



Featured Article

Assessment of the oxidative stability of lubricant oil using fiber-coupled fluorescence excitation–emission matrix spectroscopy



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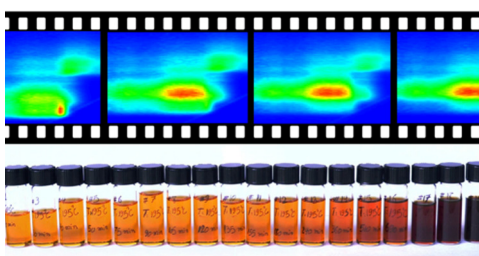
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HIGHLIGHTS

- A fiber-optic probe for engine lubricant quality has been designed.
- Fluorescence spectroscopy is used to monitor the concentration of antioxidants.
- A kinetic model for antioxidants degradation products was successfully developed.
- Fluorescence detection of antioxidants compares favorably to measurement of breakdown numbers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 August 2013

Received in revised form 9 October 2013

Accepted 10 October 2013

Available online 18 October 2013

Keywords:

Fluorescence spectroscopy

Lubricant

Oil

Fiber-optics

Kinetics

Chemometrics

ABSTRACT

The fluorescence of antioxidant additives in lubricant oil was used as an indicator of oxidative stability of the oil. It was found that the decrease in fluorescence intensities of phenyl- α -naphthylamine, its dimer, and another unidentified antioxidant coincide with the formation of decomposition products of the oil base stock. Simple kinetic models were developed that were capable of describing antioxidant reactions as a pseudo first-order processes. It is shown that fluorescence excitation emission matrix (EEM) spectroscopy coupled with an optical fiber probe can provide real-time assessment of the oxidative stability of the lubricant. Parallel factor (PARAFAC) analysis was used to correlate the component scores to the oil breakdown number.

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1. Introduction

Engine lubricants are used to reduce friction between the moving parts within an engine. Many engine lubricant oils also serve as coolants, corrosion protectors, and help remove contaminants and debris from the engine interior. By itself a lubricant oil, or “base stock”, rarely has all the required properties and many additives

have been designed to improve the performance of the base stock—either by adding and enhancing properties of the base stock or by preventing changes in its composition. Lubricants age and degrade as the machine operates. This is due to oxidation as well as thermal and mechanical decomposition. Lubricant oils may then lose some of their functions, which may, in turn, lead to machine damage or even catastrophic failure. Lubricant oxidation is one of the leading causes of the degradation of hydrocarbon-based oils and can be influenced by several factors such as high engine temperature, the exposure to oxygen, water contamination and metallic wear debris, concentration and efficiency of antioxidants

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and other additives as well as the type of hydrocarbon-based oil itself [1]. Ultimately, oil oxidation leads to the formation of acidic compounds. Lubricant quality can therefore be characterized using the total acid number (TAN), which is obtained according to the ASTM guidelines [2]. Another common metric for lubricant quality is the so-called breakdown number (BDN), which is based on the mid-infrared absorption at around the OH-stretch vibration wavenumber. The BDN is used frequently to describe ester-based lubricant oils such as the synthetic polyol esters in this study, which are commonly used as aviation and aerospace lubricants. The resulting polyol ester degradation products can be observed through their IR absorption features at 3595 cm^{-1} to 3500 cm^{-1} , and 3325 cm^{-1} to 3150 cm^{-1} , which are quoted, respectively, as breakdown number I and breakdown number II [3,4]. In addition, one can measure the oxidation stability of oils and fuels by a number of other methods [5–7].

The presence of antioxidant additives delays the oxidation of base stock either by reaction with oxygen or with primary oxidation products, such as organic radicals. The stable products of this reaction do not react further and thereby stop the radical chain reaction. Antioxidants therefore sacrificially protect the lubricant and are gradually consumed during this process. Once antioxidants are depleted, the oxidation of base stock will proceed as long as oxygen is allowed to interact with the liquid at high temperatures. For part of the base stock oxidation leads to larger oligomeric compounds and for other fractions it yields smaller oxidation products.

The Rancimat procedure measures the time it takes for volatile acids to evolve and is used in this study to characterize the oxidation stability of machinery fluids [8]. The method has been widely used for analyzing biodiesel fuels although its main application is the measurement of the oxidation stability of foodstuff. Here, an oil sample in a sealed vessel is heated while exposed to a flow of air. Once the antioxidants have been depleted, volatile organic acids are formed and are carried by the air stream into a vial of deionized water. The conductivity of the water in this vial is recorded continuously. After an induction time, which is proportional to the oxidation resistance (related to the concentration of antioxidants), a sharp increase in the water conductivity is found.

