by FTIR measurements carried out on degraded SAE-5w40 oil samples where we detected that the C-N band due to the additives observed with a high intensity on the new and slightly degraded samples [3]. The intensity of this band decreases and disappears for the high rates of lubricant degradation. Conversely, the intensity of the EPR signal increases with the degradation, due to the increase in the concentration of produced free radicals. It appears that the additives having an antioxidant effect inhibit the free radicals produced at the beginning of the degradation, which could lead to their consumption to give other reaction products. Some previous work has revealed the deposit of insoluble nitrogen products on the engine parts due to the degradation of the lubricant. As the additives disappear (from 5500 km covered by the vehicle), the concentration of free radicals continues to increase proportionally to the rate of degradation which explains the significant load of lubricating oil by the products of the degradation and the increase in viscosity about 5500 km covered.

Viscosity index results

Figure 3 shows the change in the viscosity index of the lubricating oil versus the distance covered by the vehicle engine.

As for the viscosity, the viscosity index of the used oil has decreased compared to the new oil. This result due to thermo-oxidative degradation, and mechanical shear of vehicle engine parts [12-13].

Basicity Index Results

The lubricating oils studied in this work initially have a slightly basic character. During operation, the basicity index decreases steadily according to the number of kilometers covered by the vehicle (**Figure 4**). This behavior implies that acid products such as carboxylic acid are formed during the degradation [3]. The concentration of these becomes very important at the end of life the lubricating oil. Thus, the basicity index could be used as an indicator of the rate of degradation.
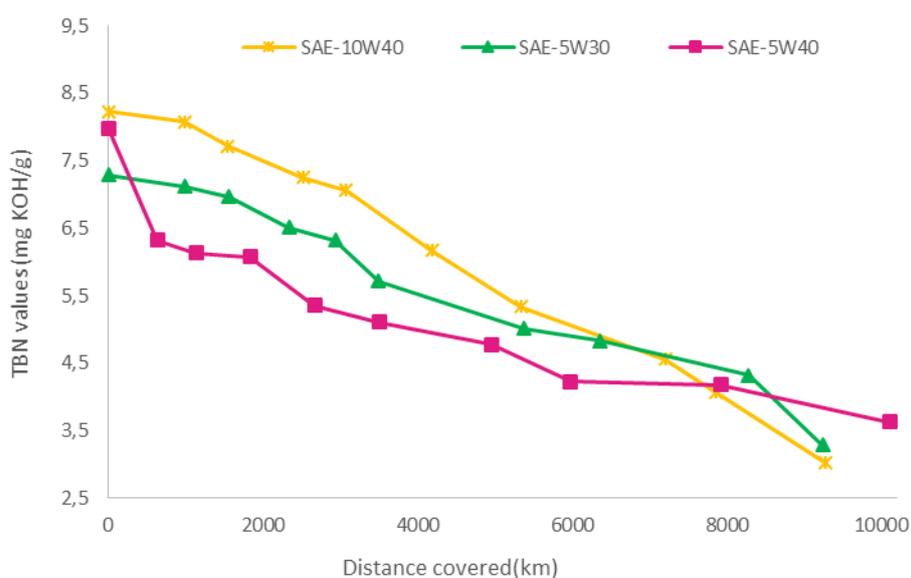
Figure 4. Evolution of the TBN of the lubricating oil versus the distance covered by the vehicle engine

Figure 5. Evolution of the flash point of the lubricating oil versus the distance traveled by the vehicle engine

Flash Point Results

Figure 5 shows the evolution of the flash point of the three categories of lubricating oils versus the distance covered by the vehicle engine.

A regular decrease of the flash point are observed versus the distance covered by vehicle. This result is probably due to the loss of thermal stability of the lubricant by the easy release of the volatile organic matter fraction, which burns in the presence of oxygen. This combustion induces an increase in the temperature of the reaction medium and thus makes the rapid decomposition of the lubricating oil [14-15].

It should also be noted an increase of this parameter nearly 5000 km of covered distance. This behaviour is in correlation with this observed on results of FTIR [3] and viscosity.

