

Article

Modeling and Forecasting of Depletion of Additives in Car Engine Oils Using Attenuated Total Reflectance Fast Transform Infrared Spectroscopy

Ronald Nguele ^{1,*}, Hikmat Said Al-Salim ² and Khalid Mohammad ³

¹ Department of Earth Resources Engineering, Resources Production and Safety Engineering Laboratory, Kyushu University, 744 Motooka Nishi-ku, Fukuoka 819-0395, Japan

² Department of Chemical & Petroleum Engineering, North Wing UCSI University, Cheras 56000 Kuala Lumpur, Malaysia; E-Mail: hikmatsaid@ucsiuniversity.edu.my

³ Division of Manufacturing and Industrial Process, Department of Chemical Engineering, University of Nottingham Malaysia Campus, Broga, 43500 Semenyih, Selangor, Malaysia; E-Mail: khalid.siddiqui@nottingham.edu.my

* Author to whom correspondence should be addressed; E-Mail: nguele.odou.548@s.kyushu-u.ac.jp; Tel.: +81-90-7531-7661.

External Editor: Sevim Z. Erhan

Received: 26 August 2014; in revised form: 28 September 2014 / Accepted: 30 September 2014 / Published: 26 November 2014

Abstract: On average, additives make up to 7% of a typical lubricant base. Commonly, they are blended with lube oils to enhance specific features thereby improving their qualities. Ultimately, additives participate in the performance of car engine oils. Using an analytical tool, attenuated total reflectance fast transform infrared spectroscopy, various grades of car engine oils, at different mileages, were analyzed. Sulfate oxidation and wear were found to trigger chemical processes which, in the long run, cause lubricant degradation while carbonyl oxidation was observed to occur only at a slow rate. Based upon data obtained from infrared spectra and using a curve fitting technique, mathematical equations predicting the theoretical rates of chemical change due to the aforementioned processes were examined. Additive depletions were found to obey exponential regression rather than polynomial. Moreover, breakpoint (breakpoint is used here to denote the initiation of deterioration of additives) and critical mileage (critical mileage defines the distance at which the lubricant is chemically unusable) of both samples were determined.

Keywords: additive degradation; antioxidants; antiwear additives; sulfonate detergents
antioxidants; FTIR

1. Introduction

Primarily, lubricating oils are designed to reduce the friction and wear between two bearing surfaces in relative motion. If manufactured from fossil resources, they are denominated as mineral oils while called synthetic oils if the feedstock, from which they are produced, is petroleum-free [1,2]. For a better performance, external materials are required to be blended with the base oil which not only upgrades both physical and/or chemical properties but also extends the useful life. Such materials are designated as additives. Additive combination, the amount to be mixed as well as the type is decided upon knowledge of lubricant application. A summary of additives, commonly used in tribology, is outlined in Table 1 [3].

Table 1. Lubricating oil additives.

Additives	Chemical Composition	Purpose
Viscosity Index Improvers	Acrylate polymers	To keep the viscosity at acceptable levels.
Anti-Foaming Agents	Dimethylsilicones (dimethylsiloxanes)	To reduce the foaming effect in oils.
Anti-Oxidants	Zinc dithiophosphate (ZDP); Alkyl sulphides; Aromatic sulphides; Aromatic amines; Hindered phenols.	To inhibit the oxidation process of oils.
Detergents	Phenolates, sulphonatesphosphonates of alkaline, alkaline-earth elements such as Mg, Ca, Na, Ba.	To neutralize strong acids present in the lubricant. To form a film on part of the surface preventing high temperature deposition of sludge.
Dispersants	Long chain hydrocarbons succinimides, such as polyisobutylenesuccinimides	To keep the foreign particles present in a lubricant in a dispersed form.
Pour Point Depressants	Co-polymers of polyalkylmethacrylates	To inhibit formation and agglomeration of wax particles

The stressful environment, into which lubricating oils are forced to operate, favors their degradations over time. This loss of performance is a result of a complex tribo-chemical (tribo-chemistry refers to chemical reactions taking place between lubricant (and/or environment) with surfaces in motion under lubrication conditions [4]) process (es) occurring within the engine [5]. Due to their active sites (functional groups) and conditions existing within the engine, additives are likely to degrade through a series of chemical reactions which invariably results in loss of their primary functions. Their chemical activities are thereby deteriorated. Various analytical tests, focusing on a particular property, have been used to monitor degradation of additives in lubricating oils including fast transform infrared spectroscopy (FT-IR) [6].

FT-IR has been found to be a reliable and sensitive technique to assess the presence of degraded materials resulting from lubricant and additive degradation [7]. Although, one may see IR spectroscopy

as a qualitative test, recent literature has revealed extensive investigations which have focused on the quantitative aspect of infrared spectroscopy. Fernandez *et al.* 1998, used mid infrared to determine pKa (pKa is a dimensionless value which tells how acidic (or not) a given hydrogen atom in a molecule is) of the contaminant inducing dehydration degree of phospholipids [8]. Similarly, the interest in contaminants in lubricants was deepened by (Borin *et al.*, 2005). Using IR spectra and through a technique known as interval least squares, they quantified the amount of poisonous components in automotive lubricating oil artificially contaminated with water, ethylene glycol and gasoline [9]. Contaminant is a generic term used in tribology science which indicates a foreign material present inside the lubricant whose action deteriorates the quality of the oil including oxidized compounds easily detectable in an IR spectrum. Based on that principle, (Van de Voort *et al.* 2003) proposed the quantification of acidic materials resulting from oxidation processes. Although, the results were supplemented by acid number (AN) and base number (BN) tests, the computations were made from the characteristic peaks of oxidized compounds [10]. Although the quantitative features of FT-IR have stimulated a certain interest, its poor selectivity has often been known to be one of its major drawbacks. However, through a combination of both chemometrics and FT-IR the chemical alterations that are not detected could be magnified [11,12]. Thus, considering lubricating oils as a case study, this research not only aimed to monitor the degradation of lubricating oils but also to propose a forecast of additive depletion based solely on infrared spectra and mathematical tools.

2. Mathematical Approach

As the engine runs, additives deteriorate until the point beyond which they become “chemically different” is reached. This point corresponds to a distance, indicated by the odometer, above which the car engine performance is reduced and it is desirable to change the oil. In this study, the distance is defined as “breakpoint” and has been determined through a mathematical model. It is believed that regression or depletion of additives follows a pattern that could be linearized. Moreover, an early detection of a breakpoint, using IR spectra, could be a stepping stone for innovative techniques including additive reconstruction and oil degradation sensors [13,14]. With regard to this, extent investigations have been conducted in the last decade. (Mujahid *et al.*, 2010) and (Irshad *et al.*, 2013) have proposed the correlation of data obtained by infrared and nanotechnology for the development of sensitive sensors to monitor the formation of carbonic materials [15,16].

Three major causes of lubricating oil degradation including carbonyl oxidation, sulfate oxidation and wear, which are believed to be the principal reasons of additive depletion, have been defined. Prior to developing a mathematical model, it was assumed that interferences between the different peaks of the spectra were minimal. Also, dimensionless parameters, which trace the fraction of degraded additives (DA) formed as a result of a specific chemical process, were defined.

- ξ_{ox} defines the fraction of oxidized materials formed because of carbonyl oxidation. Also, it accounts for the amount of antioxidants consumed during this process.
- ξ_{aw} represents the fraction of contaminants appearing because of wear metal poisoning. To an extent, it quantifies the amount of antiwear additives (AWs) depleted solely due to metal contamination.
- ξ_{su} expresses the fraction of contaminants appearing as a result of sulfate oxidation. Also, it expresses the amount of depleted sulfonate detergents.

