Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.52, 2016

FTIR Spectrum Interpretation of Lubricants with Treatment of Variation Mileage

Diana Julaidy Patty[1*] Richard R Lokollo[2]
1.Solid State Physics Laboratory-Departmen of Physics University of Pattimura, PO Box 97233 Ambon, Mollucas Indonesia
2.Atomic Physics Laboratory-Departmen of Physics University of Pattimura

Abstract

Infrared spectroscopy is a widely used technique for the analysis of lubricating oil, lubricating analyzed in this study on Motorcycle. Taking advantage of FTIR spectroscopy (Fourier Transform Infra Red) in the process of identifying the molecular structure of a compound. Samples lubricants used are mineral and Lubricants Synthetic Lubricants. The goal is to see is there a shift in the spectrum of functional groups and intensity of absorption. In the analysis of changes in or degradation of the lubricant in the FTIR spectrum, lubricants mineral or synthetic, assessed based on several parameters lubricants namely, Oxidation (carbon) (1700 cm-1), Nitration (1630 cm-1), Soot (2000 cm-1), Sulfation (1150 cm-1) and water (3400 cm-1). The results showed that based on the analysis of the spectrum for some parameter, synthetic lubricants have the advantage compared to mineral lubricants. Synthetic lubricants have better viscosity stability compared to mineral lubricants, this is because synthetic lubricants generally have better chemical properties / its chemical structure uniform than mineral lubricants. The use of synthetic lubricants have an impact on fuel consumption savings, this is because its viscosity is most stable.

Keywords: FTIR spectroscopy; synthetic lubricants; mineral lubricants; viscosity

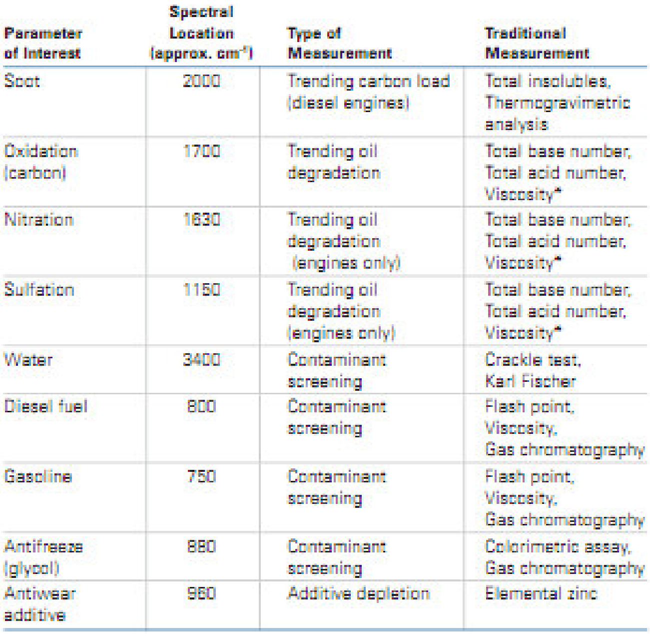
1. Introduction

Infrared (IR) spectroscopy can be used for the routine monitoring of degradation by-products, contaminants and additive levels in used lubricating oils. Acceptance of this technique as a standard method for the analysis of used oils and lubricants has been slow in coming for several reasons. The most notable hindrance is the fact, that much of the data used in assessing engine and lubricant performance have been historically obtained using traditional physical and wet chemical methods. In-service lubricating oils are tested to diagnose the lubricant's condition in order to determine when there needs to be an oil change to avoid engine damage and prolong engine life. Engine oils provide lubrication of engines moving parts and protect them from wear and corrosion. In diesel engines, the oil must also suspend soot particles resulting from incomplete combustion of fuel. The composition of the lubricating oil can indicate whether there was improper combustion seal leakage or any changes in the base oil. The analysis of in-service oils also provides information about engine-related functions to identify component failures or harmful operating conditions.