Pour Point Results

The results shown in **Figure 6**, it is found that for the used oils, the temperature of solidification and the formation of the first crystals is superior than that of the virgin oil, thus a increase of temperature, and according
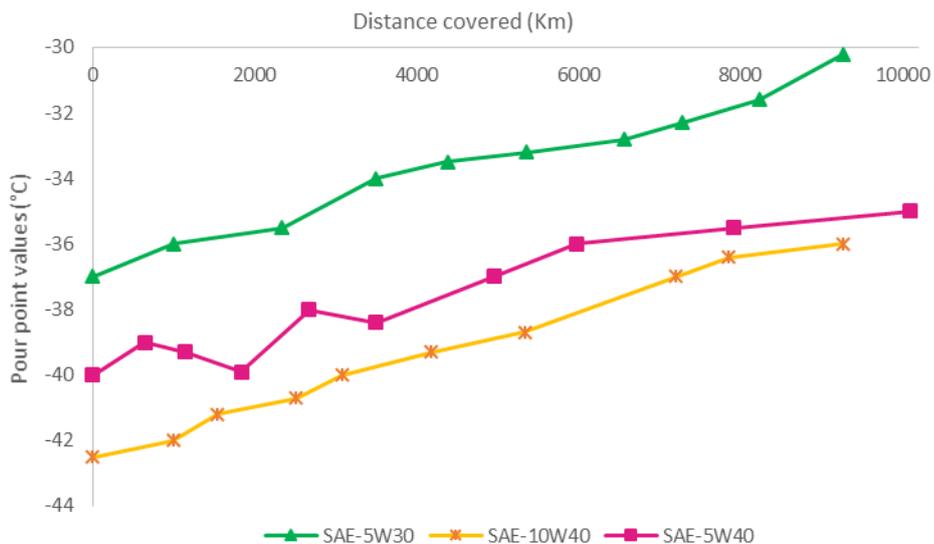
Figure 6. Evolution of the pour point of the lubricating oil versus the distance covered by the vehicle
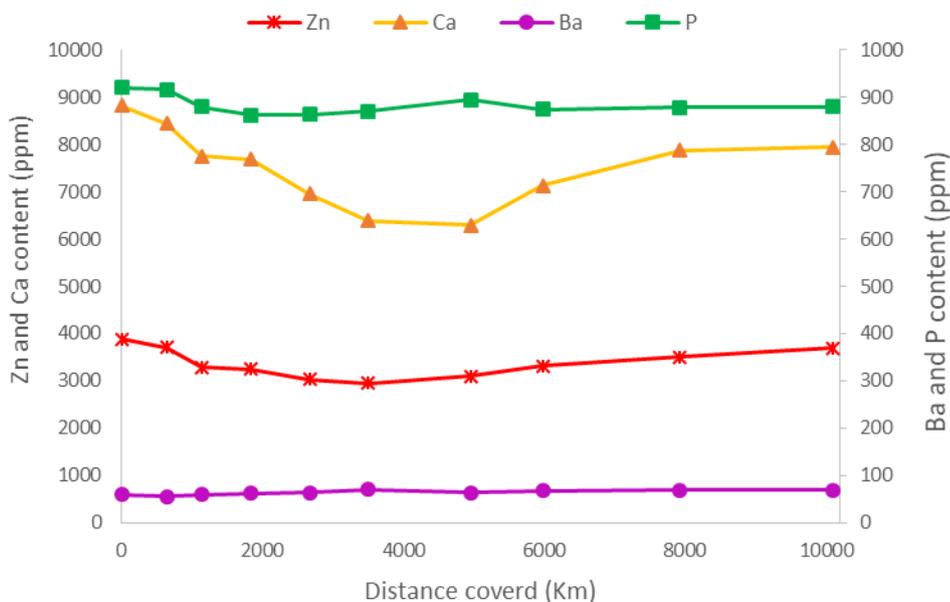

Figure 7. Evolution of metals providing from additives versus distance covered by vehicule (Lubricating oil samples of SAE-5W40)

to the literature that means the pour point depressants as polyalkylnaphthalene, polyalkyphenyl esters or polyalkylmethacrylate are decreased, plus an absence of paraffins with straight linear chains [13, 15], because at lower additive concentrations, side way growth of the crystal faces may be slightly restricted and accordingly, the crystal grows is relatively slower, however crystallization may still be able to form. On the other hand, at higher concentrations of the additives, the side way growth becomes so much more difficult for the wax crystals [16-17].

ICP-OES Results

Figure 7 shows the concentration of metals Ca, Zn, Ba and P providing from additives in lubricating oil samples of SAE-5W40 versus the distance covered. The content of these metals seems invariable [18-19]. This is obviously normal since there is no other source supplying these metals during engine operation.

In contrast, **Figure 8** shows the Mo, Cu, Fe and Mg contents are steadily increased with increasing mileage during the first 2000 Km then after, a tendency towards saturation is observed and around 5500Km the variation of the metals content becomes very weak. A similar trends observed by Zieba- Palus and Yuna Kim [19-20]. The
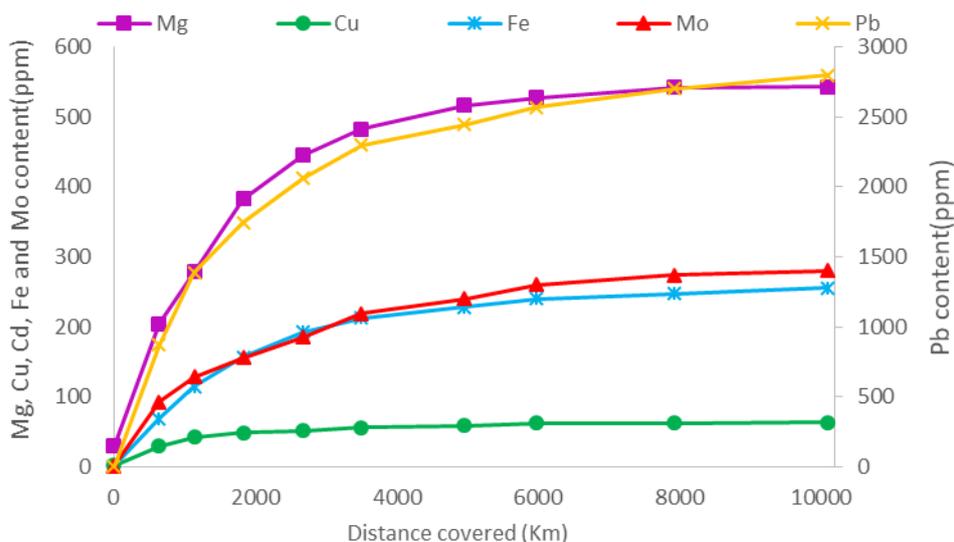
Figure 8. Evolution of metals having a different level of variation during the degradation of lubricating oil SAE-5W40

increase content of magnesium could be explained by the wear of bearings and transition of metal particles to oil during normal car service.

The increase content of Fe and Cu contents can be caused by wear of the metal motor elements during car use, including cylinder surfaces (Fe), engine (Fe) and pans (Cu). The increase of Pb content (5 × greater than the other metals) may originate from fuel containing compounds of Pb mixed with lubricating oil during driving as well as from the wear of bearings or from lubricants in the motor (**Figure 8**).

