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# Determination of the Impact of Biogas on the Engine Oil Condition Using a Sensor Based on Corrosiveness

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## 1. Introduction

Fuels, in particular low refined fuels and biofuels, may undergo considerable changes upon storage and circulation in the fuel supply system. (Bondioli et al., 2003) The knowledge of the quality of such fuels is crucial to maintain system reliability. Besides rubbing contact to parts in the fuel supply system, fuels and biofuels have also an impact on parts of the combustion section of an engine including the engine oil. (De Castro, 2007; Demirbas, 2009) Biofuels of interest are bioethanol, biodiesel and biogas. Biofuels usually differ significantly in chemistry from fossil fuels expressed by undesired interactions with oil additives accelerating oil alteration and hence significantly shortening oil intervals. (Luther, 2008)

The determination of the optimum oil change interval is increasingly important for both ecological and economical reasons. Therefore, different approaches exist to determine the right time for the oil change. For automotive applications, a common method is the forecast of the oil quality by algorithms based on indirect parameters such as the oil temperature, load profile or number of cold starts. (Fitch, 2004; Wang, 2001) For large engines or stationary machines, the current oil condition is determined by laboratory analysis of oil samples regularly taken. (Smolenski et al., 1994) The latter is the most accurate and reliable method for the determination of the current oil condition. But laboratory analysis suffers from the drawback of unacceptable time delays between sampling and analysis.

Biogas combusted in stationary gas engines is considered as one challenging renewable resource of energy. (Deublein, 2010) Besides methane and carbon monoxide as combustible compounds, undesired trace compounds can be found in biogas, sometimes at considerable levels (Harasimowicz et al., 2007). Among others, hydrogen sulphide, mercaptans, and halogen compounds are formed from processing of biomass at landfill sites, sewage plants, fermentation sites and wood gasification facilities.

These components in the biogas are able to form aggressive and potentially corrosive components during the combustion process (Abatzoglou et al., 2009; Agoston et al., 2005a). The uptake of these compounds in the lubricant results in a higher degree of oil acidification. Therefore, a higher potential for corrosion of engine parts is given and may result in engine breakdown. (Richard et al., 2010) The direct measurement of the resulting corrosiveness of the engine oil could be used as main indicator for an oil change.

Therefore, an oil condition sensor (Agoston et al., 2007) is proposed, able to measure the direct impact of the oil corrosiveness in form of a material loss of a sacrificial metal layer. Details about the principle of the proposed sensor can be found in chapter 1.3.

In this contribution, we report on the principle behaviour of the oil condition sensor for oil corrosiveness based on experiments at static conditions using defined model oils containing base oil and selected additives as well as acidic components. Furthermore, the sensor is tested with so-called artificial alteration method simulating the impact of biogases on engine oils to evaluate the online applicability of the proposed sensor concept. Results from field test gives emphases on the usefulness of the proposed sensor.

### 1.1 Biogas

Biogas as renewable source of energy is becoming increasingly important since biogas has some ecological advantages mainly being $CO_2$ neutral and hence reducing the formation of greenhouse gases. Furthermore, biogas represents a meaningful way of both waste use and waste disposal as agricultural, commercial and municipal waste from biogenic sources are used for the production of different types of biogas. The potential and possibilities for the successful application of renewable energy are illustrated by the "Modell Güssing" (EEE GmbH, 2008) – a small city in Austria which is independent from conventional energy providers as energy is entirely generated from renewable sources. A main part thereby is the gas engine driven with wood gas.

| component | concentration |
|---|---|
| methane | 40 – 75 % |
| carbon dioxide | 25 – 55 % |
| water (steam) | 0 – 10 % |
| nitrogen | 0 – 5 % |
| oxygen | 0 – 2 % |
| hydrogen | 0 – 1 % |
| hydrogen sulphide | 0 – 1 % |
| ammonia | 0 – 1 % |

Table 1. Typical components of a biogas (Schiffer, 2011)

The main components of biogas are methane ($CH_4$) and carbon dioxide ($CO_2$), but it also contains significant quantities of undesirable compounds. Table 1 shows typical compounds and their concentrations in a biogas. For the exploitation of energy gained from biogas, the amount of methane is essential: the higher the amount of methane the higher the output of energy from biogas. The other components are mostly useless for the energy production such as nitrogen or water. It is even possible that a negative impact on engine reliability can be provoked by trace components such as hydrogen sulphide ($H_2S$), ammonia ($NH_3$) and siloxanes. The trace components can be very harmful as the aggressive substances formed may destroy the engine, e.g., due to corrosion. (Harasimowicz et al, 2007; Schiffer, 2011)

