

Multichannel IR Sensor System for Determination of Oil Degradation

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Abstract :

A miniaturized infrared (IR) multichannel sensor system was realized to determine oil degradation e.g. oxidation, increasing water content etc. Different artificially aged oil samples were generated, e.g. oxidative degradation or water increase, and the characteristic degradation features of the spectrum were detected by FTIR spectroscopy. For calibration the system was tested with the oil samples to analyze the influence of different degradation effects to the measurement results.

Key words: oil degradation, oxidation, water content, NDIR

Chemistry of oil deterioration

To determine the oil degradation different features of the oil have to be observed, e.g. oxidation, nitration, sulfonation and increased water content. The speed of oxidation and the generated specific species in the oil depend on temperature. The oxidation process itself works auto catalytically. For a temperature between 30°C and 120°C the hydrocarbon reacts with metal catalysts, e.g. Co, Fe, Cr, Cu, V or Mn, to an alkyl radical depending on the strength of the C-H-bond. The alkyl radical is converted via multiple reaction paths to a hydroperoxide and another alkyl radical. Hydroperoxides are also generated via intramolecular propagation. These hydroperoxides break up into alkoxy and hydroxy radicals which take up hydrogen from the ambience. Secondary and tertiary alkoxy radicals react to aldehydes and ketones. The termination of the process occurs with the combination of radical species. Ketones and alcohols are generated. At temperatures above 120°C the reaction path is the same but the reaction speed is increased and the selectivity is reduced. Carboxylic acids and esters are formed by reactions with alcohol. At lower temperatures less alkoxy radicals are generated. At high temperatures the viscosity of the hydrocarbon increases due to polycondensation of oxygenated products. Unsaturated aldehyde or ketones are formed by aldol condensation. Alkoxy radicals can start the polymerization or polycondensation. The oxidation process can be increased with metal soaps by reducing the

activation energy for the decomposition of alkyl hydroperoxides [1].

Attain nitrogen oxides or sulfur oxides in to the oil, e.g. in case of blow by gases [2], they can react with water to acids which also support the polycondensation.

When native or phosphate esters are used as hydraulic fluids exposure to water can be dangerous because of the esters can break up into alcohol and acid components due to the increasing water content especially at high mechanical load or increased temperatures [3].

Sensor System

For the analysis of oil degradation laboratories use - amongst other methods such as viscometry or total acid number - non-dispersive infrared (NDIR) spectroscopy to determine the effects of oxidation, nitration and the concentration of water, soot and anti-wear compounds [4]. Based on this method a measurement system with an IR transparent silicon cell was developed for optical analysis of the oil [5].

Artificial oil deterioration

To prepare different samples of oxidatively deteriorated oil an experimental set up was developed as shown in Fig.1.

The set up contains a mass flow controller (MFC) which provides a stable air flow through the oil in the reactor. The MFC is connected to a drechsel head with filter, which is dipped in the oil, to generate finely distributed bubbles

while stirring the oil magnetically. The aluminum reactor is heated by a hot plate. The hot plate controls the temperature in the reactor by the external temperature sensor.

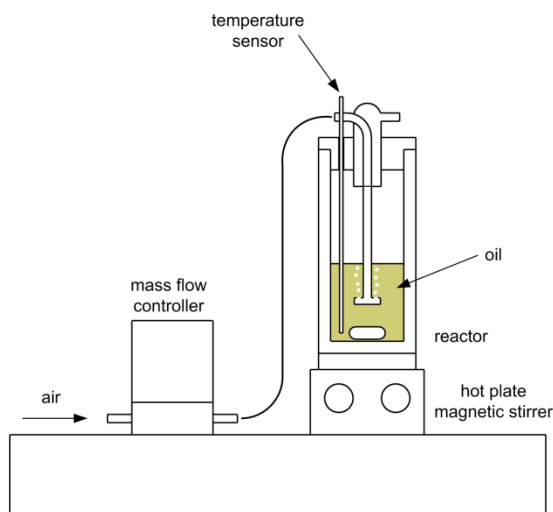


Fig. 1 Experimental set up for artificial oil oxidation [6]

Water contaminated oil samples were prepared by adding pure water (ASTM type II [7]).