ξ_{ox} , ξ_{su} and ξ_{aw} are expressed in mol_{fresh lubricant}/mol_{DA}.

Consider an additive i , with an initial transmittance $\%T_i$ on an infrared spectrum, $\%T_x$ to be its transmittance after x km as sketched in Figure 1. The fraction of DA formed at any distance x , could be computed as expressed by Equation (1)

$$\xi_i = \left[\frac{\%T_i - \%T_x}{\%T_i} \right] \times 100 \tag{1}$$

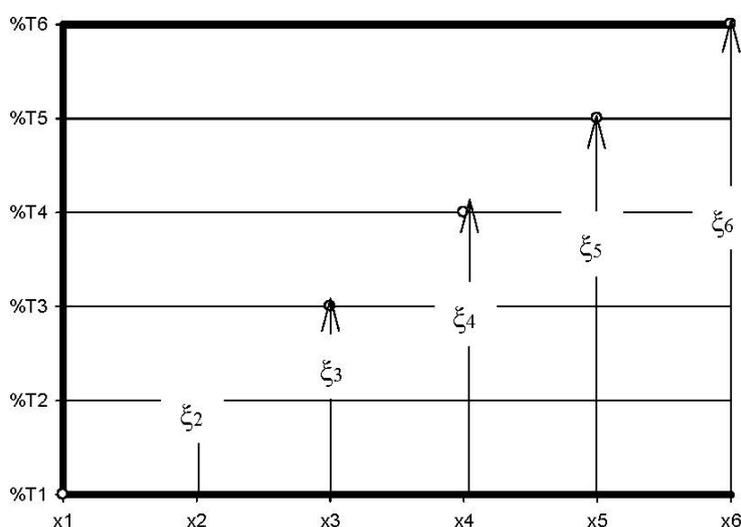
where:

$\%T_i$ is the transmittance of the fresh lubricating oil, in %.

$\%T_x$ is the transmittance of a used lubricating oil at any distance x , in %.

ξ_i is the fraction of DA appearing solely due to a specific chemical process, in mol_{fresh lubricant}/mol_{DA}.

Figure 1. Schematic of the computation of degraded additives.



The ratio of the fraction of appeared DA over the mileage outlines a chemical change occurring within the lubricant per mileage. By analogy to reaction rate in kinetics, a ratio, r_i , that expresses the rate of chemical change of a lubricating oil has been defined. Its mathematical formulation is shown by Equation (2)

$$r_i = \frac{\xi_i}{x} \tag{2}$$

where:

r_i in mol_{fresh lubricant}/mol_{DA}·km;

ξ_i , in mol_{fresh lubricant}/mol_{DA};

x , in km.

At initial conditions, $x = 0$ km *i.e.*, for a lubricant freshly introduced in the car engine, there is no chemical reaction occurrence, hence no additive depletion.

Thus, it has been postulated that the origin ($x = 0$), $\xi_1 = 1$ mol_{fresh lubricant}/mol_{DA} and $r_1 = 0$ mol_{fresh lubricant}/mol_{DA}·km.

Equations (1) and (2) were set as governing equations and were further used to develop mathematical models as discussed later.

3. Experimental

3.1. Sampling

The study, performed on a laboratory scale, considered two car engines fueled with the same gasoline, whose technical specifications as well as the type of lubricating oil used, are tabled in Table 2. The investigational study was conducted over two months. Samples were collected from engines at different distances at regular intervals of two weeks traveling mainly within a city. Prior to the experimental phase and to reduce foreign particle poisoning, the two cars underwent a thorough spot check and were cleaned. Samples were cleared of solid materials by a centrifugation process. The IR spectrum was recorded thereof.

Table 2. Model characteristics and lubricants grade.

Car Engine Specifications	Type and Lubricating Oil Grades	Experimental Code	Distance at which Samples were Collected	
			In miles	In kms
I-4, 4 Cylinders, 1.8 L	Fully Synthetic 5W-40	FS_5W	0	0
			1150	1851
			1380	2221
			1678	2700
			1818	2926
CamPro, 4 Cylinders, 125 gross	Semi Synthetic 15W-50	SS_15W	0	0
			1483	2387
			2020	3251
			2810	4522
			3175	5110

3.2. Instrumentation

The spectral analysis was performed using attenuated total resonance FT-IR (Perkin Elmer, Kuala Lumpur, Federal Territory of Kuala Lumpur, Malaysia). The values obtained were based on transmittance with a wavelength scan ranging from 500–4000 cm^{-1} . The equipment was set at 16 scans with a generated spectrum having a resolution of 0.4 cm^{-1} for 3028 cm^{-1} in the band for methane. A drop, collected from the samples at various distances, was deposited on the surface of the lens of the crystal diamond. In-built software was used to treat and process the signal and raw spectra were generated. A baseline correction was performed to give actual spectra which were used for this research.

4. Results and Discussion

A used lubricating oil spectrum should be viewed as a sum of spectra of all components contained within the car engine oil including base oil, additives, degraded products and contaminants. A comparative spectral analysis was performed, as shown on Figures 2 and 3 for both FS_5W and SS_5W respectively. A slight shift, caused by oxidation of chemical materials contained within the lubricant, was observed. It appears to be more stressed on SS_5W. The base stock or the initial

composition of lubricant is thought to be the reason for such a pattern. Moreover, the shift, herein observed, suggests a low rate of oxidation in a fully synthetic model. Certain zones of the spectra that appeared, suggest a high concentration of degraded products. Also, they indicate eventual processes responsible of additive deterioration including sulfate oxidation, ZDDP or AW depletion and carbonyl depletion.

Figure 2. Infrared spectrum of fully synthetic model.