The existence and amounts of these contaminants depend on the source of the biogas, i.e., landfill, anaerobic fermentation of manure or wood gasification. As they are aggressive to the engine, they should be removed before the gas is combusted in the engine using a biogas purification step. An important step during the purification process is to desulphurise the gas in particular by removing hydrogen sulphide. Further steps are drying to remove water from the biogas or mechanical filtering to remove dust and other particles. (Abatzoglou et al., 2009; Besser et al., 2009; Harasimowicz et al, 2007)

Generally it can be stated that the better the purification steps the less the negative impact on the engine is to expect. But in turn, the installation and running costs are significantly higher. Consequently, an engine could be driven with an unpurified biogas including several harmful compounds directly impacting the lubricant condition. In this case, the oil reaches the end of the useful life time considerably earlier than with a purified biogas. For small engines, this method could be an economical alternative. But also due to ecological reasons, a gas purification should be applied resulting in less impact on the gas engine oil with the benefit of extended oil change intervals and lower costs of used oil disposal. The decision for or against a biogas purification system, respectively, requires a careful consideration of the economical and ecological influencing factors.

### 1.2 Oil condition monitoring

Independently of the type of fuel or lubricant, oil condition monitoring is getting increasingly important. For economical and ecological reasons, it is necessary to replace the used oil only when it is required. Therefore, the knowledge about the current oil condition is a prerequisite for the determination of the remaining useful life of the lubricant and the optimum time of an oil change, respectively. Different approaches of varying value are available to characterise the oil condition as described in more details in the following.

#### 1.2.1 Fixed oil change intervals

This is the easiest method to define the time for the oil change. The lubricant is changed after a defined driven distance, a time period or after a defined number of operating hours, e.g., 15 000 km or once per year for passenger cars (Exxon Mobil Corporation, 2011) or after 500 operating hours for some biogas engines. (Riemag, 2011) This method is mostly applied to older engines.

Here, the actual stress of the engine is not noticed but requires very constant operating conditions. The latter cannot be guaranteed especially in the field of biogas as remains from seasonal crops are often processed. Hence, the different strains on a lubricant can cause that the oil is changed too late which can lead to engine damage in the worst case. On the other hand, the oil can be replaced too early when the total oil stress is lower than expected. In that case, economical losses due to early purchase of fresh lubricant and disposal of still useful lubricant have to be faced. Due to these disadvantages, the oil change after a fixed interval is not recommended. But this method is currently applied for older and inexpensive engines.

#### 1.2.2 Algorithm based oil change intervals

Algorithm based methods for determining the optimum oil change interval are very common in the automotive sector. Based on the engines operating parameters like temperature, load profile or numbers of cold starts, the oil condition is determined with special algorithms. (Fitch, 2004; Wang, 2001)

An example of such a system is the General Motors GM Oil-Life™ system (Fitch, 2004). This system divides the load profile in four groups: easy freeway driving; high temperature, high load service; city driving and extreme short, cold start driving. Thereby, the oil deterioration mainly depends on the oil temperature regarding the first three groups. At cold starts driving, the lubricant is stressed by contaminations like water: the lower the temperature the higher the contamination with water. Based on these telemetric data, the oil change interval is estimated.

This method only records indirect parameters, hence the actual oil condition is not known at any point of the oil interval. Therefore, it can only react to variations of the operating conditions, but unforeseen influences like changes in the fuel or oil quality or a water intake cannot be detected. Consequently, such systems fail in the event of unforeseen incidents.

### 1.2.3 Laboratory analysis

This method is usually applied to large engines or stationary machines. Thereby, oil samples regularly taken are sent to a laboratory to analyse the oil condition using a large number of standardised methods. The set of analytical methods significantly depends on the application but mostly include viscosity, water content, acid content, base reserve and wear elements. Based on the analytical findings and if available including the history of the engine, a recommendation whether the oil should be change or still can be used will be done. (Newell, 1999; Smolenski et al., 1994; Toms et al., 2010)

This method is currently the most accurate means to determine the condition of the lubricant. But laboratory services suffer from the drawback of considerable time delay between sampling and analyses. Therefore, the actual condition of the lubricant is not immediately known. Consequently, sudden and unforeseen dramatical changes of the oil condition, e.g., caused by a water intake, cannot be detected which can result in rapid and severe engine breakdown.

