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Determination of the total acid number (TAN) of used mineral oils in aviation engines by FTIR using regression models☆

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ABSTRACT

Total acid number (TAN) has been considered an important indicator of the oil quality of used oils. TAN is determined by potentiometric titration, which is time-consuming and requires solvent. A more convenient approach to determine TAN is based on infrared (IR) spectral data and multivariate regression models. Predictive models for the determination of TAN using the IR data measured from ashless dispersant oils developed for aviation piston engines (SAE 50) have been developed. Different techniques, including Projection Pursuit Regression (PPR), Partial Least Square, Support Vector Machines, Linear Models and Random Forest (RF), have been used. The used methodology involved a five folder cross validation to derive the best model. Then a full error measure over the whole dataset was taken. A backward variable selection was used and 25 highly relevant variables were extracted. RF provided an acceptable modelling technology with grouped dataset predictions that allowed transformations to be performed that fitted the measured values. A hybrid method considering group of bands as features was used for modelling. An innovative mechanism for wider features selection based on genetic algorithm has been implemented. This method showed better performance than the results obtained using the other methodologies. RMSE and MAE values obtained in the validation were 0.759 and 0.359 for PPR model respectively.

1. Introduction

Determining the condition of engine oil is critical for aviation safety and operation thereof. Therefore, periodic analyses of engine oils are mandatory. The conditions of aging fluids that require regular monitoring are total acid number (TAN), viscosity index (VI), wear rate and depletion of antioxidants [1]. These parameters (TAN and VI) can be determined by standard physicochemical methods. However, the main motor oil physicochemical characteristics are covered by the American Standards for Testing and Materials (ASTM) guides. Viscosity index and TAN of oils are usually measured according to standard ASTM D445 [2] and ASTM D664 [3], respectively. TAN determination is based on potentiometric titration with a base to a fixed endpoint. It is time-consuming and requires environmentally problematic solvents and reagents.

In recent years, efforts have been made to replace analytical methods based on the FTIR technique. In order to obtain analytical information in a rapid, non-destructive way, mid-infrared spectroscopy has been largely applied to study motor oils for different purposes: quantifying contaminants [4][5], or oxidation process [6][7], adulteration [8][9][10], determining the antioxidant concentration [11], determining physicochemical values (TAN [8,12,13], VI [14,15] and TBN [12,14]), and classifying them according to their origins [16].

It is well-known that hydrocarbon oxidation is an autocatalytic process governed by the initiation of a free radical chain reaction, chain propagation, chain branching, and the termination of the radical chain reaction [17]. These multiple free radical pathways produce a complex mixture of possible oxygenated products, such as hydroperoxides, alkyl

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peroxides, dialkyl peroxides, alcohols, carboxylic acids, esters, ketones, diketones, aldehydes, hydroxyketones, ketoaldehydes and unsaturated oxygenated compounds [18]. All these molecules introduce functional groups that provide characteristic FTIR spectral bands. Therefore, oil oxidation should generate visible changes in the following vibration bands: (3100–3600 cm^{-1}; 2500–3200 cm^{-1}; 1650–1730 cm^{-1}; 1680–1710 cm^{-1}; 1700–1740 cm^{-1}; 1050–1450 cm^{-1} and 1000–1250 cm^{-1}) [6].

Recently, multivariate calibration has been applied to determine the antioxidant concentration [11], and physicochemical values (TAN [8,12,13], VI [14,15] and TBN [12,14]), based on the FTIR technique. Multivariate calibration is an effective calibration method in which the chemical information (absorption, emission, transmission, etc.) of a set of standard mixtures recorded at different variables (wavenumbers) is related to the concentration of the chemical compounds present in the mixtures [19]. The popular form of calibration used in chemical analyses is univariate calibration, in which the chemical information of a set of solutions recorded at one variable (i.e., wavenumber) is related to the solute concentration in the solution. The most applied multivariate methods are classical least squares (CLS) [14], principal-component regression (PCR) [14] and partial least squares (PLS) [7,8,11,14,15].

In the present study, the TAN (total acid number) of turbine engine oils from military aircrafts was estimated by FTIR spectroscopy with multiple regression by using two different strategies. Instead of using the classic PCA for dimension reduction, we used both the PCA and the Independent component analysis (ICA), which slightly outperforms the PCA. By employing this backward variable selection, 25 highly relevant variables were extracted. After this variable selection, predictive models were built by different techniques, including Projection Pursuit Regression (PPR), Partial Least Square (PLS), Support Vector Machines (SVM), Linear Models, Generalized Linear Models (GLM) and Random Forest (RF). In addition, an innovative mechanism for wider features selection based on genetic algorithm has been implemented, which outperforms the previously used techniques.