The analysis of the metals contained in the degraded lubricating oil can be a good indicator to highlight the metals resulting from the wear of the metal parts of the engine, and even to identify the metal parts of the latter having undergone this wear.

GC/MS Results

GC-MS methods are suitable for evaluating degradation of synthetic lubricating oils. These methods can detect new products that are not present in the original samples, but are forming in the degradation reactions.

Analysis of the new lubricating oil SAE-5W40

The chromatogram obtained on the new lubricating oil SAE-5W40 shows that saturated alkanes and unsaturated alkanes identified (**Figure 9**). It appears that the broad band present on the chromatogram correspond to the base oil consists mainly of linear and / or branched hydrocarbons and naphthenic hydrocarbons. It is therefore a base oil of good quality, which does not contain aromatic hydrocarbons, this is in keeping with the fact that the base of lubricating oil is of group III and IV (hydro-fissured or hydroisomerized oil).
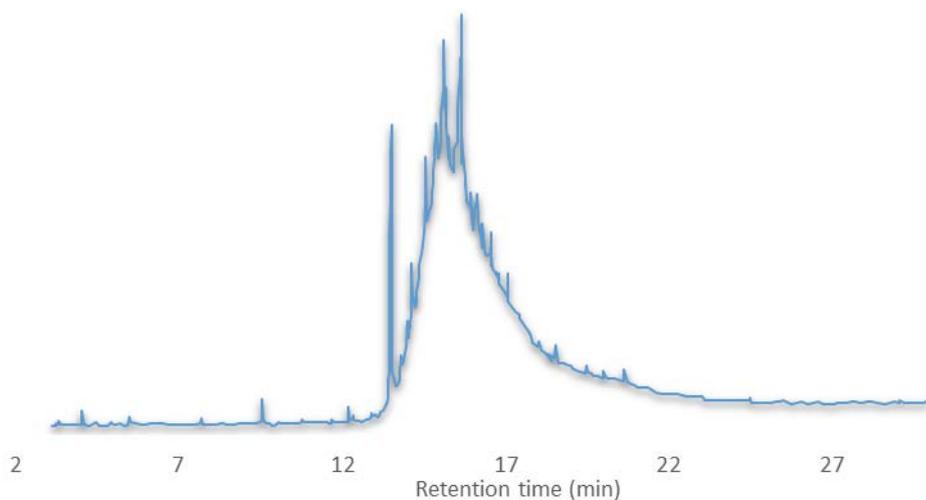
Figure 9. Chromatogram of the new lubricating oil SAE-5W40
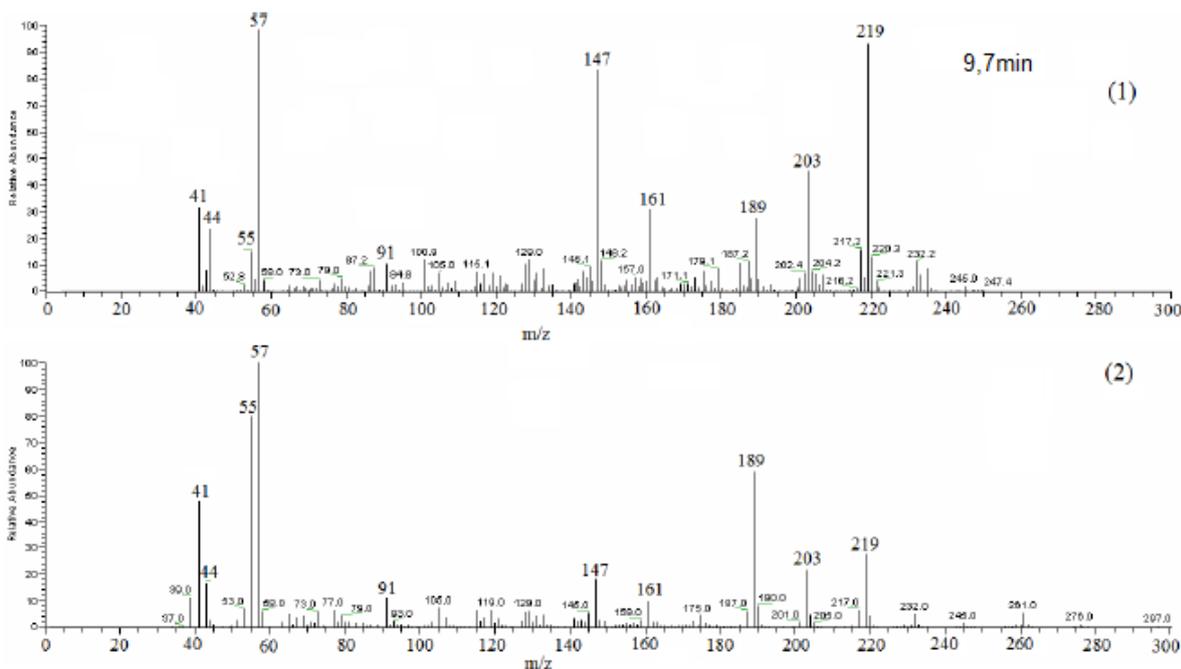

Figure 10. (1) Experimental mass spectrum and (2) Theoretical mass spectrum of 4-(3,5-di-tert-butyl-4-hydroxyphenyl) butyl acrylate

Moreover, **Figure 10** shows the mass spectrum (1) of the product of one of the small bands observed, and that (2) of 4- (3,5-di-tert-butyl-4-hydroxyphenyl) butyl acrylate ($C_{21}H_{32}O_3$) whose mass spectrum is available in the NIST spectrum library. The comparison of these two mass spectra reveals that the structure of the products observed in GC in the form of small bands corresponds to a phenolic type antioxidant structure [21].