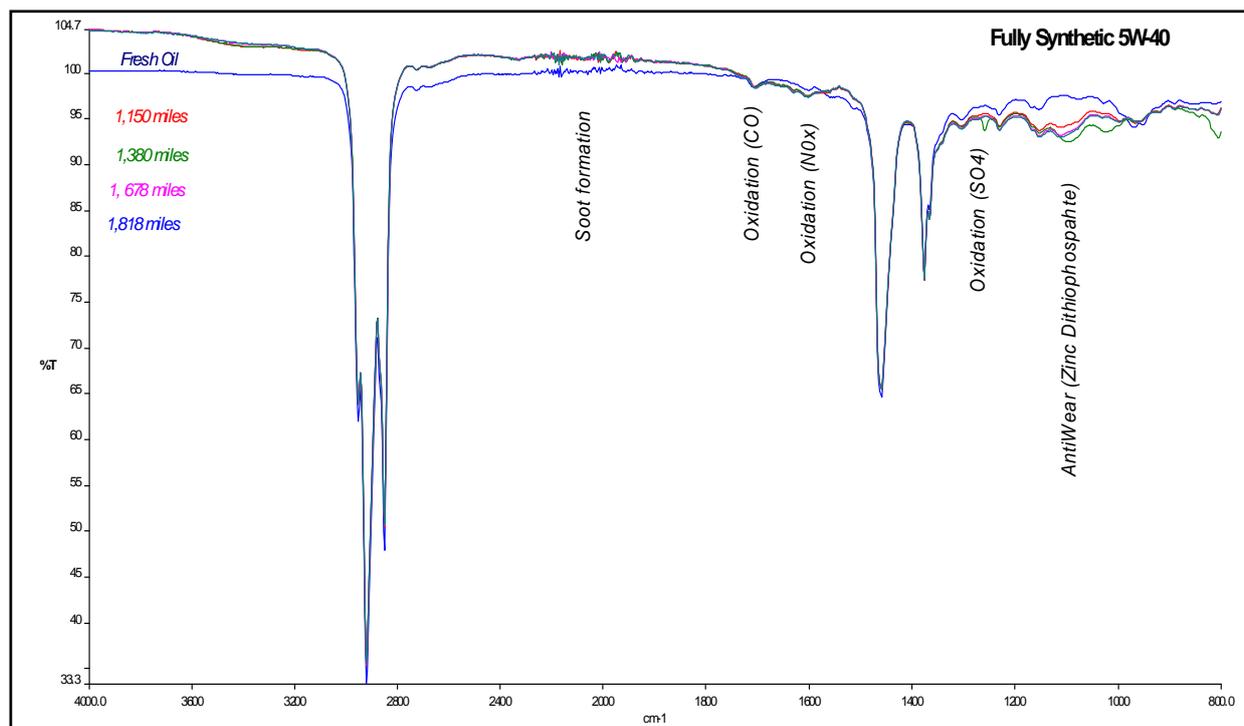
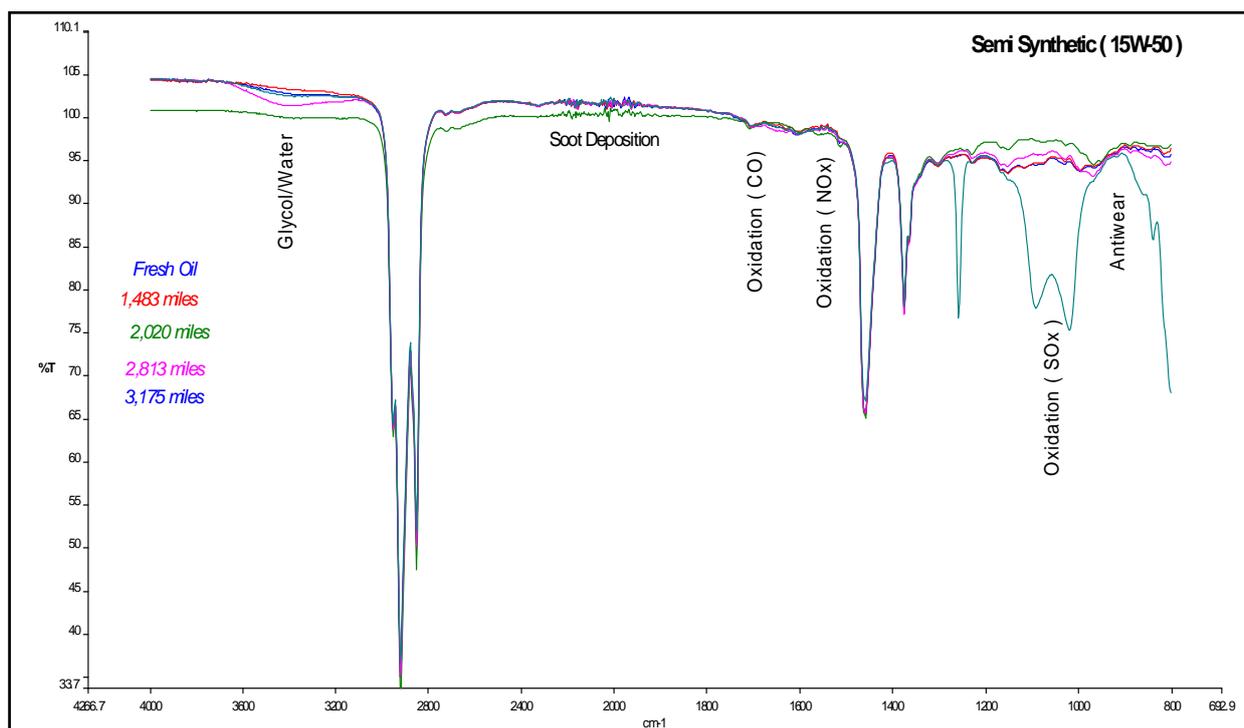


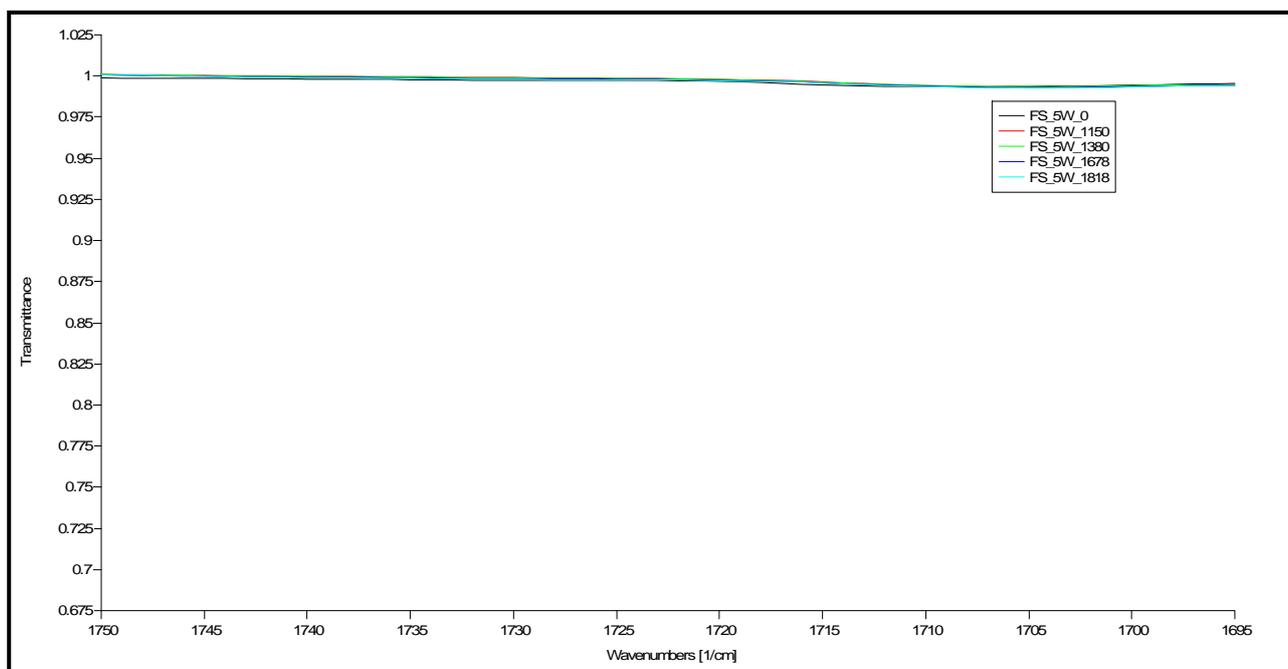
Figure 3. Infrared spectrum of semi-synthetic synthetic model.