The spectra of the oil samples were measured with a fluid cell with 0.2 mm film thickness in a FTIR spectrometer (Bruker Vertex 80V).

IR Spectra and limit values

For analyzing spectral degradation features different oils were used:

- mineral hydraulic oil (Shell – Tellus Oil 46)
- native hydraulic fluid (Meguin – HETG 37)
- synthetic gas engine oil (Mobil 1 – Pegasus)

The spectrum of synthetic oil used in a gas engine shows multiple characteristic effects with increased deterioration as shown in Fig. 2.

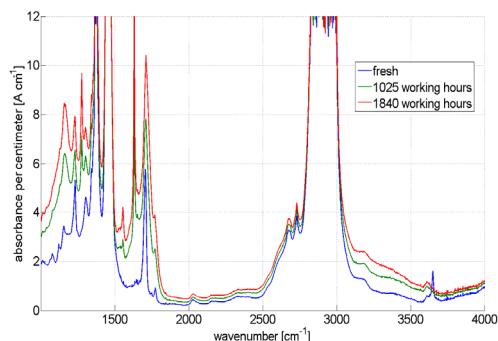


Fig. 2 IR spectra of a synthetic motor oil from a gas engine (combined heating and power unit) at different stages of aging.

The oil shows a slight increase of broad band absorption caused by an increase of soot

particles in the oil. In the region 3100...3500 cm^{-1} it shows an increase of OH absorption feature, which can be found in alcohols or water. Usually the peak of alcohols is shifted toward smaller wavelengths [8]. The fresh oil shows a peak at 1700 cm^{-1} which can be caused by an additive with a C=O double bond feature, e.g. an ester. With increased deterioration a strong increase can be observed in this region caused by a rise of oxidized molecules with C=O double bond features, e.g. aldehydes, ketones and carboxylic acids. At 1630 cm^{-1} a nitration feature increases due to influences of the blow-by effect in combustion engines. The presence of an increase at 1555 cm^{-1} , 1150 cm^{-1} and 1277 cm^{-1} suggests contamination with sulphuric acid. At 3650 cm^{-1} the spectrum shows decreasing absorption. This is caused by the decomposition of a phenolic antioxidant additive [9, 10].

For calibration of the sensor system [5] the different degradation effects in the oil spectrum have to be analyzed separately to ensure the independency of the multiple measurement channels.

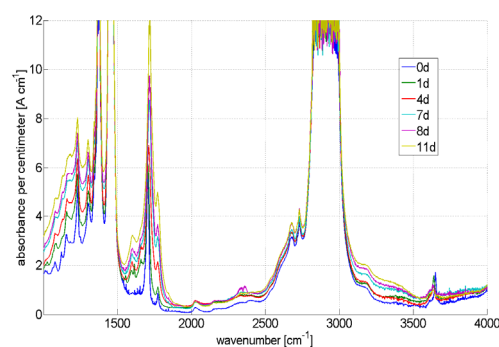


Fig. 3 IR spectra of synthetic motor oil artificially aged at 160°C with 50 cm^3/min air flow over 11 days.

The spectrum of the synthetic gas engine oil deteriorated by artificial oxidation shows a characteristic increase of the C=O double bond feature (at 1700 cm^{-1} , see Fig. 3). After 8 days artificial aging the oxidation peak value of the real samples is reached. Also an increase of the OH feature at 3100...3500 cm^{-1} is observed.

Additional contamination of the synthetic motor oil with water results in an increase of the OH feature (see Fig. 4). Compared with the spectrum of Fig. 2 and Fig. 3 the spectral absorption is shifted to larger wavelengths.

The spectrum of the artificially aged mineral hydraulic oil shows a strong increase of C=O double bond feature corresponding to the behavior of the artificially aged synthetic oil (see Fig. 5).