The lubricating oil that was chosen in the chromatographic study, is a multigrade oil 5W40. The GC/MS analyzes have shown that is a well refined oil, composed of aliphatic hydrocarbons (linear and / or branched) and naphthenic, characteristic of group III oil bases (hydro-cracked or hydro-isomerised oils). For lubricants, especially those of engines, it is desirable to have saturated compounds and little reactive, since they are the only ones with better aging stability. These compounds thus allow longer emptying intervals without significant changes in the properties of the lubricating oil. In this, the results obtained are in agreement with the expected characteristics of the reference lubricating oil.
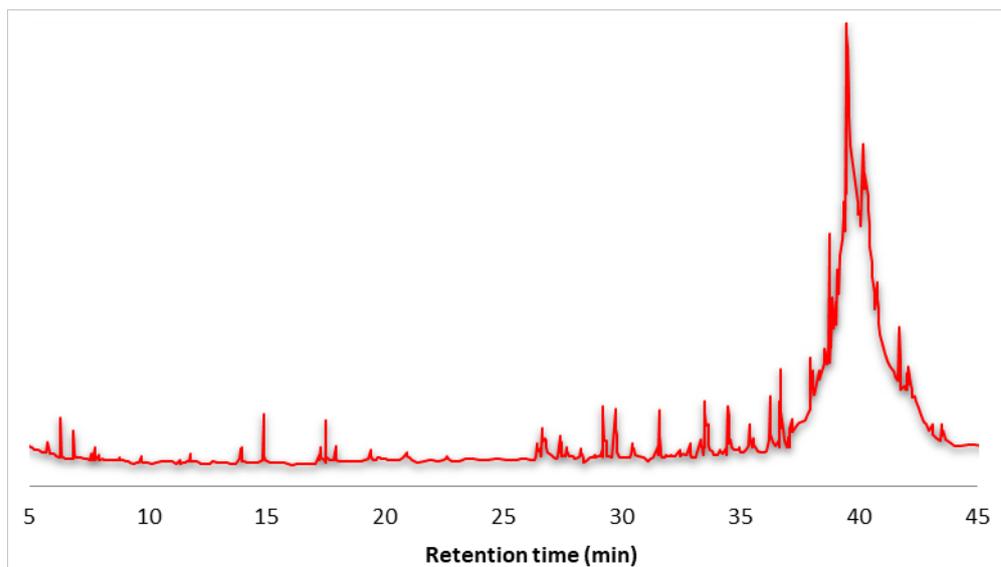
Figure 11. Chromatogram of the degraded lubricating oil SAE-5W40

Analysis of the used lubricating oil SAE-5W40

In order to characterize the products formed during degradation, the degraded samples of lubricating oil SAE-5W40 analyzed by gas chromatography coupled with the mass spectrometer using the previously described GC / MS Varian apparatus.

Product identification was carried out using mass spectra of the National Institute of Standards and Technology (NIST) library and the molecular mass deduced from the mass spectra obtained by chemical ionization; and finally by comparing retention times with those of standard products when uncertainties remained at the level of allocations.

The results of these analyzes made it possible to show the presence of several families of products such as light hydrocarbons (alkanes, alkenes), oxidation products (alcohols, aldehydes, ketones, acids), heavier products, which appear at retention times greater than that of the new lubricating oil, there by demonstrating the existence of a polymerization process during degradation (**Figure 11**).

