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Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation

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ABSTRACT

The influence of ethanol in gasoline and its partial combustion products on the engine oil performance was investigated by joint use of IR spectroscopic data and chemometrics. Oil samples obtained from artificial alteration in the laboratory and engine alteration in a chassis dynamometer were compared. Quantification of residual amounts of antioxidant and antiwear additive (ZDDP) in the oil samples by FTIR spectroscopy showed depletion of phenolic antioxidant during engine alteration but ZDDP degradation during artificial alteration. Different chemometrical models using principal component analysis (PCA) elucidated similarities and differences between both alteration types, proving the findings of FTIR spectroscopy. Additionally, laboratory-based artificial alteration was mainly driven by oxidative processes whereas engine alteration showed higher amounts of both oxidation and nitration products.

1. Introduction

For various reasons [1,2], there has been paid more and more attention to bio-fuels – especially fatty acid methyl esters for diesel substitution and ethanol for gasoline substitution, respectively – with the consequence that their production increased dramatically in the last decades and is still rising. At the present day, the quantities produced correspond only to 1% of fuel requirements but is expected to reach 7% until 2030 [3].

Legislation related to energy and fuels was the driving force concerned with these strategic, economical and environmental issues resulting in the directive 2003/30/EC [4], commonly known as the “bio-fuels directive”, released by the European Union in May 2003. In this non-binding directive the replacement of 2% of all fossil fuels used in the transportation sector is demanded until December 31, 2005 as well as a further increase in substitution to 5.75% until December 31, 2010. With the new directive 2009/28/EC (RED—renewable energy directive) [5] from 2009 compulsory targets were introduced to replace 10% of common fuels by bio-components until 2020.

Intense research has been carried out on the topic of bio-diesel and its impact on the engine performance, on the lubrication system, and on the emission profile [6]. On the contrary, the interactions of bio-ethanol and its combustion products with the engine oil are still widely unknown resulting in a demand for detailed investigation due to highly usage as fuel in passenger cars. In Brazil, for example, ethanol became the second most consumed liquid fuel after diesel in 2008. This development is mainly attributed to the growing sales of flexible fuel vehicles. This technology enables the usage of gasoline–ethanol mixtures (also called gasohol) of any percentage in the same engine simultaneously and without any operational reconstruction [7].

In a recent study, Besser et al. [6] developed a novel thermo-oxidative alteration method to evaluate the impact of ethanol and its partial combustion products acetaldehyde and acetic acid on the engine oil while not yet considering other processes occurring in an engine like nitration or the impact of metal surfaces. It was clearly shown that ethanol and acetaldehyde have only marginal effects on the oil performance in comparison with artificial alterations using only air, but acetic acid decreased the oil stability resulting in accelerated degradation as well as a higher tendency towards sludge formation. In this paper, it is reported on complementary chassis dynamometer bench tests that have been performed to transfer the alteration system from the laboratory to the engine regime. As long as modern engine oils provide good stability, long-term engine bench tests are needed, exceeding 25,000 km, to provide differentiation between performances of individual oil formulations. In order to achieve accelerated deterioration of the lubricant during special time-saving bench tests, artificial alteration taking place directly in the engine was proposed to provide a significant shortening of test duration.

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Usually, a well-founded evaluation and in-depth understanding of oil deterioration mechanisms are based on the generation of extensive oil data by time and resources consuming methods, preferably by engine bench tests. This fact suggests the need to find different procedures being appropriate for a rapid and easy evaluation of the stability performance of novel oil formulations, in particular when a large number of oil samples has to be considered during such assessments. For this purpose, chemometrics is regarded to be thoroughly helpful as these statistical methods proved to provide substantial support in different fields of chemistry: Purcell et al. developed a rapid at-field screening method for sugarcane clonal performance using NIR spectra of the surface of sugarcane clones and chemometrics instead of a laboratory GC instrumental approach [8]. Friedl et al. presented a chemometric model to predict the higher heating value, the enthalpy of complete combustion of a fuel including the condensation of formed water, from the elemental composition of different biomass [9]. In lubricant chemistry, Gracia et al. combined mid-infrared (IR) spectroscopy with chemometrics to study oxidation processes occurring in lubricating base oils with and without the influence of iron by the means of principal component analysis. They showed that the first principal component is similar for oxidation with and without iron, but the second principal component reveals that iron provokes the formation of alcohols and esters, especially in the very first moments of the oxidation [10]. Gracia et al. presented in another publication investigations about the role of diphenylamine as an antioxidant in lubricating oils by combination of mid-IR spectroscopy with curve resolution methods [11]. Lima et al. investigated the carcinogenic potential of base oils as function of its concentration of polycyclic aromatic hydrocarbon compounds determined by near-IR spectroscopy utilising the tools of principal component analysis and principal component regression [12]. Sepcic et al. identified fresh and used engine oils based on the content of volatile compounds over the oils collected via headspace technique using solid phase microextraction and analysed by a time of flight mass spectrometer. Principal component analysis and cluster analysis were carried out to correlate these compounds with miles used in the engine [13]. Felkel et al. used chemometric tools to determine the total acid number of various gas engine oils from different gas engines using IR spectroscopic data [14]. By principal component analysis they proved that IR spectroscopic data reflect alteration mechanisms: qualitative differences between two engines types as well as between different oil fillings could be detected. They developed a partial least-squares model to predict the total acid number of used gas engine oils from IR spectroscopic data with a repeatability in the same range or better than potentiometric titration according to ASTM D 664 [15].