In this research, the test lubricant with FTIR spectroscopy method on samples of mineral lubricants and synthetic lubricants with variations mileage treatment of motorcycle. The main analysis of FTIR invitation to provide information whether the change in the intensity of the absorption and bonding groups on each sample. Research quality lubricants also aims to provide accurate and objective information about the quality of some brands of oil that has been circulating in the market.

The parameters typically analyzed using FT-IR are listed in Table 1. This table presents the parameters of interest and information on obtaining and using them. The spectral plot in Figure 1 shows a used oil difference spectrum and labels the peaks of interest indicated in the table.

Table.1 The parameters typically analyzed using FT-IR



Parameter of Interest	Spectral Location (approx. cm^{-1})	Type of Measurement	Traditional Measurement
Soot	2000	Trending carbon load (diesel engines)	Total insolubles, Thermogravimetric analysis
Oxidation (carbon)	1700	Trending oil degradation	Total base number, Total acid number, Viscosity*
Nitration	1630	Trending oil degradation (engines only)	Total base number, Total acid number, Viscosity*
Sulfation	1150	Trending oil degradation (engines only)	Total base number, Total acid number, Viscosity*
Water	3400	Contaminant screening	Crackle test, Karl Fischer
Diesel fuel	800	Contaminant screening	Flash point, Viscosity, Gas chromatography
Gasoline	750	Contaminant screening	Flash point, Viscosity, Gas chromatography
Antifreeze (glycol)	880	Contaminant screening	Colorimetric assay, Gas chromatography
Antiwear additive	960	Additive depletion	Elemental zinc

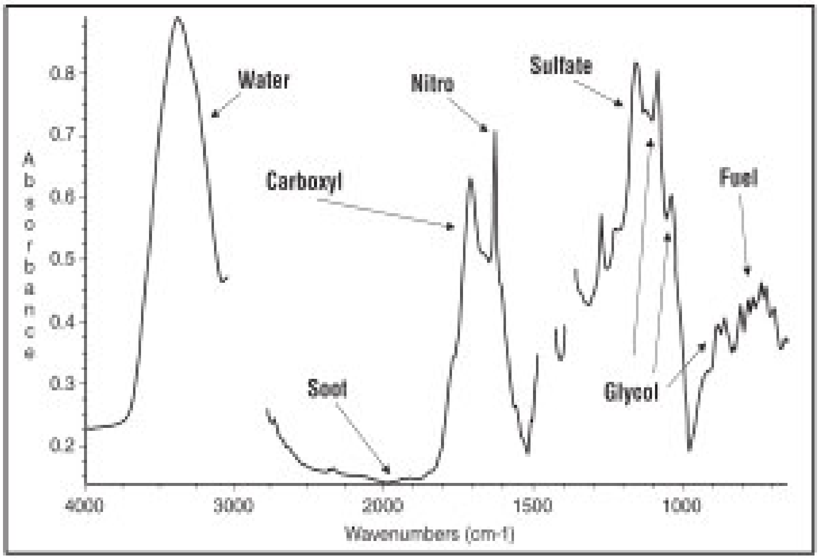


Figure 1: Used oil difference spectrum

2. Electromagnetic Radiation

The visible part of the electromagnetic spectrum is, by definition, radiation visible to the human eye. Other detection systems reveal radiation beyond the visible regions of the spectrum and these are classified as radiowave, microwave infrared, ultraviolet, X-ray and γ-ray. These regions are illustrated in Figure 2, together with the processes involved in the interaction of the radiation of these regions with matter. The electromagnetic spectrum and the varied interactions between these radiations and many forms of matter can be considered in terms of either classical or quantum theories.