### 1.2.4 Sensors for online oil condition monitoring

Sensors and sensor systems, respectively, directly installed in the lubricated system are proposed as the best way for condition monitoring as the current oil condition is immediately known and oil changes can be performed without delay especially in critical situations. Due to this crucial advantage over laboratory analysis, an extensive portfolio of different sensor systems exists on the market capable to measure various relevant oil parameters using a large number of sensor principles. But not every sensor principle is suitable for each oil application as the operating conditions as well as fuel and lubricant chemistry have to be considered. For this reason, the knowledge about the biofuel properties and critical oil parameters is indispensable for the selection of an appropriate sensor system.

Recently, a couple of sensor principles have been proposed aiming at the detection of physical or chemical properties of the oil. One typical parameter detected by sensors is the viscosity. (Agoston et al., 2004; Agoston et al., 2005b; Ronaldson et al., 2006) Here, it has to be pointed out that each sensor principle measures a different aspect of the viscosity. Electrical parameters of the oil such as permittivity or conductivity (Agoston et al., 2004; Basu et al., 2000; Gegner et al., 2010) are easy to measure and can be realized in robust devices. But the interpretation of the sensor signals is difficult as many factors influence permittivity or conductivity. The contribution of each factor cannot be clearly attributed without the knowledge of other oil parameters. Infrared sensors as proposed in (Agoston et al., 2008; Kudlaty et al., 2003) enable the measurement of several oil parameters, among others oxidation and additive depletion, but the constructional implementation of the interaction between infrared beam and oil is considered as largest difficulty.

In the case of online sensors, a similar thinking as for laboratory based analytical services should be considered: a single parameter is not sufficient to obtain reliable information about the oil condition. Therefore, the use of online systems equipped with multiple sensors able to measure several oil parameters should be implemented in the engine.

Particularly in stationary engines driven by gaseous biofuels, acidification is a crucial parameter for the evaluation of the condition of the engine oils (Felkel et al., 2008) as a correlation to corrosion of engine parts is expected. Here, elevated levels of acidification showed to be one of the main indicators for an oil change. For this reason, online monitoring of the engine oil corrosiveness by means of a chemical sensor is highly beneficial which is described in the following chapter.

### 1.3 Oil condition sensor based on corrosiveness

The proposed oil condition sensor is used to measure the corrosiveness of lubricants. For this purpose, a metal film acting as sacrificial layer is exposed to the lubricant. Due to the corrosive attack by the oil, a material loss of the metal film occurs which can be monitored by electrical means.

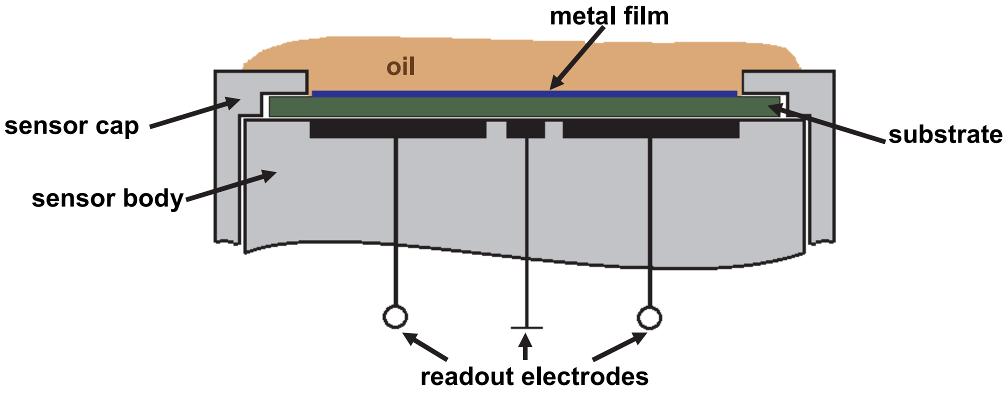

Fig. 1. Schematic setup of the proposed oil condition sensor for corrosiveness using capacitively coupled electrodes