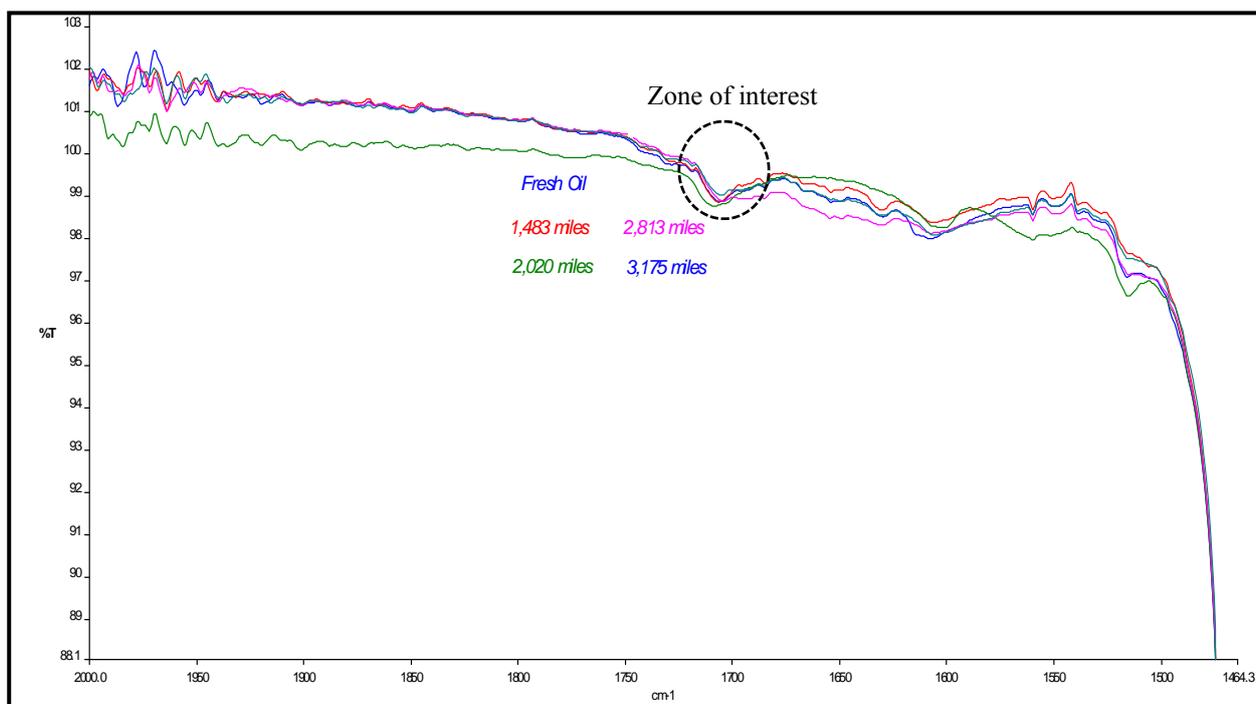
4.1. Carbonyl Oxidation or Carbonylation

Around 1700–1750 cm^{-1} , the differential spectrum exhibited a fair but broad peak for the semi-synthetic model while being nearly undistinguishable for the fully synthetic. Figure 4a,b depict the aforementioned observations.

Figure 4. (a) Carbonyl oxidation in FS_5W; (b) Carbonyl oxidation in SS_15W.

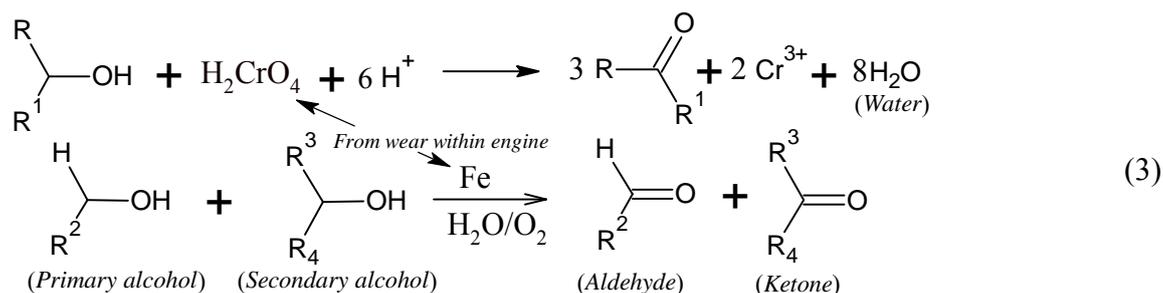


(a)



(b)

Nevertheless, an absorption, around that region of the IR in tribology, is characteristic of a carbonyl absorption (stretching motion). The functional group is representative of aldehydes, carboxylic and/or ketone type compounds which result from a series of chemical reactions which convert hydroxyl compounds. The conversion is thought to be catalyzed by wear metals such as iron, chromium and copper. A nano-scratch, on the surface of engine parts in motion, is sufficient to release an amount of metal which latter behave as catalyst [17]. With usage, an acidic environment builds up within the engine and thereby promotes the formation of oxidizing agents including H_2CrO_4 and Fe(III) which combine further with oxygen (O_2) and water (H_2O) to form a cationic complex [18]. Ultimately, conversion of alcohols, following the chemistry below is likely to occur [19].



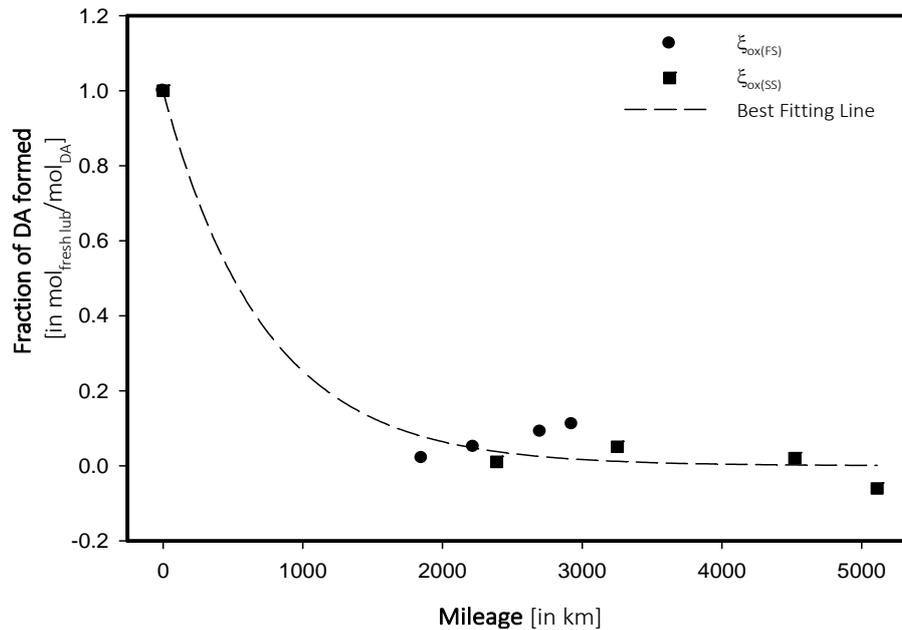
R , R^1 , R^2 and R^3 are either phenyl, alkylene or aliphatic groups which usually form the base stock of the lubricating oils. The broadness of the observed peak suggests a wide variety of acidic materials formed. Transmittances corresponding to carbonyl absorption were measured in percentage and are outlined in Table 3.

Table 3. Carbonyl oxidation results.

