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COMPRESSOR OIL ASSESSMENT BY USING FT-IR SPECTROSCOPY

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Abstract

An experimental assessment of compressor oil degradation was carried out in order to establish its degradation. The monitored screw compressor is using poly-alpha-olefin synthetic oil to compress natural gas. Gas composition and working conditions are continuously affecting the oil, which in this type of compressor exerts multiple functionalities: lubrication, cooling, sealing and compression.

Taking into account the gas composition, the oil type used within the screw compressor directly influences its performances and life span. The literature highlights that a thorough monitoring and analyze of the oil is, in fact, one of the most important ways to assess the performances and usage of a screw compressor. Thus, many of the compressor maintenance issues can be identified and solved resulting in both the increase of its life span and the minimization of the maintenance expenditures. Therefore, basic characteristics determinations - flash point and cinematic viscosity were performed as well as FTIR testing for the collected samples. The degradation tendency of the oil based on the influence of gas characteristics was assessed. FTIR spectra evaluation, highlighted the degradation tendency for base oil at chemical level, leading towards a better understanding of both degradation phenomena and altering of oil characteristics.

Key words: Poly-alpha-olefin, FT-IR spectroscopy, screw compressor, oil degradation,

1. Introduction

Oil injected screw compressors are widely used for medium pressure applications in many industries. Low cost compressors can be adopted for compression of helium or other gases, leading to significant cost savings [1].

Synthetic hydrocarbon lubricants are engineered for particular applications. For compressor applications, poly-alpha-olefin (PAO) based oil is commonly used. PAO provide many of the best lubricating features of a mineral oil and without its drawbacks. Although PAO components are derived from petroleum base stock, they are chemically re-engineered to have a consistent, controlled molecular structure of fully saturated hydrogen and carbon. Because

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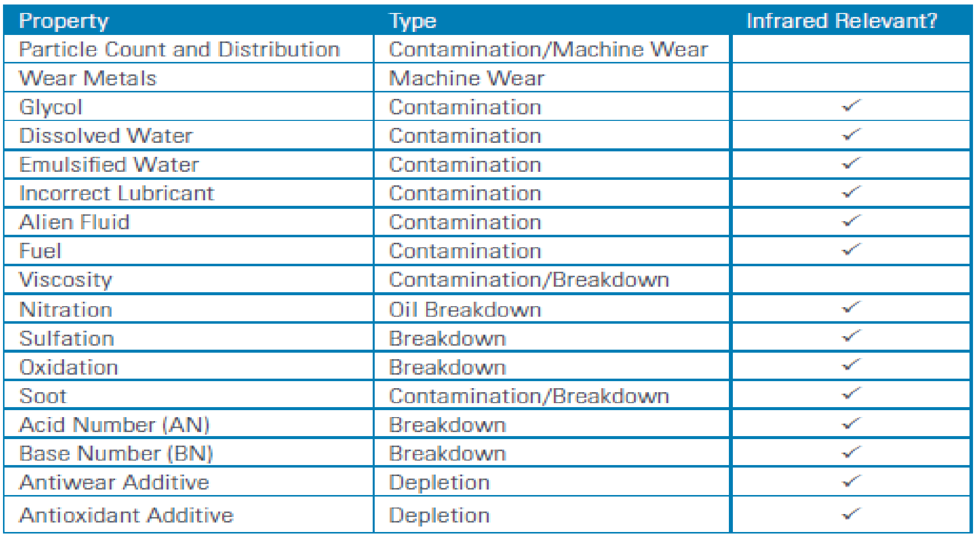
their molecules structure is homogenous, their properties and characteristics are predictable. PAO separate water extremely well, are chemical stabile and have low toxicity. PAOs, however, are not good solvents. The additive chemistry must be adjusted for this fact [2].

Machine conditioning monitoring or predictive maintenance is a practice of assessing a machine's condition by periodically gathering data on machine-health indicators to determine when to schedule maintenance. Knowing to interpret the changes observed in the lubricants properties facilitates the increase of both the uptime and the lifespan of the equipment.

Lubricants are the life blood of wetted machinery. As an important element of predictive maintenance technologies, in-service oil analysis, can provide trace information about machinery wear condition, lubricant contamination and as well as lubricant condition. The immediate benefits of in-service oil analysis include avoiding oil mix up, contamination control, condition based maintenance and failure analysis [3].

Solid contamination (sand and dirt) accelerates the formation of abrasive wear. Liquid contamination such as moisture in oil accelerates machine corrosion. Fuel or coolant dilution will decrease the viscosity, therefore generating more abrasive wear (rubbing wear). It is critical to keep the lubricating oil clean and dry all the time. This requires set cleanliness limits and continue monitoring the contamination during the machine operation [3].