In this follow-up research work, statistical mathematical tools of chemometrics have been selected on the one hand to differentiate the stability performance of the engine oils and on the other hand to evaluate the correlation between artificial alteration in the laboratory and the natural as well as artificially accelerated alteration in the engine system. Chemometrics, especially principal component analysis (PCA), was selected as method of choice in this research work to evaluate the usefulness of statistical mathematical techniques for the investigation of engine oil degradation. In detail, PCA has been applied for the qualitative evaluation of differences or similarities in lubrication properties using variables derived from IR spectroscopic data. To our best knowledge, this is the first description reporting on the joint use of IR spectroscopic data and chemometrical tools for the interpretation of natural and artificial degradation of lubricating oils.

2. Experimental

2.1. Oil samples

In this study, oil samples from artificial alteration in the laboratory, from natural alteration in the engine regime as well as from artificially accelerated alteration in the engine regime were investigated. The procedures of sample generation are described in Sections 2.2.1 and 2.2.2.

Two fully formulated engine oils for the usage in passenger cars were chosen from a consecutive sequence of advancing engine oil technologies. Oil A with the viscosity grade SAE 15W-40 and the ACEA specification A3/B4 contains group I mineral base oil. It was selected to represent a common engine oil technology currently available on the market. Based on the performance of this oil during artificial alteration, improved formulations were developed, resulting in – among others – oil C with the viscosity grade SAE 5W-30 and exceeding ACEA specification A3/B4/C3. The main physical–chemical properties of oils A and C are given in Table 1 and discussed in detail in [6].

The elemental content was determined by optical emission spectroscopy with inductively coupled plasma of the aqueous solutions of the oils derived from microwave digestion with nitric acid. IR spectroscopic analysis showed the presence of aminic antioxidants in both oils, whereas phenolic antioxidants were found only in oil C.

2.2. Oil alteration

2.2.1. Artificial alteration in the laboratory

For the investigation of the influence of ethanol and its partial combustion products on engine oil, the above-mentioned fully formulated engine oils were altered with a novel artificial alteration method described in detail in [6]. The conditions for artificial alteration are summarised as follows: 300 g of the respective lubricating oil was placed in a round bottomed three-neck glass flask kept at 160 °C by a heating oil bath. The oil was brought into contact with dried air via a glass tube. The air gas flow was adjusted to 10 l/h by a flow controller. The flask was also equipped with a cooler to avoid considerable loss due to oil evaporation. One neck of the flask was used for periodical sampling and subsequent condition monitoring. The alteration duration was always 96 h, sampling was carried out every 24 h.

Three different liquid contaminations were added over the whole alteration period in order to simulate the influence of biofuels and its anticipated partial combustion products brought into the lubricant via blow-by gases and by down-washing from the cylinder liner wall. In detail, these compounds were ethanol and – as partial oxidation products and combustion by-products of ethanol – acetaldehyde as well as acetic acid. These combustion products were selected on the base of a literature research, where scientific work was found proving a correlation between the

Table 1
Physical—chemical properties of engine oil A and C [6].

Oil parameter	Oil A	Oil C
SAE grade	15W-40	5W-30
Total base number (mg KOH/kg)	8.1	7.2
Neutralisation number (mg KOH/kg)	2.0	1.4
Ca content (mg/kg)	2300	1900
P content (mg/kg)	700	700
S content (mg/kg)	4900	2100
Zn content (mg/kg)	900	800
Antioxidants	Aminic	Aminic, phenolic