Mileage (in km)	Transmittance (in %)	ξ_{ox} , (in $\text{mol}_{\text{fresh lubricant}}/\text{mol}_{\text{DA}}$)	r_{ox} , (in $\times 10^{-5} \text{mol}_{\text{fresh lubricant}}/\text{mol}_{\text{DA}} \cdot \text{km}$)
FS_5W			
0	99.48	1.0000	0.0000
1851	99.46	0.0201	1.0861
2221	99.43	0.0503	2.263
2700	99.39	0.0905	3.3508
2926	99.37	0.1106	3.7790
SS_15W			
0	98.96	1.0000	0.0000
2387	98.95	0.0101	0.4233
3251	98.91	0.0505	1.5542
4522	98.94	0.0202	0.4470
5111	99.02	-0.0606	-1.1863

Data from Table 3, were used to obtain Figure 5, from which the fraction of degraded materials due to carbonyl oxidation was computed.

Figure 5. Carbonyl oxidation profile.



Let $\xi_{ox.(FS)}$ and $\xi_{ox.(SS)}$ be the fraction of consumed antioxidants of FS_5W and SS_15W respectively. Antioxidant depletion, in Figure 6, was found to follow an exponential decay regression whose general expression is:

$$\xi_{i,x} = a \times \exp(-bx) \quad (4)$$

Solving for the rate of appearance of DA,

$$r_{i,x} = \frac{b}{x} \exp(-bx) \quad (5)$$

where

a and b are constants to be determined, in $\text{mol}_{\text{fresh lubricant}}/\text{mol}_{\text{DA}}$ and $1/\text{km}$ respectively.
 x the distance covered by the engine, in km.

Nonlinear least squares fitting technique was iteratively applied to both models and the regression coefficient (R^2) was found to be 0.9875 with the sum of squares $\Sigma(y_i - y)^2 = 0.0228$.

The rates of chemical change credited to carbonyl oxidation of fully synthetic and semi synthetic samples at any distance x are expressed respectively by Equations (6) and (7):

$$r_{ox.(FS),x} = \frac{0.9981}{x} \exp(-0.0014x) \quad (6)$$

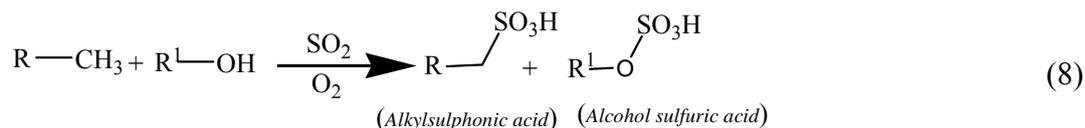
$$r_{ox.(SS),x} = \frac{0.9656}{x} \exp(-0.0003x) \quad (7)$$

Both $r_{ox.(FS),x}$ and $r_{ox.(SS),x}$ are expressed $\text{mol}_{\text{fresh lubricant}}/\text{mol}_{\text{DA}} \cdot \text{km}$.

4.2. Sulfate Oxidation: Sulfation and Sulfonation

Sulfonates are present in the base stock of lubricating oils as detergent additives. In the IR spectrum, they are detected around 1150 cm^{-1} in the form of oxidized materials (sulfur oxides). Sulfate oxidation implies either sulfation and/or sulfonation. Sulfation is a process by which esters or salts of sulfuric acid (sulfates) are formed while sulfonation refers to a chemical reaction where sulfonic acids are formed.

As the car engine runs, detergent additives are degraded following the chemistry described by Equation (8) with sulfuric acid formed as a side product (9) [20].



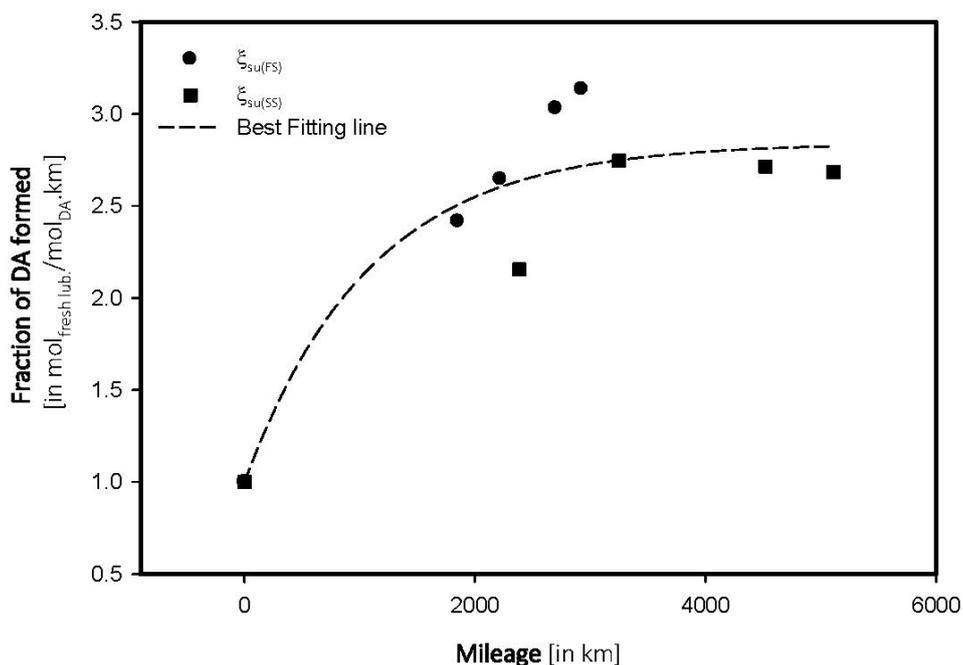
R and R¹ refer to alkylic, aliphatic and/or phenylic groups forming the base stock of the lubricant. Sulfur oxides and other acidic materials formed during the combustion process, when accumulated within the oil, lead to corrosion of the moving parts of the engine. They are detected because of the asymmetric stretching motion of the bond S=O. A strong absorption for SS_5W and a fair one for FS_5W were observed; suggesting the inclination of the semi-synthetic model towards sulfation and/or sulfonation compared to a fully synthetic archetype. By determining transmittance values, Table 4 was assimilated.

Table 4. Sulphation/Sulphonation results.

Mileage (in kms)	Transmittance (in %)	ξ_{ox} , (in mol _{fresh lubricant} /mol _{DA})	r_{ox} , (in $\times 10^{-4}$ mol _{fresh lubricant} /mol _{DA} ·km)
FS_5W			
0	96.04	1.0000	0.0000
1851	93.72	2.4157	0.1305
2221	93.50	2.6447	0.1191
2700	93.13	3.0300	0.1122
2926	93.03	3.1341	0.1071
SS_15W			
0	96.52	1.0000	0.0000
2387	94.44	2.1550	9.0280
3251	93.87	2.7456	8.4452
4522	93.90	2.7145	6.0028
5111	93.93	2.6834	5.2502

Both alkylsulfonic and alcohol sulfuric acids later combine with metals encountered in the lubricating oils as corrosion inhibitor or antiwear additives including sodium (Na), zinc (Zn), calcium (Ca) to form alkylsulfonic and alcohol sulfuric salts. Thus, the wide variety of compounds yielded explains the broadness of the absorption peak observed. The sulfation and/or sulfonation profile observed across the samples was obtained by plotting the fraction of degraded additives and the rate of change *versus* the distance run as shown in Figure 6.

Figure 6. Sulfate oxidation analysis.



Abrupt increase, followed by an apparent steadiness was observed in the sulfate oxidation analysis. The curve fitting technique ($R^2 = 0.8929$ and $\Sigma(y_i - y)^2 = 0.5628$), suggested an exponential rise to a maximum pattern whose general expression is given by (10):

$$y(x) = y_0 + a(1 - \exp(-bx)) \tag{10}$$

By analogy in this research: y_0 is the initial concentration/fraction of an additive i (in mol_{fresh lub.}/mol_{DA}) that increases at a rate of $a(1 - \exp(-bx))$ per x km.