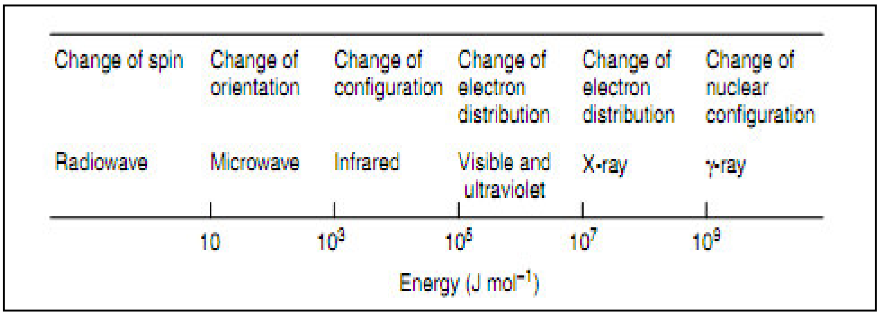


Figure 2. The Electromagnetic Spectrum

The nature of the various radiations shown in Figure 2 have been interpreted by Maxwell's classical theory of electro- and magneto-dynamics – hence, the term electromagnetic radiation. According to this theory, radiation is considered as two mutually perpendicular electric and magnetic fields, oscillating in single planes at right angles to each other. These fields are in phase and are being propagated as a sine wave. The magnitudes of the electric and magnetic vectors are represented by E and B, respectively.

3. Fourier Transform Infrared (FTIR)

Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram. The latter is a signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier-transformation. The basic components of an FTIR spectrometer are shown schematically in Figure 4. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation.

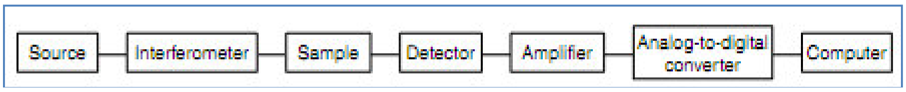


Figure. 3 Basic components of an FTIR spectrometer.

Fourier Transform Infrared spectroscopy is a technique used to determine qualitative and quantitative features of IR-active molecules in organic or inorganic solid, liquid or gas samples. It is a rapid and relatively inexpensivemethod for the analysis of solids that are crystalline, microcrystalline, amorphous, or films. Samples are analyzed on the scale of microns to the scale of kilometers and new advances make sample preparation, where needed, relatively straightforward. Another advantage of the IR technique is that it also can provide information about the "light elements" (e.g., H and C) in inorganic substances.

To obtain the best possible IR spectra of samples it is necessary to choose the appropriate IR source, detection method and accessories. First, the analyst needs to determine the appropriate region of the infrared spectrum, in which the sample under investigation has diagnostic features. These regions are defined using wavelengths (λ) in microns (μm) or wavenumbers (*ν)* in reciprocal centimeters (cm^{-1}), where $\lambda = 10^4/ \nu$. In terms of frequency, 1 cm^{-1} = 2,9979 10^{10} Hz ~ 30 GHz. Different users have difined the near-, mid- and far- IR region differently (Hirschmugl 2004), based on the practical limits of their instruments.

Two types of interactions-absorption and transmission-are important in the typical IR experiment. When the molecule in the sample compartment of the spectrometer is exposed to a source of continuous IR radiation, the photons of discrete energy units that are absorbed by the molecule do not reach the detector.