Figures 12, **13**, **14**, **15** and **16** show the experimental mass spectra of some aromatic compounds and their identification by their concordance with the theoretical mass spectra listed in the NIST library.
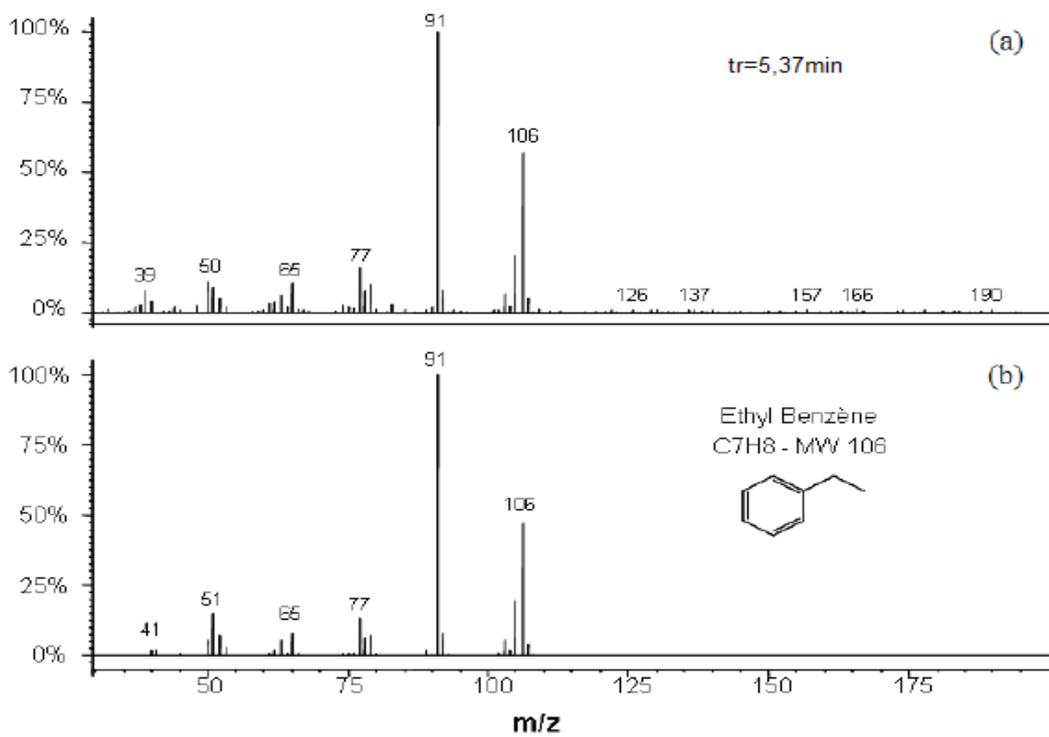
Figure 12. (a) Experimental mass spectrum and (b) Theoretical mass spectrum of product eluted at 5.37 min in lubricating oil chromatogram SAE-5W40
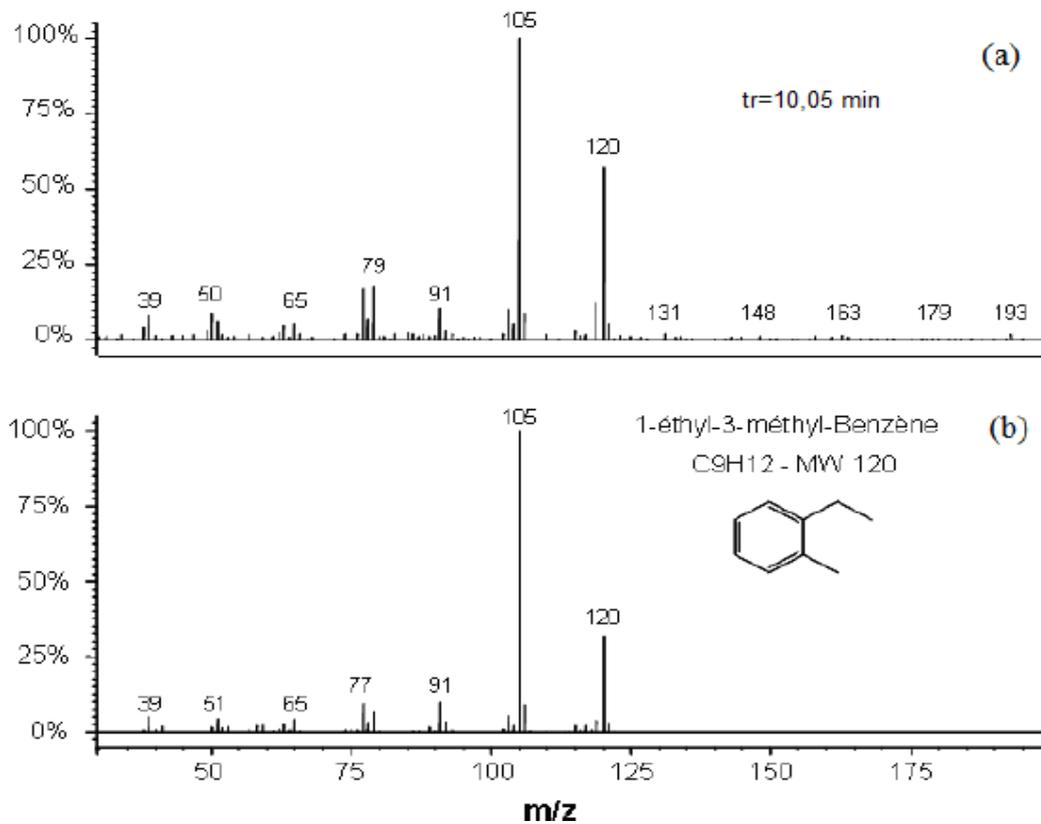

Figure 13. (a) Experimental mass spectrum and (b) Theoretical mass spectrum of product eluted at 10,05 min in lubricating oil chromatogram SAE-5W40

Figure 14. (a) Experimental mass spectrum and (b) Theoretical mass spectrum of product eluted at 14,05 min in lubricating oil chromatogram SAE-5W40