The rates of chemical change due to sulfate oxidation for FS_5W and SS_15W are expressed as shown in Equations (11) and (12) respectively:

$$r_{su.(FS),x} = \frac{0.9947}{x} + \frac{1.846}{x} [1 + \exp(-0.0092x)] \tag{11}$$

$$r_{su.(SS),x} = \frac{0.9947}{x} + \frac{2.84}{x} [1 + \exp(-0.0011x)] \tag{12}$$

where $r_{su.(FS),x}$ and $r_{su.(SS),x}$ are expressed in mol_{fresh lub.}/mol_{DA}.km.

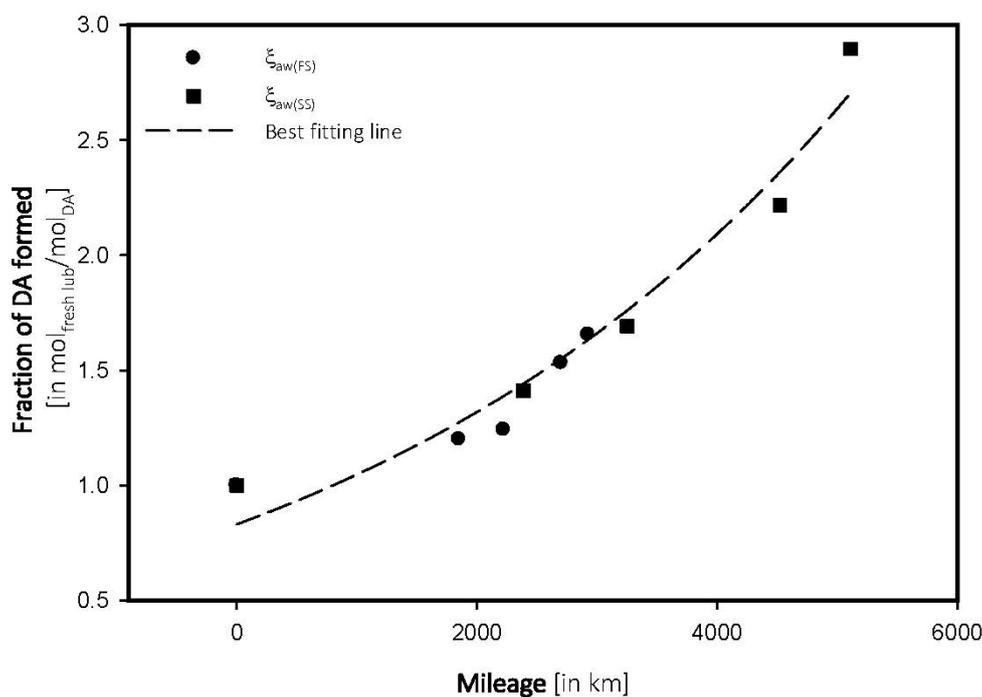
4.3. Antiwear Depletion

Wear, in car engines, is mainly due to friction within the moving parts. The infrared spectrum showed a strong peak of absorption around 1050 cm⁻¹ which is believed to be the response of the P–O–C bond, originating from zinc dithiodiphosphate (ZDDP) present among antiwear additives (AWs). ZDDP was found to degrade at different rates for both models. Various factors may favor this deterioration e.g., foreign materials and soot deposition [21]. Lubricant degradation, due to antiwears and ZDDP depletion, is outlined in Table 5 and plotted as shown in Figure 7.

Table 5. Antiwears and zinc dithiodiphosphate (ZDDP) depletion results.

Mileage (in km)	Transmittance (in %)	ξ_{ox} , (in mol _{fresh lubricant} /mol _{DA})	r_{ox} , (in $\times 10^{-4}$ mol _{fresh lubricant} /mol _{DA} ·km)
FS_5W			
0	96.68	1.0000	0.0000
1851	95.52	1.1998	6.4821
2221	95.48	1.2412	5.5885
2700	95.20	1.5308	5.6696
2926	95.08	1.6549	5.6558
SS_15W			
0	97.02	1.0000	0.0000
2387	95.65	1.4121	5.9158
3251	95.38	1.6904	5.1996
4522	94.87	2.2160	4.9005
5111	94.21	2.8963	5.1996

Figure 7. Antiwear/ZDDP additives depletion profile.



In both samples, ZDDP was found to deplete steadily with a peak around 2000 km. This observation was observed for both samples. Based upon regression technique, a steady formation of contaminants which is believed to follow an exponential growth pattern was observed; its general formulation is given by Equation (13):

$$y(x) = a \times \exp(-bx) \tag{13}$$

where a and b are constants to be determined, in mol_{fresh lubricant}/mol_{DA} and 1/km respectively.

Let $r_{aw.(FS)}$ and $r_{aw.(SS)}$ be the rates of chemical degradation of lubricating oils due to wear metal poisoning of FS_5W and SS_5W respectively, in mol/mol·km.

Considering the best fitting line technique ($R^2 = 0.9524$ and $\Sigma(y_i - y)^2 = 0.1483$), the theoretical rates of chemical change credited to depletion in AWs are expressed by Equations (14) and (15):

$$r_{aw(FS),x} = \frac{0.8301}{x} \exp(0.0002x) \quad (14)$$

$$r_{aw(SS),x} = \frac{0.9505}{x} \exp(0.0002x) \quad (15)$$

4.4. Determination of Breakpoint

Based upon the results of infrared, the depletion trend of antioxidants, sulfonates and antiwears as well as antioxidants expressed mathematically, r_{ox} , r_{su} and r_{aw} were modeled. When plotting the aforementioned parameters *versus* the mileage run by the engine as depicted in Figure 8a,b respectively for fully synthetic and semi synthetic models, characteristic points were found; which were used to determine the distance x' , above which a lubricant is said to be chemically degraded; x' refers to the breakpoint.

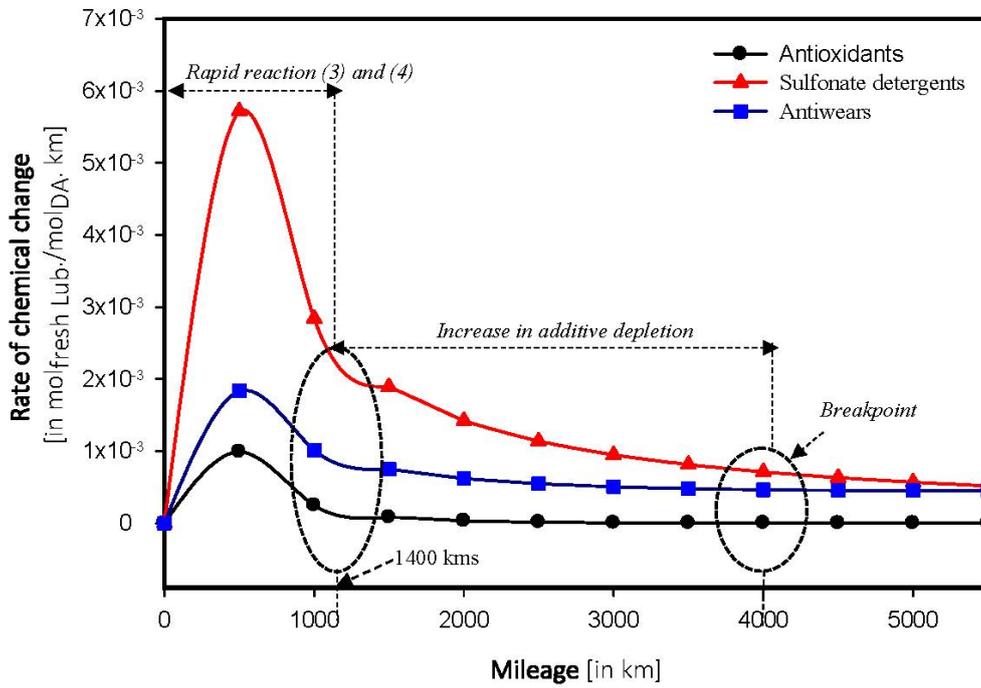
Graphically, the breakpoint for the fully synthetic model was found at $x' = 4000$ km above which a steadiness in additive decomposition was noticed. Moreover, the plots suggest that sulfation/sulfonation (8) are favored to the detriment of carbonyl oxidation (3). Therefore, a fully synthetic lubricant is believed to degrade primarily due to oxidation of sulfur materials, which invariably, consumes sulfonate additives.