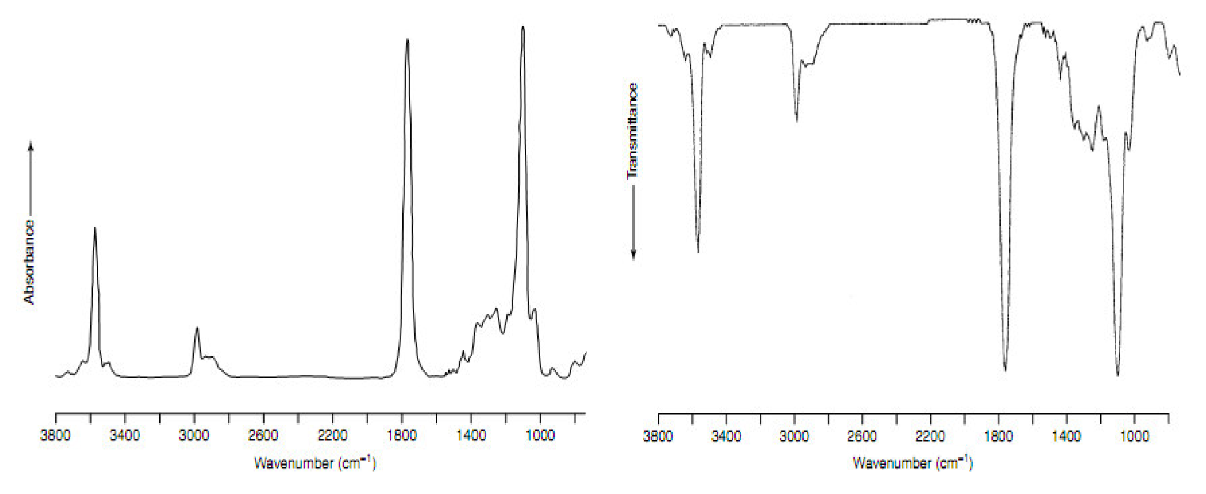


Figure 4. Absorbance spectrum and Transmittance spectrum

The IR spectrum reveals these missing photons, or absorptions, as a series of well-defined, characteristic, and reproducible absorption bands. Photons that are not absorbed by the sample are transmitted to the detector essentially unaltered.

3.1 Group frequencies

Within any molecule, a given functional group (a combination of atoms such as a carbonyl group or an amide group) is responsible for IR absorptions at or near the same frequency, regardless of the rest of the molecule. The position (i.e., frequency or wavenumber) of an absorption band depends on the mass of the atoms in the absorbing group, along with the strength and angles of the connecting bonds. A mathematical equation for the vibrational frequency of a two-body system (Hooke's law) can be used to predict the absorption band position for simple molecules (Smith 1979). However, only a limited number of small molecules have vibrational spectra simple enough for complete theoretical analysis and interpretation.

The majority of IR spectra-structure correlations are empirical, having been determined by the analysis of a large number of compounds. The vibrational frequencies for any particular functional group are characteristic of that group-e.g., most carbonyl stretches occur between 1650 and 1750 cm-l , and most carbon-hydrogen stretches occur near 3000 cm -1. These characteristic vibrations are termed group frequencies and are used for the identification of materials and for the determination of structure in an unknown pure compound.

3.2. Oil Quality

All lubricants will undergo degradation while in use. The most often common signs of base oil degradation are increased oxidation and shear thinning. Oxidative degradation occurs as a result of reactions with oxygen in the environment in which a lubricant resides. Shear thinning is a physical breakdown of the oil due to pressure and temperature conditions to which the lubricant is exposed. These and other degradation processes of the lubricant make it unable to provide adequate lubrication for mechanical moving engine parts. Therefore test methods to assess the levels of degradation by-products are paramount to determining the condition of the oil. Three classes of reactions are dominant in the oil degradation process:

3.2.1 Soot Particles

Suspended soot is the result of the incomplete combustion of fuel. This is usually only a consideration in diesel engines but could be indicative of carburetor or injector problems with other fuel systems. While it has no specific frequency of absorption in the infrared spectrum, soot causes a shift in the baseline of the spectrum due to absorption and scattering of light. Since there are no other spectral features in the region around 2000 cm-1, this area is used to assess the level of soot in a sample.

3.2.2 Carbonyl Oxidation Products

The broad feature centered around 1730 cm^{-1} is due to the presence of carbonyl-containing degradation products of oil. These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts, as well as others. The broadness of the peak is because of the wide variety of materials present. The point of maximum intensity will vary as the oil and conditions of its use are changed. The increase in peak height that occurs as the number of hours the oil has been run in the engine increases has a greater significance in the measurement of degradation than total acid number (TAN) or viscosity.