Figure 15. (a) Experimental mass spectrum and (b) Theoretical mass spectrum of product eluted at 35,34 min in lubricating oil chromatogram SAE-5W40
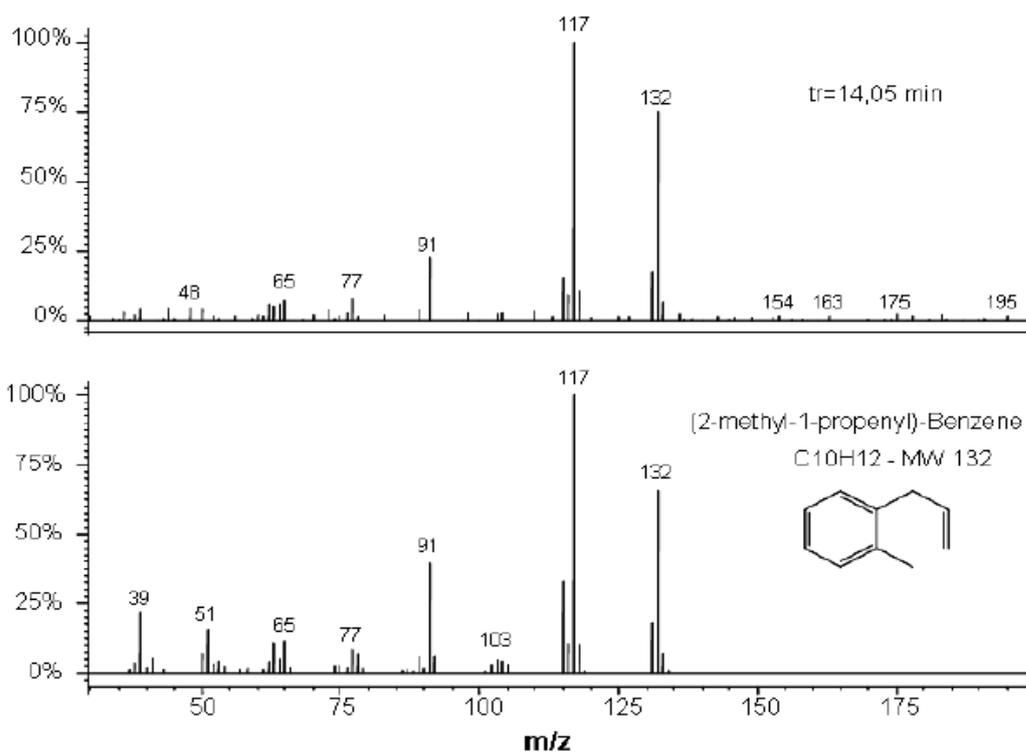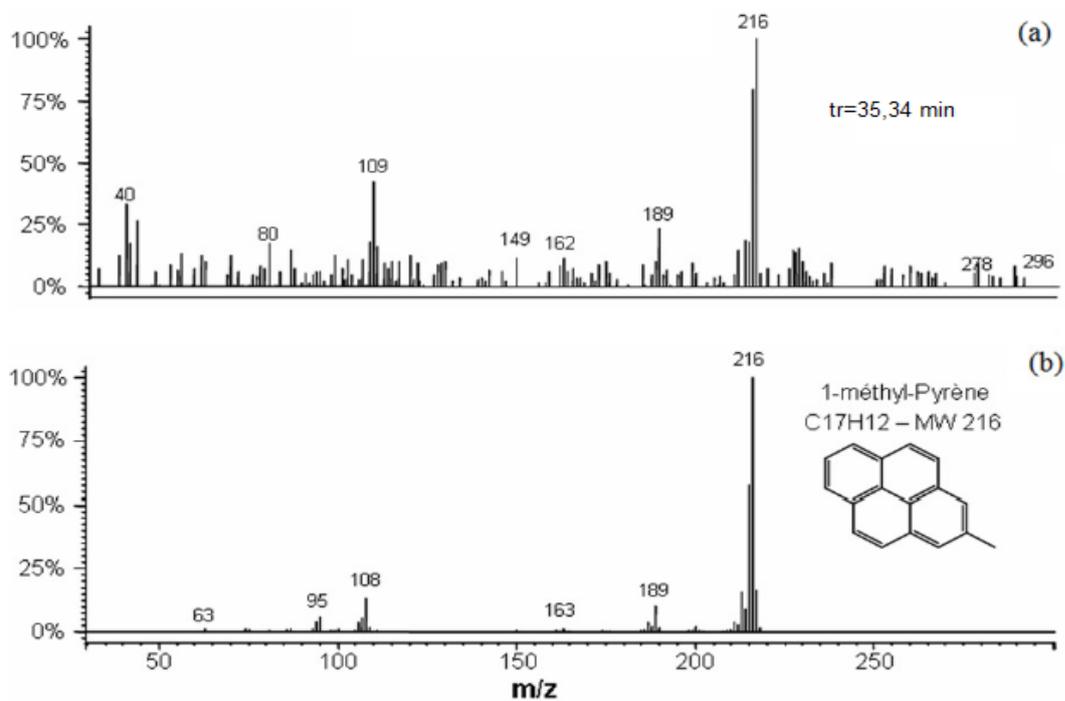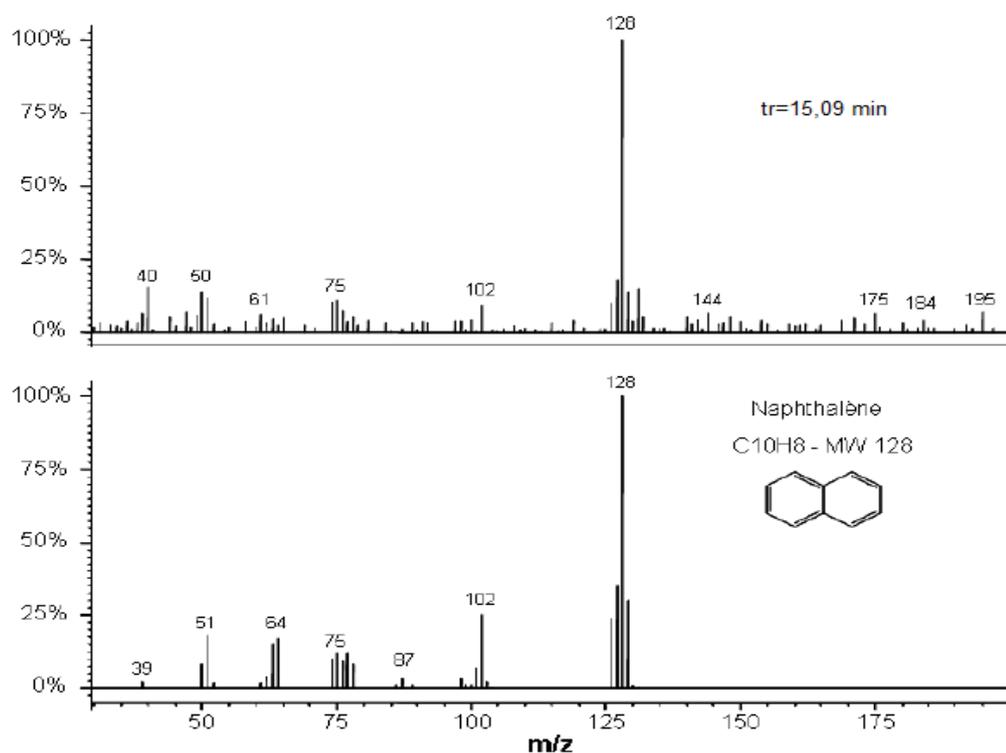
Figure 16. (a) Experimental mass spectrum and (b) Theoretical mass spectrum of product eluted at 15,09 min in lubricating oil chromatogram SAE-5W40