Fourier transformed Infrared spectroscopy can be used for monitoring in-service lubricants, since, as shown in figure 1, 14 out of 17 in-service lubricant's properties of interest can be monitored by this technique.



Property	Type	Infrared Relevant?
Particle Count and Distribution	Contamination/Machine Wear	
Wear Metals	Machine Wear	
Glycol	Contamination	✓
Dissolved Water	Contamination	✓
Emulsified Water	Contamination	✓
Incorrect Lubricant	Contamination	✓
Alien Fluid	Contamination	✓
Fuel	Contamination	✓
Viscosity	Contamination/Breakdown	
Nitration	Oil Breakdown	✓
Sulfation	Breakdown	✓
Oxidation	Breakdown	✓
Soot	Contamination/Breakdown	✓
Acid Number (AN)	Breakdown	✓
Base Number (BN)	Breakdown	✓
Antiwear Additive	Depletion	✓
Antioxidant Additive	Depletion	✓

Fig. 1 Typical lubricant parameters that are measured and the relevance of FT-IR spectroscopy per property [4]

The general trend in the analysis of petroleum products is to use different types of spectroscopy: IR, Raman, etc. since these techniques are becoming more and more adapted and accepted as standard tools of choice to perform tests which previously required wet chemical analysis. The infrared spectroscopy of lubricants rely on a very simple method. You observe how much IR radiation the lubricant absorbs as a function of frequency of the radiation. In general, different lubricants have different spectra, so the main issue is to be sure that an accurate IR spectrum is acquired. [4]

2. Experimental

In order to achieve the fully characterization of the oil degradation it is compulsory to perform a set of determinations. Firstly, the analysis of basic characteristics is needed in order to make a comparison with the characteristics provided by the oil's datasheet. Thus the most important base (basic) characteristics that are firstly measured are flash point and cinematic viscosity. After that, a thorough investigation must be done in order to establish oil degradation at molecular level and the most appropriate way to do this is by the means of FT-IR spectroscopy.

The determination of the flash point can be performed in both open or closed cup apparatus. The one used in this paper is an open cup Scavini automatic flash and fire point tester, as shown in figure 2.

Fig. 2. Scavini automatic flash and fire point tester

Flash point measures the tendency of the sample to form a flammable mixture with air under controlled lab conditions. Flash point is used for shipping and safety regulations to define flammable and combustible materials. Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively non-volatile or non-flammable material. For example an abnormally low flash point in a sample of kerosene can indicate gasoline contamination. [5]

The test cup is filled to a specific level with the sample. The temperature of the sample is increased rapidly at first and then at a slow constant rate as the flash point is approached. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. [5]

The cinematic viscosity determination is, along with flash point determination one of the most important methods to test basic characteristics of an lubricating oil. The viscometer used in this paper is a Scavini ubbelhode viscometer, as shown in figure 3.

Fig. 3. Scavini ubbelhode viscometer

Basically, the viscometer consists of the capillary tube, venting tube and filling tube, capillary with the measuring sphere and reference level vessel. Above and below the measuring sphere there are two markers indicating the timing of oil level.

The sample runs down from the capillary as an thin film under atmospheric pressure, while the time in which the sample flows is clocked. The diameter of the capillary should be selected accordingly with the viscosity of the measured (analyzed) sample. For samples with low viscosity values a smaller capillary is recommended in order to mitigate the measurement errors. [6]

For all the oils used in industrial applications, the datasheet provided by the producer gives the viscosity at 40°C, so all the measurements are made in a thermostatic bath. Depending on the heating fluid used the temperature in the thermostatic bath can vary from room temperature up to 150°C.

FT-IR analysis is a versatile tool for detecting usual contaminants, forming of secondary products and degradation of the additives packages or base oils, thus becoming a wide spread technique related to multiple evaluation of oils degradation. The FT-IR technique is based on the mathematical operation called Fourier transform and the adsorption lines of the sample are correlated with the ones already known for each type of chemical bond. So, initially a reference spectra is acquired for a fresh sample of oil. Then, the spectra for the sample is acquired and after that, the two spectra are compared and registered differences can provide info related to the changes within oil composition, degradation, contamination and equipment wear.