2. Material and methods

2.1. Oil samples

Oil samples have been used in airplanes with fixed or reciprocating piston engines installed on a private aircraft (not including freight or passenger) with a maximum certified take-off weight of up to 5700 kg. These aircrafts are included in the *Schedule of Condition Based Maintenance* (SCBM) of the Venezuelan National Institute of Civil Aviation (Instituto Nacional de Aeronáutica Civil, INAC). INAC provides an alternative to extend the service up to 8 more years for these engines for a 12-year calendar time to perform reconditioning or overhaul, but which have not yet reached the limit in flight hours (1200–1700 h) specified by the manufacturers.

Oils were used in engines of the brands Teledyne Continental Motors and Textron Lycoming. The owners of these aircrafts operate their units at fewer than 100 h per year, and make engines work under tropical climate conditions (heat and moisture). This tends to accelerate oxidation processes and oil degradation, thus promoting corrosion and rust formation, mainly in those parts exposed to engine elements, such as cylinders. The SCBM program includes some preventive and predictive parameters, such as compression checks, boroscopic inspection, and the flow testing of cylinders, oil filters inspection, oil consumption verification, complete engine inspection, plus the prior inclusion of an oil analysis that the inspector should have before aircraft assessment begins.

Eighty ashless dispersant oils (AeroShell W 100, SAE 50) were collected from aviation piston engines used during the 2009–2012 period of engines of the brands Teledyne Continental Motors with operation times within the 600–2000 h range and oils with a 50 h operation. Table 1 shows the complexity of the samples in a variety of engines, times of operations and acidity.

2.2. Infrared spectra

Infrared spectra were obtained in a Fourier Transform spectrometer, Perkin Elmer model Spectrum 100, within a spectral range of 450–4000 cm^{-1}, with a resolution of 1 cm^{-1} and 16 scans per sample, corresponding to 3551 data points per spectrum (original variables). The cells used were zinc selenide (ZnSe) transmission cells and path length was fixed at 0.1 mm.

The FTIR equipment was kept in a cabin at low humidity (under 45%) and was usually purged with nitrogen gas every 6 months. The background analysis and cleanliness of cells were performed between each determination in an estimated time of 5 minutes.

Oil samples were subjected to ultrasonic agitation for a time longer than 5 minutes, but shorter than 10 minutes, and 6 mL were extracted with a Pasteur pipette and analysed. No dilution was employed. Cells were cleaned with N-heptane before each determination. Spectra were collected in duplicate per sample and the % of transmittance and absorbance of the spectra were recorded with the FTIR software.

2.3. TAN Determination

TAN values were measured according to the ASTM D664 method [3]. For potentiometric titration, previously standardized potassium hydroxide (0.1 mol/L) was used to neutralize all the acidic constituents. Titrations were carried out in a mixture of toluene, isopropanol and water (volumetric ratio of 500:495:5). The amount of acidic constituents is given in mg of potassium hydroxide (KOH) per g of oil. A sample pretreatment was done by heating to 60 °C and filtering through 100 µm mesh filters. Each analysis was done 3 times to determine an average. The standard deviation was established in 0.08 mg/KOH.

3. Results and discussion

3.1. Spectroscopic results

The FTIR spectra of the motor oil samples were recorded within the 450–4000 cm^{-1} range and are illustrated in Fig. 1. To obtain clearer FTIR graphics, the full spectra were divided into three regions: 3000–2850, 1800–1500 and 1000–450 cm^{-1}. The spectra of the motor oils clearly overlapped within the entire spectral region and no certain wavenumber was found. Fig. 1 shows three typical infrared spectra of engine oils which corresponded to oils with different acidities, low, medium and high, and characteristic changes due to acidity and oxidation.

Gracia et al. [6] reported a large absorption band between the absorption bands for (C=O) corresponding to esters (1740 cm^{-1}) and cyclic esters (lactones, 1780 cm^{-1}). These changes indicate typical oxidation products and aging products caused by contaminants in oil. Other authors have considered simplifying the spectrum and have eliminated several spectral ranges using criteria such as regions with total absorbance, regions with bands from strong C-H and C-C vibrations from hydrocarbons contained in base oil (typically 3100–2750 cm^{-1}, 1500–1300 cm^{-1}, and 800–700 cm^{-1}) and regions with no significant absorbances (typically 2750–2000 cm^{-1}, 1600–1500 cm^{-1}, and 700–600 cm^{-1}) [13].

3.2. Data analysis methods

This section presents the data analyses carried out. The available dataset involved 76 oil samples. For all these samples, the FTIR spectra from 4000 to 450 cm^{-1} were available, as well as the TAN in accordance with ASTM D-664 [3].