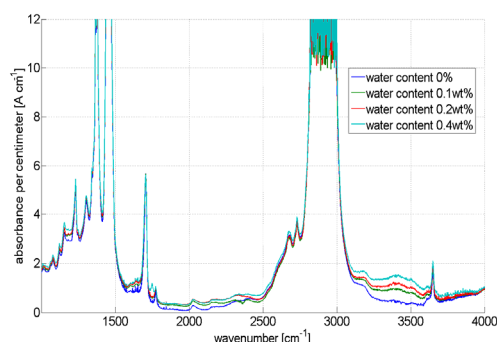


Fig. 4 IR spectra of synthetic motor oil with added water (ASTM type II, 0, 0.1, 0.2 and 0.4 wt%)

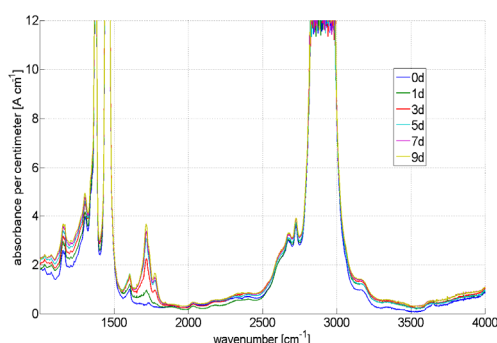


Fig. 5 IR spectra of mineral hydraulic oil artificially aged at 160°C with 50 cm³/min air flow over 9 days.

The spectra of artificially aged native hydraulic fluid shows different oxidation features at 1700 cm⁻¹ comparable to the petroleum based oils caused by an overlay of the C=O double bond feature due to an oxidation via hydroperoxides [11] and the C=O double bond of the acid part of the ester (see. Fig. 6) [3]. A broad spectral increase at 3500 cm⁻¹ is observed with increasing aging. Comparing this result with the water contamination of the petroleum based synthetic engine oil shown in Fig. 4 an increase of the water content would interfere with the oxidation in this area [4].

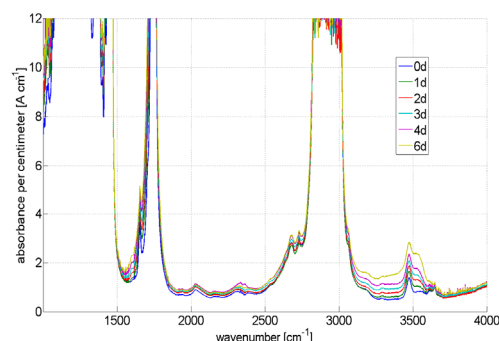


Fig. 6 IR spectrum of native hydraulic oil artificially aged at 130°C with 40 cm³/min air flow over 6 days

For determining the quality of the oil the kinematic viscosity was measured with an Ubbelohde viscometer at 40°C(η)for the

petroleum based oils and the total acid number was additionally determined with Schott Titroline 6000(TAN ASTM D664) for the native hydraulic fluid and compared with limit values of literature [12],[13](see Tab. 1-4).

	0h	1025h	1840h	Limit
η [mm²s ⁻¹]	92	123	163	±35%

Tab. 1 Kinematic viscosity for Mobil 1 Pegasus; real samples taken from the gas engine.

	0d	3d	7d	9d	Limit
η [mm²s ⁻¹]	90	94	101	110	±35%

Tab. 2 Kinematic viscosity for synthetic motor oil; artificially aged samples, cf. Fig. 3.

	0d	3d	7d	Limit
η [mm²s ⁻¹]	44	49	56	±10%

Tab. 3 Kinematic viscosity for mineral hydraulic oil; artificially aged samples.

	0d	2d	4d	6d	Limit
TAN [mgKOH/g]	-	1,5	4,1	5,6	>5*
η [mm²s ⁻¹]	35	42,3	50	59,5	±10%*

Tab. 4 TAN and kinematic viscosity for native hydraulic fluid; artificially aged samples (*limit values for mineral hydraulic fluids)

The limit values for kinematic viscosity and TAN given in the tables show the maximum deviation to fresh oil. As the oxidation peak at the C=O double bonds is comparable for the synthetic oil samples aged in real applications and the artificially aged samples the difference of the viscosities is based on the increase of nitric and sulphuric acids which increase polycondensation in the oil. The mineral hydraulic fluid reaches the limit value after 3 days oxidation, the native hydraulic fluid already within 2 days.