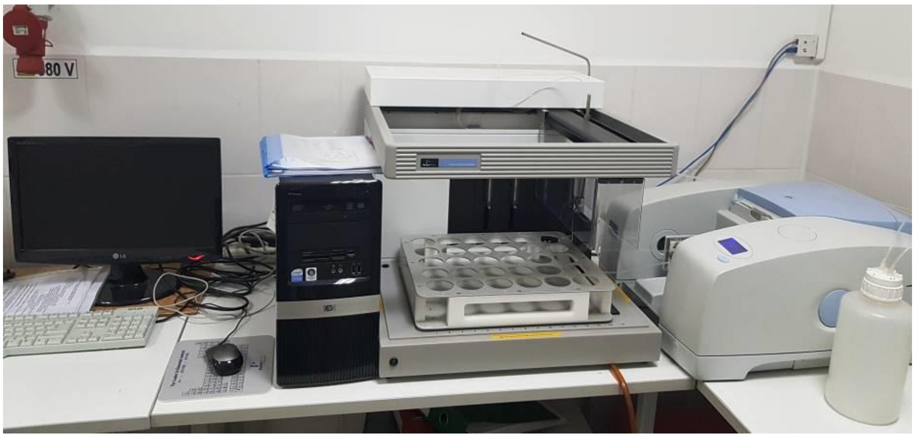


Fig. 4. Perkin Elmer oil spectrometer and autosampler

The analytical instrument used for determinations is a Perkin Elmer oil spectrometer equipped with auto sampler, as shown in figure 4, and provides important information regarding the lubricating oil degradation at several levels as follows):

- degree of oxidation. The oil exposed to oxygen at elevated temperatures will oxidize to a variety of compounds, the majority of which are carbonyl compounds, including carboxylic acids. These acids contribute to the acidity of the oil, depleting the basic additives present in the oil and contributing to corrosion. The degree of oxidation is a good indicator of oil degradation. A rapid increase in oxidation may indicate an overheating or a depletion of the anti-oxidant additive due to an over-extended oil change period.

- nitration value. Nitrogen oxides produced form the oxidation of atmospheric nitrogen during the process, react with the oil. Nitration increases the viscosity of the oil and is the major cause of build-up of varnish. A high nitration value, known as NO_x, indicates excessive loads and/or low operating temperature.

- sulfate value. Sulfur oxides are produced by the reaction of sulfur compounds present in oil with water and can lead to the formation of sulfuric acid. The sulfuric acid is neutralized by the oil's basic additives. A rapid increase of the sulfate value may indicate a high value of sulfur in the compressed gas or a rapid depleting of anti-wear additive.

- ester breakdown. Synthetic oil usually contain a high proportion of poly-ol esters. These esters are susceptible to breakdown in the presence of water and acids (hydrolysis). Ester breakdown contributes to the acidity of the oil and can result in the formation of crystals of the base poly-ol and clogging the filters.

- anti-wear additive depletion. Anti-wear additives are consumed during the normal life of the oil. The consumption of the anti-wear additives is accelerated by the presence of water. A rapid loss of anti-wear additive may indicate excess load or water contamination.

- IR spectra. Having the reference spectra of the analyzed oil, a comparison between the fresh and used oil spectra can be made in order to assess the oil degradation. Although all oil producers do not make public their oil recipe and, thus, it cannot be anticipated which are the degradation products that should be contained by an used oil, a correlation of the information regarding gas composition, physical characteristics and the possible structures that absorb IR radiation at certain wavelengths can result in an appropriate assessment of the oil degradation. It is to be known that the spectrometer's software is provided with its own libraries making possible the visualization of almost all possible structures. [7]

3. Results and discussions

The monitoring protocol states that oil sampling should be made every 500 operating hours, in order to assess oil degradation. Also the sampling protocol must be followed in order to obtain the most representative samples.

Thus, 3 samples have been brought to the lab in order to be analyzed, until the oil has been changed. Table 1 provides a comparison between the values of flash point and cinematic viscosity determined for the used oil samples and the ones stated in the oil's data sheet.

Table 1

Basic characteristics determination

Characteristic	***Cinematic viscosity at 40 °C, mm^2/s (cSt)***	***Flash point,° C***
Method	*SR ISO 3104-2002*	*ASTM D92 - 05a*
Equipment	*SCAVINI ubbelhode viscometer*	*SCAVINI Flash point*
Datasheet values	***100***	***>240***
Stabio S100 - 493 h	49,6	36,9
Stabio S100 - 991 h	33,4	27,6
Stabio S100 - 1487 h	24,34	25,8

As it can be observed in Table 1, the basic parameters of the oil rapidly decrease during working hours. In a screw compressor the oil has three main functions: lubrication, cooling and compression. Thus, unlike other compressor types, the oil comes in direct contact with the gas.

Since the gas in this extraction plant is a "rich" one, it can be anticipated that lubricating oil basic characteristics may decrease. Although the lubricating oil basic characteristics provides valuable information regarding its degradation, it is compulsory to perform its chemical degradation assessment, before taking any decision.