3.2.3 Nitrogen Oxidation Products

The sharp feature at 1630 cm^{-1} is the result of nitrogen oxide fixation into the oil. The materials that create this feature are due mostly to nitrate esters. Nitrogen fixation products are most significant in gasoline and natural gas engines and some diesel systems that use exhaust gas recirculation.

3.2.4 Sulfur Oxidation Products

Another broad spectral feature, centered around 1150 cm^{-1}, is the result of sulfate compounds as well as overlap with oxidation products. Sulfate material is a result of the introduction of sulfur from fuels or from the oxidation of sulfur from the base oil and additives. This band is a fairly specific measure of over basing additive consumption and relates to total base number (TBN).

3.2.5 Fuel Residue

The measurement of fuel residues or raw fuel is difficult by any method. The main difference between the fuel and base oil is in molecular weight or boiling range and the percentage of aromatic materials. Fuel has a lower boiling range and significantly higher percentage of aromatic material. Conventional methods make use of the lower boiling range, while the infrared approach examines the aromatic content to indicate if fuel is present. The spectral features around 800 cm-1 are used for this purpose.

3.3 Oil analysis by Fourier transform infrared spectroscopy

Used oil samples are complex mixtures of a large number of different compounds and include compounds derived from the original formulation of the base oil and its additives, oil degradation by-products and contaminants. The challenge of the analysis is to determine the small concentrations of degradation by-products and contaminants in the presence of the base oil and additives. In FT-IR spectroscopy, to subtract out the spectrum of the base oil and additives from the used oil sample spectrum to obtain a differential spectrum and which represents only the changes in the oil. In that way, the changes in the oil due to accumulation of degradation by-products, additive depletion and contamination levels can be more readily visualized. Due to the the digital data handling of FT-IR spectrometers, the spectra of many reference oils simply samples can simply be stored to the hard disk and compared to their respective used oil sample analysis results at a later time. This allows for the condition of the lubricant to be trended at different sampling time points while it is in-service.

4. Experimental Method

This Research was done in Lab solid-state physics, Faculty of Mathematics and Science UNPATTI . The main tool used is ABB type MB3000 FTIR spectrometer. The samples used are mineral and synthetic lubricants , which were treated with vehicle mileage 5 Km, 10 Km, 15 Km, 20 Km.

FTIR spectroscopy (Fourier Transform Infrared) is equipped with infrared spectroscopy Fourier transform for the detection and analysis of the results spectrum. Core FTIR spectroscopy is a Michelson interferometer is a tool for analyzing frequencies in the combined signal . The infrared spectrum pentrasmisian generated from the light passing through the sample , the measurement of the intensity light with a detector and compared with the intensity without the sample as function of wavelength . The infrared spectrum obtained is then plotted as a function of energy intensity , wavelength (μm) or wave number (cm^{-1}).

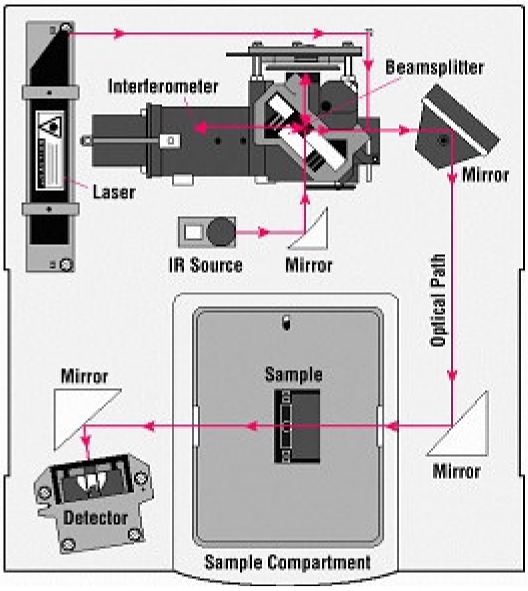


Figure 5. A Simple Spectrometer Layout

Analysis of functional groups of a sample is done by comparing the absorption band that formed in the infrared spectrum using spectrum correlation table and use comparative compounds (already known).