Table 2. The degradation products identified in the SAE-5W40 lubricating oil

Retention time (min)	Molecular weight	Formula	Attribution
5.37	92	C_7H_8	Benzène-C_1
6.67	106	C_8H_{10}	Benzène-C_2
10.05	120	C_9H_{12}	Benzène-C_3
13.39	118	C_9H_{10}	Benzène-C_3-Insat.
14.3	134	$C_{10}H_{14}$	Benzène-C_4
14.05	132	$C_{10}H_{12}$	Benzène-C_4-Insat.
13.92	130	$C_{10}H_{10}$	1H-Indène-C_1
15.09	128	$C_{10}H_8$	Naphtalène
17.52	144	$C_{11}H_{12}$	Napht.-dihydro-C_1
17.54	146	$C_{11}H_{14}$	Benzène-C_4-Insaturé
17.13	142	$C_{11}H_{10}$	Naphtalène-C_1
19.27	158	$C_{12}H_{14}$	1H-Indène-C_3
18.44	156	$C_{12}H_{12}$	Naphtalène-C_2
31.67	170	$C_{13}H_{14}$	Naphtalène-C_3
29.12	168	$C_{13}H_{12}$	Naphtalène-C_3-Insaturé
18.13	154	$C_{12}H_{10}$	Acénaphtène
34.08	180	$C_{14}H_{12}$	Fluorène-C_1
32.45	178	$C_{14}H_{10}$	Phénanthrène / Anthracène
34.68	202	$C_{16}H_{10}$	Pyrène / Fluoranthène
35.34	216	$C_{17}H_{12}$	Pyrène-C_1
37.15	228	$C_{18}H_{12}$	Chrysène

These results show that under the real operating conditions of the vehicle engine, polycyclic aromatic hydrocarbons (PAHs) formed. The PAH formation mechanisms have been the subject of numerous studies, and several pathways have been proposed. Indeed, following the formation of the first aromatic rings by the mechanisms of deoxygenation and dehydrogenation, the growth of aromatic polycyclic aromatic products can occur by direct combination of aromatic rings following the removal of hydrogen (**Table 2**).

In addition, some authors have suggested that Diels-Alder type reaction mechanisms may also be responsible for the formation of these compounds [22]. They hypothesized that, under the effect of temperature, the pyrolysis

of long alkane chains can occur, resulting in the formation of alkenes and dienes by dehydrogenation reactions. Then by cyclization mechanisms (Diels-Alder type reaction), then aromatization [23], these products could lead to the formation of these aromatic compounds.

In our present study, we believe that both of these reactions are considered, and we can even assume that both would occur in our experiments.

Indeed, as we have already mentioned, the formation of aromatic molecules supports the idea of mechanisms of deoxygenation and dehydrogenation.

In addition, we also noted the formation of saturated light hydrocarbons (alkanes) and unsaturated hydrocarbons (alkenes, naphthenes). These two families of compounds, under the effect of temperature and pressure, are likely to undergo Diels-Alder type reactions to produce the first aromatics, which would also react in the same way to form PAH under conditions extreme experience.

CONCLUSION AND OUTLOOKS

The evaluation of the degradation phenomenon of the synthetic lubricating oils during the operation of the vehicle diesel engine and according to the covered distance led us to carry out several analysis techniques such as viscosity measurements, Basicity index measurement, ICP/OES, GC/MS.

The various measurements developed on the lubricating oil samples versus the number of kilometers covered by the vehicle made it possible to follow the evolution of their physical properties, their rheological parameters and their chemical composition, according to their degradation rate.

Thus, the experimental results proved that:

- The lubricant begins to lose its thermal stability, its anti-acid property and its strong rheological character according the distance covered by the vehicle engine.
- The important degradation of the additives tends to thicken the lubricating oil and consequently the continuous increase in the pour point.
- The basicity index could be used as an indicator of the rate of degradation.
- Near 5500Km, the viscosities (kinematic and dynamic) increase due to the thickening of the lubricating oil.
- The ICP/OES emission spectrometry study of the various samples detected the progression of the load, lead, iron and magnesium generated by engine and fuel wear.
- The characterization of the new lubricating oil and that degraded by gas chromatography coupled with mass spectrometry reveals the formation of polycyclic aromatic hydrocarbons, as described by Diels-Alder, followed by dehydrogenation and deoxygenation reactions.

The next works will treat the regeneration of lubricating oils by using extracts of vegetable oils with a good anti-radical power using other analysis techniques.