Results

The different oil samples were analyzed with the measurement system to evaluate the oxidation for the oils and the water content for the synthetic oil. For the petroleum based oils the system was equipped with a quadruple IR detector with filters for 1730 cm⁻¹(TP1), 2500 cm⁻¹(TP2), 3350 cm⁻¹(TP3) and 3500 cm⁻¹(TP4). For the native hydraulic fluid a filter set

with 3875 cm^{-1} (TP1), 3663 cm^{-1} (TP2), 3484 cm^{-1} (TP3) and 3322 cm^{-1} (TP4) was used. The oils were analyzed in continuous flow at room temperature. The first harmonic FFT component is evaluated from the thermopile signals for a measurement cycle with 12 rectangular pulses of the IR source at 0.2 Hz.

The measurement results of the oxidation of the synthetic oil show a strong decrease of channel TP4 according to the spectrum in Fig. 3 (see Fig. 7). Also a slight decrease of TP3 can be observed which results from an increase of the OH-feature. The reference TP2 is decreasing due to an increase of soot particles in the oil.

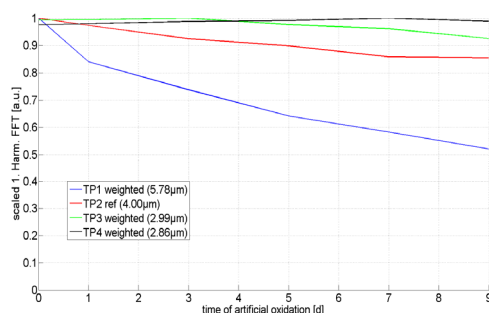


Fig. 7 Synthetic motor oil artificial oxidation

An increase of water according to Fig. 4 can be observed with a strong decrease of measurement channels TP3 and TP4 (see Fig. 8). TP1 stays mainly constant so that increasing water content and oxidation can be determined with the measurement channels TP1 and TP3.

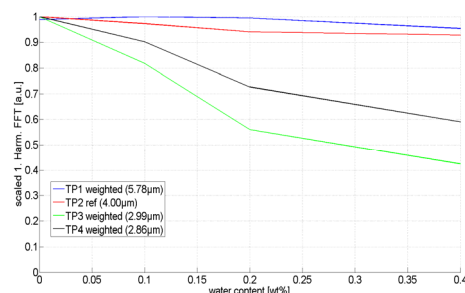


Fig. 8 Synthetic motor oil with water contamination 0 wt%, 0.1 wt%, 0.2 wt%, 0.4 wt%

Increased oxidation can be observed for the artificially aged native ester for measurement channels TP3 and TP4. Also a slight decrease of the first harmonic in TP2 and TP1 can be observed (see Fig. 9).

Conclusion and Outlook

Synthetic, mineral oils and native esters were analyzed by FTIR, viscosity and TAN measurements. The FTIR analysis showed the interference effects for water increase and oxidation. The measurement system was able to differentiate between both effects at two

different samples. It was also able to measure the oxidation status of native esters.

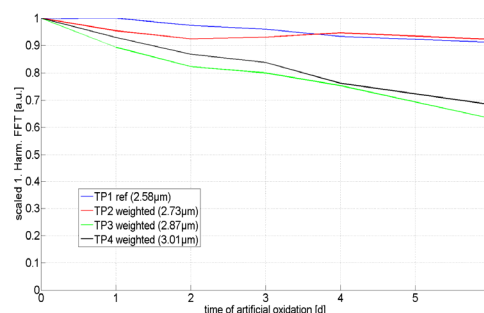


Fig. 9 Native hydraulic fluid artificial aging

Next measurements will include a mixture of artificially aged oils with additional water. Also the increase of nitric acid components will be analyzed by using an adequate filter and an experimental set-up simulating the blow by effect by bubbling NO in N₂ through the oil.

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