FTIR spectroscopy is an analytical measurement method to characterize and identify the structure of organic molecules. In oil analysis, we are analyzing in-service ubricants to detect the presence of any contaminants or by-products formed. The lubricant, the by-products and the contaminants, all absorb IR energy at specific and reproducible wavelengths.

5. Results and Discussion

FTIR spectroscopy of the test with a sample of lubricant obtained spectrum IR as below.

A. Mesran Lubricants

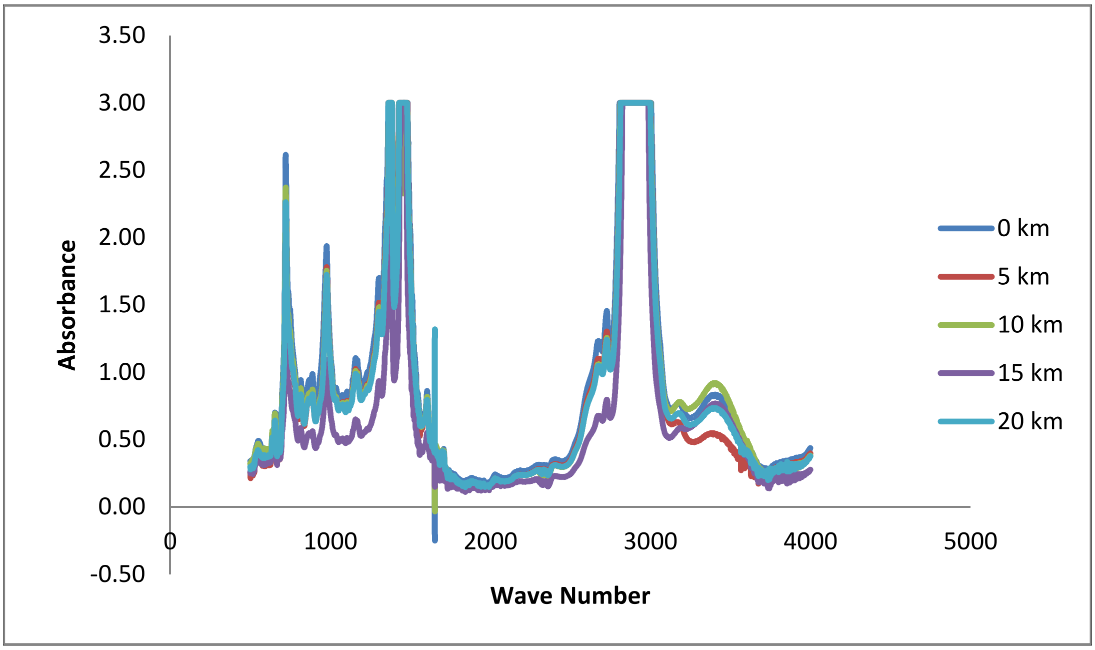


Figure. 6. Spectrum Of Mesran Lubricants

B. MPX Lubricants

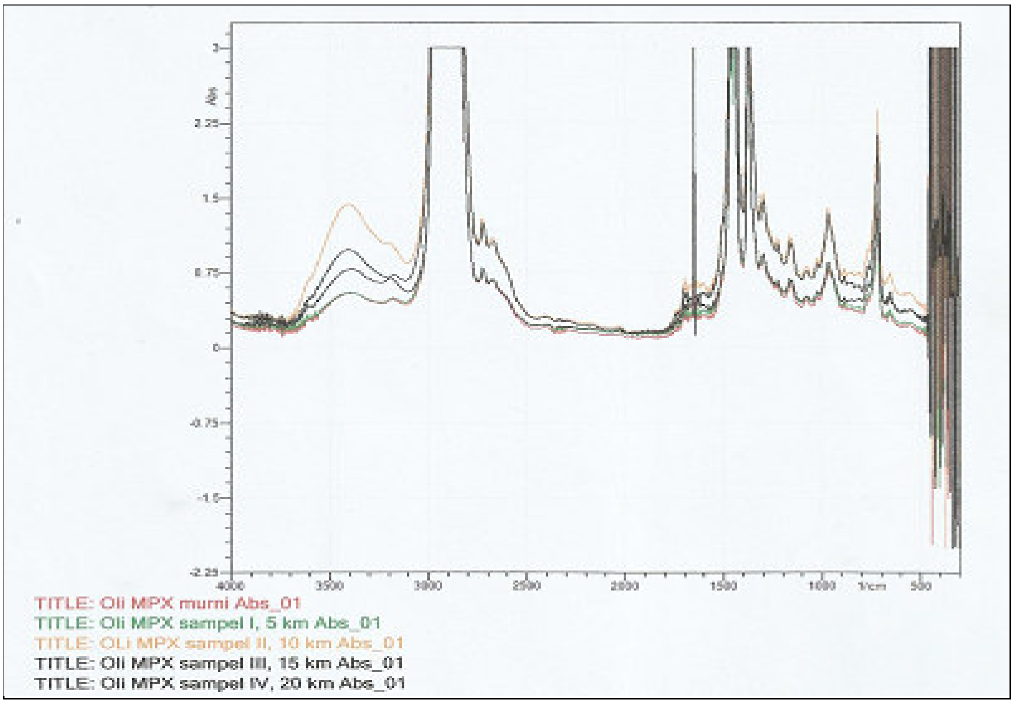
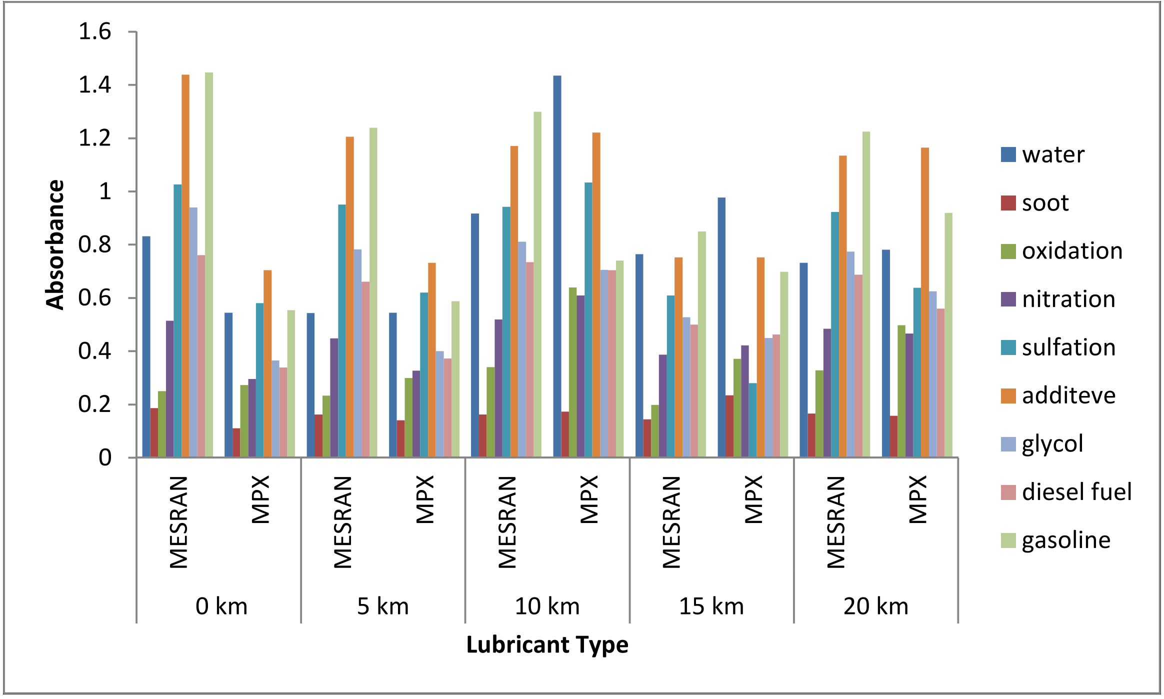