The breakpoint for SS_5W was found graphically around 2500 km. Also, ZDDP and sulfonate detergents were found to trigger the loss of performance of semi-synthetic lubricants while antioxidants were observed to deteriorate at a rate slower than ZDDP and sulfonates; the process of depletion of additives is similar to a fully synthetic model. However, the severity was found to hasten lubricant degradation which partially explains the breakpoint found.

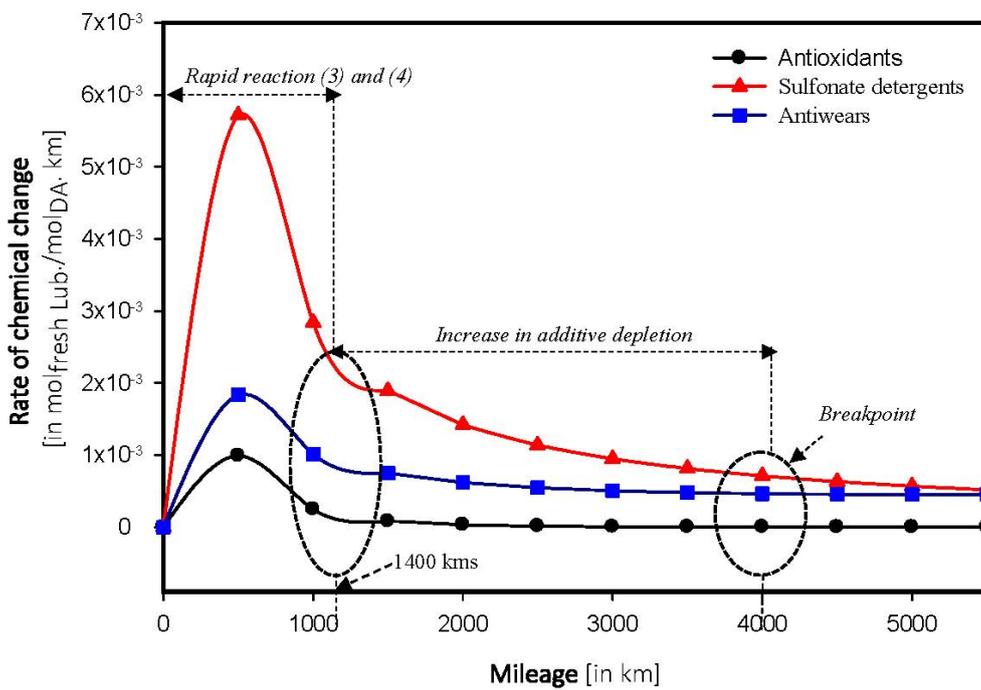
4.5. Forecasting of Depletion in Additives

Oil condition monitoring was conducted on engines which were serviced every 6000 km. Considering a scenario, whereby the lubricants were used for an additional 2500 km, a forecast was made; by which, the extent of chemical reactions on the depletion in additives as well as the behavior of the lubricants throughout their life service could be monitored. Based upon mathematical equations developed previously, antioxidants, antiwears and sulfonate detergents profiles were investigated and are illustrated in Figure 9.

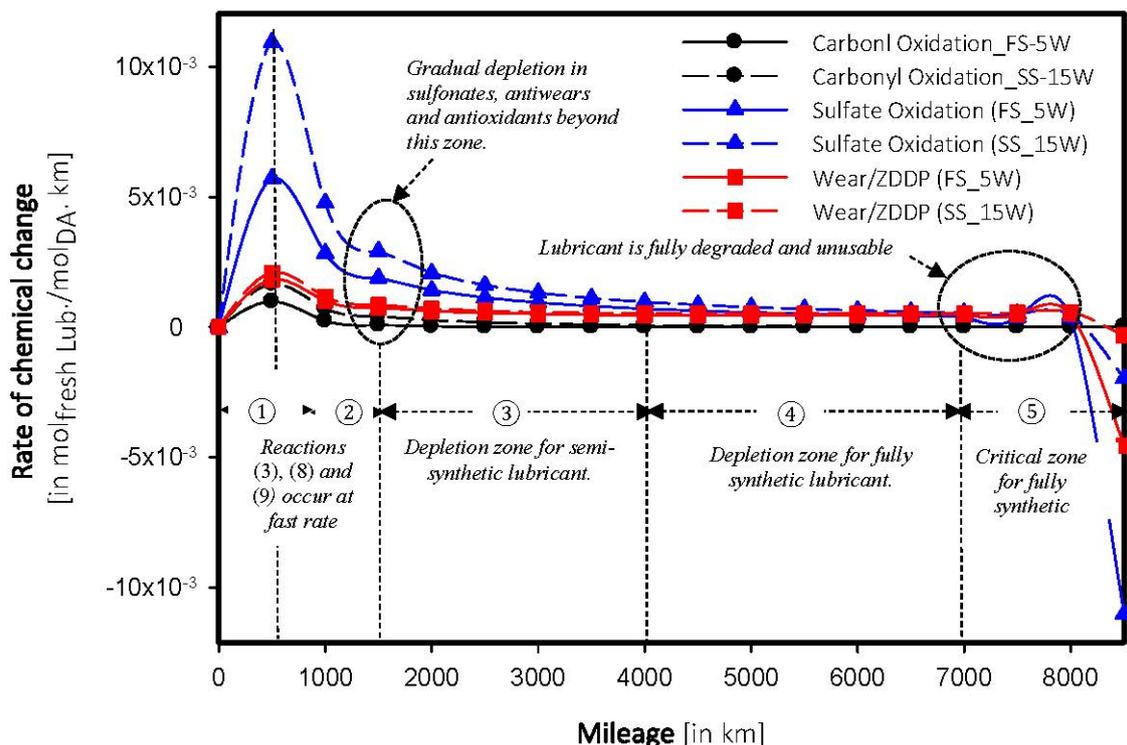
Figure 8. (a) Graphical determination of breakpoint for the fully synthetic model; (b) Graphical determination of breakpoint for the semi synthetic model.



(a)



(b)

Figure 9. Comparative analysis of depletion in additives.