Having in mind the above mentioned aspects, FT-IR spectroscopy has been made in order to assess the chemical degradation of the oil.

So, a reference spectra has been acquired using new, unused oil and the first sample's spectra has been compared with it, as shown in figure 5

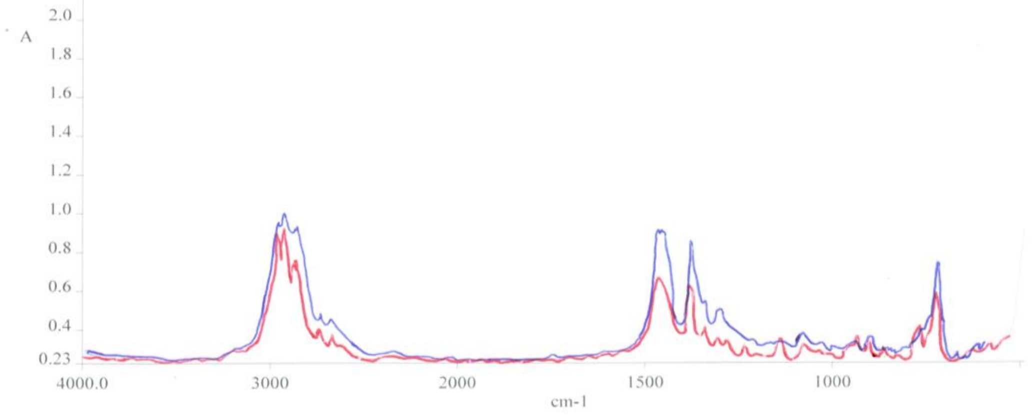


Fig. 5. Comparison between Sample 1 spectra and reference spectra

In table 2, the main indicators regarding oil chemical degradation are shown. It must be emphasized that provided values, represents only the difference between the two spectra.

Table 2.

Sample 1 compared with reference

Characteristic	Values
Antiwear (A/cm)	0.00
Ester BD (A/cm)	1.27
Hydroxy (A/cm)	0.00
NO_x (A/cm)	1.24
Soot 1980 (A/cm)	0.50
Soot 3800 (A/cm)	1.48
Sulfate (A/cm)	0.00
Water (%)	0.00

As it can be seen in tables 1 and 2, during the first 500 working hours, the gasoline present in the natural gas determined both an oil "dilution" (low flash point and low cinematic viscosity) and a slightly depletion of the esters content in the oil. Also the presence of NO_x in the used lubricating oil along with an increased value of Soot indicates an compressor overload.

Anti-wear additive has not been affected during the operation and also, there is no oxidation since, it is well known that "rich" gas contains only trace amounts of water.

After analyzing the IR spectra, and correlating it with gas composition, chemical degradation indicators and possible structures that may occur at different wavelengths, it results that the base oil has been degraded due to the gas composition in short chain substitutes, namely: short chain - methyl, ethyl, propyl, and long chain C_4 mainly with straight chain.

This analysis highlights the fact that the gasoline within the natural gas has blended with the oil thus introducing these substituents in its chemical structure.

The second sample has been brought in the lab after another 500 or so working hours. As it can be seen in table 1, the basic characteristics of the oil continued to decrease but at a slower rate, meaning that the oil is almost saturated in gasoline.

A new IR spectra has been obtained and compared with the previous one, as shown in figure 6.

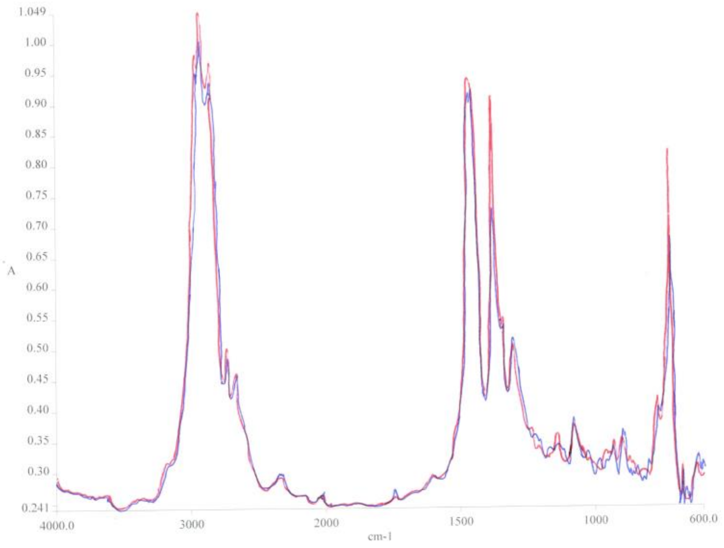


Fig. 6. Comparison between Sample 2 spectra and Sample 1 spectra

In table 3 are shown the main indicators of oil chemical degradation. As mentioned above, the values are for the differences between the two samples.