Previous concepts measured the electrical resistance of a metal film (Agoston et al., 2005a; Agoston et al., 2007). This assembly requires a resistive connection between metal film and electronic measuring equipment. Experiments with this type of sensor setups clearly showed that corrosion occurred preferably at these contact points of the sacrificial layer. Furthermore, corrosion of the sacrificial layer was observed as even loss of material or as blotch type corrosion. In the latter case, the position of the blotches or spots on the sacrificial layer showed an influence on the sensor signal. (Agoston et al., 2006)

In order to overcome these shortcomings, a novel readout method was presented (Dörr et al., 2009) which is based on corrosion measurement without the need of an electrical contact using capacitively coupled planar electrodes. As shown in Figure 1, the novel sensor consists of an inert nonconductive substrate with a metal film as sacrificial layer on one side which is directly exposed to the corrosive medium. The material loss due to corrosion is monitored by measuring the capacitive coupling between the sacrificial layer and the readout electrodes on the backside of the substrate.

Using this setup, no resistive contact between the sacrificial layer and the electronic measurement equipment exists and hence no contact points with the danger of undesired corrosive attack exist, too.

## 2. Experimental setup

### 2.1 Sensor design and fabrication

The main part of the proposed sensor is the sacrificial element that consists of a metal film – the sacrificial layer – deposited on an inert substrate. For these experiments, a ceramic substrate from CeramTec AG was used. As metal film selected for these evaluations, lead was applied with a thickness of 600 nm. After this fabrication process, the metal films of the sensor were covered with a protective lacquer to avoid an undesired surface passivation by air during storage (prior to use).

For the implementation in corrosion experiments, a defined setup was fabricated consisting of the sensor body including the electrodes for the readout and a sensor cap for fixing the sacrificial element to the sensor body. The readout electrodes were mounted in a defined mould which was cast with epoxy resin afterwards. The sensor cap was also fabricated by casting of an other defined mould with epoxy resin. Figure 2 shows the setup of the manufactured sensor.

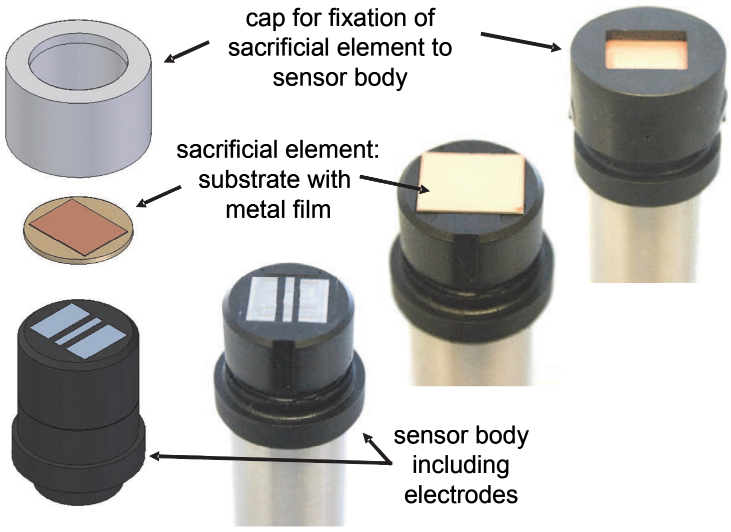

Fig. 2. Setup of the sensor for evaluation in the laboratory

An appropriate electronic measurement circuit which was directly connected to the readout electrodes evaluated the resonance frequency of the capacitive coupling between the electrodes and the metal film in combination with a constant resistor. For laboratory evaluations, the sensor was operated with a voltage output. This way, the resonance frequency was converted into a respective voltage. In the case of the field test also performed, the resonance frequency was transformed into an appropriate current.

As parameter for the corrosiveness of the lubricant monitored, the initial time (onset) for corrosion can be used representing the time when the sensor signal began to increase. Alternatively, the end time defined as the time when the sensor signal reached the end value can be determined. Hence, the end time refers to the moment when the entire metal film has been corroded away. Furthermore, an average corrosion rate can be easily calculated from the metal film thickness divided by the end time in (nm/h).

For the evaluation in laboratory, the sensor body was mounted on a tube for fixing the whole setup while immersing the sensor head with the sacrificial layer in the respective oil during the experiment. In this embodiment, the electronic measurement equipment was separated from the sensor body because of the high temperature effected by artificial alteration (see 2.3). Accordingly, a higher stray capacity due to longer cables between sensor and electronics had to be accepted.