Since the useful lifetime of lubricant is determined by the concentration of remaining antioxidants, it appears more useful to monitor the antioxidant level and not the concentration of degradation products [9]. Monitoring antioxidants as proxy for lubricant quality has the additional advantage of a reduced occurrence of “false positive” warnings for low lubricant quality. Present methods that rely on the chemical or spectroscopic signatures of products will give false positives, whenever adequate oil is contaminated with oxidation products, but this may easily occur during an oil change when the engine interior has not been cleaned.

An additional concern with the accepted lubricant assessment methods lies in the required effort and expertise. All commonly accepted techniques used to determine lubricant oxidation require removal of a sample and off-line analysis. Even for large industrial machinery, a change of lubricants is therefore performed typically after a specified number of hours of operation (equivalent to the distance travelled in motor vehicles), but not when the lubricant has started to degrade.

We attempt to develop real-time and in-line methods and protocols to monitor the degradation of lubricant oils using fiber optic probes [10]. The ultimate goal of the work is development of a robust sensor and a continuous read-out system that contains a probe submersed permanently in the lubricant volume or flow. In this study, we use fluorescence excitation emission matrix (EEM) spectroscopy to characterize antioxidant performance as a polyol ester-based aviation lubricant oil is degraded by oxidation at elevated temperatures.

Fluorescence EEM produces three-dimensional spectra, *i.e.* a matrix of intensities that is obtained by recording fluorescence spectra at a variety of excitation wavelengths. The technique is now used in the analysis of different liquids in various fields from environmental [11,12] and bio-medical research [13] to foodstuff [14–16]. Fluorescence EEM has also been applied to petroleum products and other industrial liquids [17–20] and its many applications were reviewed recently [21–23]. Fiber-coupled EEM spectroscopy has already demonstrated potential for the identification and quantification of jet fuel and jet turbine oil and lends itself to in-line and real-time analysis. [10] In this previous article we showed that contamination of jet fuel with jet turbine oil can be detected and quantified between 10 ppm and 1000 ppm using a bifurcated fiber probe similar to that employed in the present study.

Fortunately, synthetic lubricant oils, such as the polyol ester-base stock used in this study, and also silicone oils, do not exhibit strong fluorescence when excited in the 220–450 nm region, whereas the polycyclic aromatic compounds that are added as antioxidants do fluoresce. It will be shown that the fluorescence signature of one of these antioxidants, phenyl- α -naphthylamine (PAN), changes with time as the oil is heated and the PAN-dimer is formed as is apparent by the dimer's fluorescence EEM signature. The fluorescence of PAN, the PAN-dimer and another, unidentified antioxidant could be correlated to the established lubricant assessment methods such as the BDN measurements and the Rancimat procedure.

To investigate deterioration of the aviation lubricant oil, a laboratory bench simulation test has been developed. The lubricant oil was heated to temperatures that are typical for an aircraft turbine engine (150–220 °C) [24,25]. We also collected oil samples, which have been degraded during aircraft engine operation. All lab and field samples were studied using fiber-coupled EEMS followed by chemometric data analysis using the parallel factor (PARAFAC) method.

2. Materials and methods

2.1. Chemometric analysis

EEM spectra contain quantitative analytical information, which is multidimensional in nature [26]. Several chemometric techniques are typically used for the necessary multivariate data analysis. Principal Component Analysis (PCA) and Regression (PCR) is one of the more popular chemometric methods because of its robustness and universality. Parallel Factor Analysis (PARAFAC) is another multi-way data decomposition model which can be applied to interpret the EEM data [27–30]. PARAFAC is less robust compared to PCA/PCR but has the advantage that the EEM signatures of the PARAFAC components can sometimes be related to chemical constituents, especially when a small number of distinct species contribute to a composite EEM spectrum as is the case in this study [31]. Stacking 2-dimensional EEM spectra from a series of samples creates a data cube that can be mathematically decomposed into a set of trilinear components and then modeled by PARAFAC in a matrix equation,

$$X_{ijk} = \sum_{f=1}^F A_{if} B_{jf} C_{kf} + E_{ijk}$$

where X_{ijk} is the fluorescence intensity of sample k at the excitation wavelength i and the emission wavelength j . F is the number of unique spectral profiles (“components”) found in the data cube. The columns of the A , B , and C matrices are the estimates of the pure excitation, emission, and concentration profiles, respectively,

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