Table 3

Sample 2 compared with sample 1

Characteristic	**Values**
Antiwear (A/cm)	0.00
Ester BD (A/cm)	1.22
Hydroxy (A/cm)	0.00
NO_x (A/cm)	1.44
Soot 1980 (A/cm)	0.33
Soot 3800 (A/cm)	1.54
Sulfate (A/cm)	0.00
Water (%)	0.00

As it can be seen from table 1 and 3, during the first 1000 working hours, the oil kept degrading, but at a slower rate than in the first 500 working hours. Nevertheless almost the same oil constituents have been degrading and, after analyzing IR spectra it is clearly shown that more and more functional C_1 to C_4 substituent occur in oil's chemical structure with a higher ratio of C_4 substituents, also with straight chains.

The third sample was brought in the lab after almost 1500 working hours, and the above mentioned analysis has been performed.

Table 4 contain the most important indicators for chemical degradation.

Table 4

Sample 3 compared with sample 2

Characteristic	Values
Antiwear (A/cm)	0.75
Ester BD (A/cm)	1.27
Hydroxy (A/cm)	0.00
NO_x (A/cm)	1.82
NO_x vs Oxid (A/cm)	4.00
Oxidation (A/cm)	1.41
Soot 1980 (A/cm)	0.00
Soot 3800 (A/cm)	2.02
Sulfate (A/cm)	0.00
Water (%)	0.00

As it can be seen in Table 1, the basic characteristics continued to decrease, reaching a critical value for compressor's integrity. Also, in Table 4, two new indicators are shown: Oxidation and NO_x vs. Oxid, so the oil started to oxidize. The presence of oxidation indicates a depleting of base additives of the oil that causes the compressor corrosion and also it shows that the oil change period has been over-extended. It can be stated also that the anti-wear additive started to deplete.

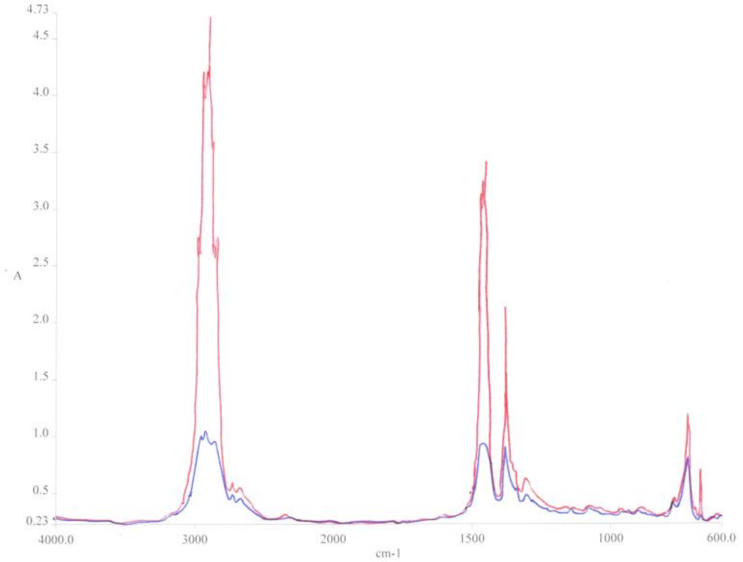


Fig. 7. Sample 3 compared with sample 2 spectra (Comparison between Sample 3 spectra and Sample 2 spectra)

By analyzing the comparative IR spectra (Fig.7), it can be emphasized that a main part of the oil has been transformed in C4 substituents, thus causing the loss of almost any oil like characteristics.

6. Conclusions

- A "rich" natural gas is constantly affecting a PAO based oil, even more when the oil is in direct contact with the gas as the case in screw compressor. So, it can be concluded that PAO based oil may be suitable for other types of compressor applications where the oil it is not in direct contact with the gas, or PAO based oil can be used in screw compressors but in "poor" gas extraction sites.
- FT-IR spectroscopy is a very useful tool to assess oil degradation since it provides valuable information regarding the chemical structure of the compounds of a sample.
- By coupling FT-IR spectroscopy with other analysis, a complete "picture" of oil degradation can be acquired, thus minimizing the risk of compressor breakdown and also its maintenance can be made more easily.
- It is well known that gasoline, acting as diluents is constantly affecting the oil, but the degree of this action can only be assessed by using deep analysis techniques as FT-IR spectroscopy.

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