For the experiments in the field, the sensor body was built on a flange for easy integration in the oil circulation system of the observed gas engine (Figure 3). In this version, the electronic measurement equipment was also integrated in the same setup on the backside of the flange. So, a compact device could be integrated into the engine. Advantageously, the stray capacity was possible to be kept lower, too, because of short cables between readout electrodes and electronics.

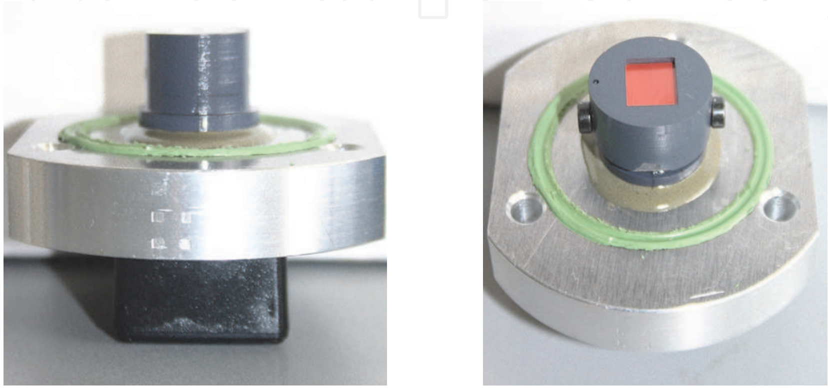

Fig. 3. Setup of the sensor for the evaluation in the field without cap for fixing the sacrificial element and with electronics at the bottom (LEFT), and fully mounted with cap and sacrificial element (RIGHT)

### 2.2 Experiments at static conditions

For corrosion experiments at static conditions, the substrates with the sacrificial layer were cleaned by a solvent to remove the protective layer. Afterwards, the dried substrate was mounted on the sensor base body and fixed with the sensor cap. After these preparatory steps, the fully assembled sensor was immediately immersed into 40 mL of the oil sample in a hermetically sealed vessel. In such a vessel, a further chemical alteration of the oil was prevented and hence allowed constant (static) conditions. The assembled test units were kept at 100 °C and 120 °C, respectively, to monitor the corrosion process at an elevated rate. The chosen elevated temperature accelerated the corrosion process due to a higher rate of the chemical reactions initiated. At these conditions, the corrosion process of the metal film depends mainly on the current corrosiveness of the oil sample; therefore, the metal films corrode faster in more corrosive oils. In the event that after 100 hours no corrosion of the sacrificial layer could be observed, the experiment was aborted and consequently the oil investigated was classified as non-corrosive to the used metal for the sacrificial layer.

The sensor was tested at these conditions with a series of defined model oils containing acidic compounds and/or selected additives. Table 2 lists the oil samples used for these investigations as well as the chosen temperature and acid number (AN) according to (DIN 51558-1, 1979) of the selected oil samples. AN refers to the amount of acidic components in an oil given in (mg KOH/g oil).

The model oils M1 to M3 were used to evaluate the principle behaviour of the novel sensor setup. Therefore, a base oil was mixed with different amounts of acidic component (here naphthenic acid). The model oils containing mineral base oil and only one additional component (oil additive or acid) were used to investigate the sensitivity of the used sacrificial layer to different components of the oil. The oil samples with both additive and acid were used to describe the interaction (competition) between the components and the impact on the corrosion process of the metal film, respectively.

| sample no. | oil type | experimental temperature [°C] | AN [mg KOH/g] |
|---|---|---|---|
| **M1** | base oil + 3 mg/g naphthenic acid | 100 | 0.6 |
| **M2** | base oil + 6 mg/g naphthenic acid | 100 | 1.3 |
| **M3** | base oil + 10 mg/g naphthenic acid | 100 | 2.3 |
| **BO** | base oil | 120 | - |
| **AO** | base oil + 0.5% antioxidant | 120 | - |
| **DET1** | base oil + 2.0% detergent A | 120 | - |
| **DET2** | base oil + 2.0% detergent B | 120 | - |
| **S1** | base oil + 1mg/g organic acid of middle chain length | 120 | 0.4 |
| **S2** | base oil + 1mg/g organic acid of long chain length | 120 | 0.2 |
| **DET1 + 0.1% S2** | base oil + 2.0% detergent A + 1 mg/g long chain length organic acid | 120 | - |
| **DET1 + 0.5% S2** | base oil + 2.0% detergent A + 5 mg/g long chain length organic acid | 120 | - |
| **AO + 0.1% S2** | base oil + 0.5% antioxidant + 1 mg/g long chain length organic acid | 120 | - |