Figure 7. Spectrum of MPX Lubricants

Figure 6 and Figure 7, shows five different spectrum oils. The plot shows the differences in spectral features resulting from the variation in base oils and additives used to make the lubricants. These differences must be taken into account, Because of this, spectral subtraction of the proper new oil reference spectrum is applied to obtain correct used oil analysis results. The difference spectrum is shown with a much expanded y-scale.

C. The Changes of Lubricants parameters with vehicle mileage



The results of spectral analysis on both lubricants, shows the basic lubricant, oil Mesran, at 0 km has a value for each parameter higher than MPX, and the most prominent is sulfation, additives, glycol and gasoline.

Oxidation stability. The lubricant should not undergo undesirable oxidative changes when used within the applicable temperature range. it looks at the results of the comparison lubricant Mesran and MPX , reasksi oxidation showed no significant changes , or fairly stable in both lubricants.

At each change of vehicle mileage, changes in the structure of the lubricant that show changes in parameters and gasoline additive always coincide. Additives can be defined as compounds that can improve or strengthen the specifications or characteristics of lubricating oil base oil. Some multipurpose additives can improve some of the characteristics of the base oil, while some other additives to function as a complement. complex mixtures of additives are added to the base oil to obtain the desired level of performance. Interactions between several different additives can be either synergistic or antagonistic.

Of all the properties of fluid lubricants, viscosity is the most important, since it determines the amount of friction that will be encountered between sliding surfaces and whether a thick enough film can be built up to avoid wear from solid to-solid contact. Viscosity customarily is measured by a viscometer, which determines the flow rate of the lubricant under standard conditions; the higher the flow rate, the lower the viscosity. on previous testing for second-viscosity lubricants, showed results that the viscosity of the lubricant MPX better than Lubricants Mesran

6. Conclusion

The results showed that based on the analysis of the spectrum for some parameter, synthetic lubricants have the advantage compared to mineral lubricants. Synthetic lubricants have better viscosity stability compared to mineral lubricants, this is because synthetic lubricants generally have better chemical properties / its chemical structure uniform than mineral lubricants. The use of synthetic lubricants have an impact on fuel consumption savings, this is because its viscosity is most stable.

Reference

Barbara Stuart, Infrared Spectroscopy: *Fundamentals and Applications*, 2004. John Wiley & Sons, Ltd.

D. Michele R,. Dusan Stulik, James M. Landry, 1999. *Infrared Spectroscopy in Conservation Science*. The Getty Conservation Institute, Los Angeles.

Michael C. Garry, John Bowman, Thermo Fisher Scientific, Madison,FT-IR *Analysis of Used Lubricating Oils –* General Considerations,WI, USA. 2007 Thermo Fisher Scientific Inc.

Toms Allison M. *Fourier-Transform Infrared (Ftir) Spectroscopy – Applying The Correct Method For Your Application,* 2007. Society of Tribologists and Lubrication Engineers (STLE) 62nd Annual Meeting - May 6-10, 2007 Philadelphia, Pennsylvania, USA.

Stretching Vibrations15 Infrared Spectroscopy: Theory. Online edition for students of organic chemistry lab courses at the University of Colorado, Boulder, Dept of Chem and Biochem. (2002)

Used Lubricating Oil Analysis by FT-IR, 2008. www.bruker.com/optics.