ACKNOWLEDGEMENTS

REFERENCES

1. Aucelio RQ, Roseli MS, Reinaldo CC, Miekeley N, Carmem LP. The determination of trace metals in lubricating oils by atomic spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy. 2007;62:952. https://doi.org/10.1016/j.sab.2007.05.003
2. Kamalakar K, Manoj GN, Prasad RB, Karuna MS. Influence of structural modification on lubricant properties of salfat-based lubricant base stocks. Industrial Crops and Products. 2015;76:456. https://doi.org/10.1016/j.indcrop.2015.07.050
3. Zzeyani S, Mikou M, Naja J, Elachhab A. Spectroscopic analysis of synthetic lubricating oil. Tribology International. 2017;114:27. https://doi.org/10.1016/j.triboint.2017.04.011
4. Diaby M, Sablier M, Negrate A, El Fassi M, Bocquet J. Understanding carbonaceous deposit formation resulting from engine oil degradation. Carbon. 2009;47:355. https://doi.org/10.1016/j.carbon.2008.10.014
5. Al-Ghouti MA, Al-Atoum L. Virgin and recycled engine oil differentiation: A spectroscopic study. Journal of environmental management. 2009;90:187. https://doi.org/10.1016/j.jenvman.2007.08.018
6. Trevelin MA, Rúbia ES, Eustáquio VR, Geisamanda PB, Ricardo JC, Carneiro MT. Extraction induced by emulsion breaking for determination of Ba, Ca, Mg and Na in crude oil by inductively coupled plasma

optical emission spectrometry. Microchemical Journal. 2016;124:338. https://doi.org/10.1016/j.microc.2015.09.014

7. Brandenberger S, Mohr M, Grob K, Neukom HP. Contribution of unburned lubricating oil and diesel fuel to particulate emission from passenger cars. Atmospheric Environment. 2005;39:6985. https://doi.org/10.1016/j.atmosenv.2005.07.042

8. Maricq M. Chemical characterization of particulate emissions from diesel engines: a review. Journal of Aerosol Science. 2007;38:1079. https://doi.org/10.1016/j.jaerosci.2007.08.001

9. Zeigler C, MacNamara K, Zhendi W, Robbat A. Total alkylated polycyclic aromatic hydrocarbon characterization and quantitative comparison of selected ion monitoring versus full scan gas chromatography/mass spectrometry based on spectral deconvolution. Journal of Chromatography A. 2008;1205:109. https://doi.org/10.1016/j.chroma.2008.07.086

10. Frederik R, Sedman J, Cocciardi R, Juneau S. An automated FTIR method for the routine quantitative determination of moisture in lubricants: An alternative to Karl Fischer titration. Talanta. 2007;72:289. https://doi.org/10.1016/j.talanta.2006.10.042

11. Fernando L, et al. Application of the extraction induced by emulsion breaking for the determination of Cu, Fe and Mn in used lubricating oils by flame atomic absorption spectrometry. Talanta. 2013;110:21. https://doi.org/10.1016/j.talanta.2013.03.017

12. Nejjar K. Etude de la Réactivité Thermique d'une Huile de Lubrification des Moteurs Diesel. Mohamed V University. 2011;66:7. Retrieved from http://toubkal.imist.ma/bitstream/handle/123456789/9196/THESE_NEJJAR.pdf?sequence=3

13. Pranab G, Moumita D. Study of the influence of some polymeric additives as viscosity index improvers and pour point depressants – Synthesis and characterization. Journal of Petroleum Science and Engineering. 2014;119:79. https://doi.org/10.1016/j.petrol.2014.04.014

14. Azim AA, Nasser AM, Ahmeh NS, El Kafrawy AF, Kamal RS. Multifunctional Additives Viscosity Index Improver, Pour Point Depressants and Dispersants for Lube Oil. Petrol. Sci. Technol. 2009;27:20. https://doi.org/10.1080/10916460701434621

15. Kalam MA, et al. Influences of thermal stability and lubrication performance of biodegradable oil as an engine oil for improving the efficiency of heavy duty diesel engine. Fuel. 2017;196:36. https://doi.org/10.1016/j.fuel.2017.01.071

16. Al-Sabagh AM, Sabaa MW, Saad GR, Khidr TT, Khalil TM. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. Egyptian Journal of Petroleum. 2012;21:19. https://doi.org/10.1016/j.ejpe.2012.02.003

17. Briant J, Denis J, Parc G. Propriétés rhéologiques des lubrifiants. 1985. Retrieved from https://www.amazon.com/Propriétés-rhéologiques-lubrifiants-Publications-lInstitut/dp/2710804352

18. Toivo K, Paavo P, Ilkka V, Rönkkömäki H. Determination of Heavy Metals in Waste Lubricating Oils by Inductively Coupled Plasma–Optical Emission Spectrometry. Inter. J. of Envir. Anal. Chem. 2001;81:89. https://doi.org/10.1080/03067310108044347

19. Yuna K, Nam YK, Seh YP, Dong L, Hoon L. Classification and individualization of used engine oils using elemental composition and discriminant analysis. Foren. Sci. Inter. 2013;230:58. https://doi.org/10.1016/j.forsciint.2013.01.013

20. Palus Z, Kościelniak P. An analysis of the similarity of motor oils on the basis of their elemental composition. Foren. Sci. Inter. 2000;112:81. https://doi.org/10.1016/S0379-0738(00)00172-9

21. Diaby M, Kinani S, Genty C, Bouchonnet S, Sablier M, Negrate A, El FassI M. Analysis of the Volatile Organic Matter of Engine Piston Deposits by Direct Sample Introduction Thermal Desorption GC/MS. Anal. Chem. 2009;81:9764. https://doi.org/10.1021/ac901652j

22. Fairburn JA, Behie LA, Svrcek WY. Ultrapyrolysis of n-hexadecane in a novel micro-reactor. Fuel. 1990;69:1537. https://doi.org/10.1016/0016-2361(90)90203-3

23. Williams PT, Besler S. polycyclic aromatic hydrocarbons in waste derived pyrolitic oils. J. Anal. Appl. Pyrol. 1994;30:17. https://doi.org/10.1016/0165-2370(94)00802-7

http://www.eurasianjournals.com