Depletion in additives, hence degradation of lubricants, forecasted for 8500 km showed five distinct phases which every lubricant is believed to follow. The first 500 km (①) an abrupt increase, followed by a sudden decrease (②) in additives, is to be expected with a high rate consumption of sulfonate materials. Reactions (3), (8) and (9) are believed to occur concurrently reaching their highest formation rates at 500 km. However, it is believed that regardless of the occurrence of the aforementioned reactions, within ①, the concentration in additives within the engine is still at an acceptable level. Moreover, the base stock of the lubricant is thought to play a key role during the degradation process as a semi synthetic model is expected to deteriorate faster than a fully synthetic model.

Depletion in additives is expected to decrease continuously (③), even more after the inflexion zone, which is characteristic of the response of the engine oil towards various forms of oxidation. Above this zone, semi synthetic lubricants tend to degrade faster as the breakpoint is found within this distance range. The same pattern is to be found for fully synthetic lubricating oils. However, depletion will occur between 4000–7000 km (④). As the moving parts are in contact, wear detaches metals from the surface, which subsequently, poison lubricating oils; thereby enhancing sulfonate detergents depletion [8,22]. Furthermore, the chemical hindrance of ZDDP is to be expected. It could be argued henceforth that the critical mileage for a semi synthetic lubricant is found within this range, more accurately around 5000 km.

The critical stage, ⑤, is found to occur above 7000 km at which major additives are largely depleted with inclined stress for antiwears and sulfonate detergents. Such a pattern is forecasted for both fully synthetic and semi synthetic lubricants. At this level of the process, the engine oil is “chemically broken” and therefore unusable for an engine, which is left unprotected against corroding agents. Therefore, the critical mileage for a fully synthetic model is around 7000 km.

5. Conclusions

Degradation of lubricating oils is ascribed to a series of chemical reactions occurring within the car engine oil at different rates. Based upon infrared spectra combined with a curve fitting technique, mathematical models, that describe the behavior of additives within the engine, have been developed. The following conclusions have been drawn:

1. Depletion in additives within a car engine follows an exponential regression rather than polynomial.
2. Chemical breakpoint—distance above which the lubricant starts to degrade, depends on the composition of the base stock. The breakpoint was found to be two times higher in a fully synthetic model than a semi synthetic model.
3. Sulfate oxidation and wear poisoning were found to be the primary sources for lubricating oils.

Acknowledgments

This investigation was partially funded by Perkin Elmer Malaysia. The authors want to extend their gratitude to Soon Hua Siew for her kind support.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Mang, T.; Dresel, W. *Lubricants and Lubrication*, 2nd ed.; WILEY-VCH Verlag GmbH & Co.: Weinheim, Germany, 2007; pp. 2–7.
2. U.S. Army Corps of Engineers. *Engineering and Design Lubricants and Hydraulic Fluids*; EM 1110-2-1424; Department of the Army: Washington, DC, USA, 1999; pp. 1–10.
3. Mann, D. Chemical Breakdown and Deterioration of Motor Oil during Use. In *A Comprehensive Technical Handbook on Motor Oil, Lubrication and Filtration*; Motor Oils and Engine Lubrication ed.; Motor Oil Engineers, L.L.C: USA, 2008; pp. 5–7.
4. Hsu, S.M.; Zhang, J.; Jin, Z. The nature and origin of tribochemistry. *Tribol. Lett.* **2002**, *13*, 131–139.
5. Stavinoha, L.L.; Wright, B.R. Spectrometric analysis of used oil. *SAE Tech. Pap.* **1969**, doi:10.4271/690776.
6. Garry, M.C.; Bowman, J. *FT-IR Analysis of Used Lubricating Oils—General Considerations*; 50731; Thermo Fisher Scientific: Madison, WI, USA, 2007.
7. Gómez-Fernandez, J.C.; Villalaín, J. The use of FT-IR for quantitative studies of the apparent pKa of lipid carboxyl groups and the dehydration degree of the phosphate group of phospholipids. *Chem. Phys. Lipids* **1998**, *96*, 41–52.
8. Borin, A.; Poppi, R.J. Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil. *Vib. Spectrosc.* **2005**, *37*, 27–32.

9. Van de Voort, F.R.; Sedman, J.; Yaylayan, V.; Saint Laurent, C. Determination of Acid Number and Base Number in Lubricants by Fourier Transform Infrared Spectroscopy. *Appl. Spectrosc.* **2003**, *57*, 1425–1431.
10. Van de Voort, F.R.; Sedman, J.; Cocciardi, R.A.; Puncuk, D. FTIR Condition Monitoring of In-Service Lubricants: Ongoing Developments and Future Perspective. *Tribol. Trans.* **2006**, *49*, 410–418.
11. Kuhnen, S.; Ogliari, J.B.; Dias, P.F.; Boffo, E.F.; Correia, I.; Ferreira, A.G.; Delgadillo, I.; Maraschin, M. ATR-FTIR spectroscopy and chemometric analysis applied to discrimination of landrace maize flours produced in southern Brazil. *Int. J. Food Sci. Technol.* **2010**, *45*, 1673–1681.
12. Calvo, N.L.; Maggio, R.M.; Kaufman, T.S. A dynamic thermal ATR-FTIR/chemometric approach to the analysis of polymorphic interconversions. Cimetidine as a model drug. *J. Pharm. Biomed. Anal.* **2014**, *92*, 90–97.
13. Basu, A.; Berndorfer, A.; Buelna, C.; Campbell, J.; Ismail, K.; Lin, Y.; Rodriguez, L.; Wang, S.S. Smart Sensing of Oil Degradation and Oil Level Measurements in Gasoline Engines. In Proceedings of the SAE 2000 World Congress, Detroit, MI, USA, 6–9 March 2000; pp. 1–3.
14. Jakoby, B.; Vellekoop, M.J. Physical Sensors for Water-in-Oil Emulsions. *Sens. Actuators A* **2004**, *110*, 28–31.
15. Irshad, M.; Iqbal, N.; Mujahid, A.; Afzal, A.; Hussain, T.; Sharif, A.; Ahmad, E.; Athar, M.M. Molecularly Imprinted Nanomaterials for Sensor Applications. *Nanomaterials* **2013**, *3*, 615–637.
16. Mujahida, A.; Afzal, A.; Glanzing, G.; Leidl, A.; Lieberzeit, P.A.; Dickert, F.L. Imprinted sol-gel materials for monitoring degradation products in automotive oils by shear transverse wave. *Anal. Chim. Acta* **2010**, *675*, 53–57.
17. Anderson, R.J.; Bendell, D.J.; Groundwater, P.W. Ultraviolet-Visible (UV-Vis) Spectroscopy. In *Organic Spectroscopic Analysis*; Royal Society Chemistry: Cambridge, UK, 2004; pp. 8–10.
18. Bhushan, B.; Lowry, J.A. Friction and wear studies of various head materials and magnetic tapes in a linear mode accelerated test using a new nano-scratch wear measurement technique. *Wear* **1995**, *190*, 1–3.
19. Patnaik, P. *Handbook of Inorganic Book Chemistry*; Mc Graw Hill: New York, NY, USA, 2002; pp. 225–227.
20. Masoudian, S.; Yahyaee, H. Oxidation of alcohols with hydrogen peroxide catalyzed by supported Fe (III) porphyrins. *Indian J. Chem.* **2011**, *50A*, 1002–1005.
21. Foster, N.C. *Sulphonation and Sulphation Processes*; Chemithon: Seattle, WA, USA, 1997; pp. 1–3.
22. Mc Kenzie, T. Atomic Absorption Spectrophotometry for the Analysis of Wear Metals in Oil Samples. *Varian Techtron* **1981**, *AA-10*, 2–4.