Table 2. Defined model oils for corrosion experiments at static conditions; the amount of components is given in percent by weight

### 2.3 Experiments at dynamic conditions using artificial alteration

The online applicability was investigated by the integration of the oil condition sensor for corrosiveness in a novel artificial alteration apparatus. This lab-based apparatus is specifically designed for the simulation of the impact of biogases to lubricants during the application.

Artificial alteration means applying harsh conditions to the oil sample to accelerate oil degradation in a short-term scale. Nevertheless, an artificial alteration procedure should remain as close to reality as possible. This way, the quality of lubricants at special operating conditions and the usefulness of sensor systems for special applications can be investigated without the need to perform expensive field tests.

Currently used standardized methods for the artificial alteration of engine oils evaluate different parameters of the oil performance. Most standards examine the thermal-oxidative stability of oils by exposing the lubricant to elevated temperatures and oxygen from air. (ASTM D4871, 2006; DIN 51352, 1985)

| sample no. | alteration hours [h] | KV @ 100 °C [mm²/s] | TBN [mg KOH/g] | AN [mg KOH/g] |
|---|---|---|---|---|
| **A-A-0** | 0 | 14.2 | 9.0 | 1.5 |
| **A-A-1** | 16 | 14.1 | 8.5 | 1.3 |
| **A-A-2** | 32 | 14.2 | 7.9 | 1.4 |
| **A-A-3** | 48 | 14.3 | 7.9 | 1.6 |
| **A-A-4** | 64 | 14.4 | 7.5 | 1.8 |
| **A-A-5** | 80 | 14.5 | 7.1 | 2.1 |
| **A-A-6** | 96 | 14.6 | 6.4 | 2.2 |
| **A-A-7** | 112 | 14.8 | 5.9 | 2.4 |
| **A-A-8** | 128 | 15.0 | 5.4 | 2.6 |
| **A-A-9** | 144 | 15.0 | 5.1 | 3.0 |

Table 3. Oil samples taken during artificial alteration with "air" (A-A-0 to A-A-9) including alteration hours and oil properties determined by laboratory analysis

Based on the existing methods, an adapted alteration method was used to simulate oil life cycles in gas engines. Therefore, the lubricant was deteriorated at high temperature – in this case 160 °C – in a defined vessel able to blow gas into the oil. Additionally, a fixation was used to implement the proposed sensor setup in the artificial alteration device.

In order to simulate the impact of different fuel qualities on lubricant degradation, two different alteration methods were chosen. According to the first method, air was blown through the lubricant at a rate of 10 L/h. This method denoted with "air" should simulate mild conditions in an engine, e.g., the operation with natural gas almost free from contaminants forming aggressive compounds.

The conditions for the second method called "biogas" were based on the "air" method and adjusted to simulate the impact of biogas on accelerated oil degradation.

The lubricant was artificially altered at these conditions for 72 hours for "biogas" alteration and 144 hours for alteration "air", respectively. For oil condition monitoring and observation of the trend of oil degradation during the alteration procedure, oil samples were taken every 8 hours or 16 hours, respectively, and analysed in the laboratory. Table 3 for alteration "air" and Table 4 for alteration "biogas" summarise the most important properties of the oil samples: kinematic viscosity (KV) at 100 °C according to (ASTM D7042, 2010) using the so-called Stabinger viscosimeter, total base number (TBN) according to (DIN ISO 3771, 1985) and AN. TBN indicates the amount of bases in an oil possible to neutralise acidic components taken up or formed upon lubricant alteration. TBN is given in (mg KOH/g oil).

| sample no. | alteration hours [h] | KV @ 100 °C [mm²/s] | TBN [mg KOH/g] | AN [mg KOH/g] |
|---|---|---|---|---|
| **A-B-0** | 0 | 14.2 | 9.0 | 1.5 |
| **A-B-1** | 8 | 14.0 | 8.3 | 1.9 |
| **A-B-2** | 16 | 14.1 | 7.0 | 2.4 |
| **A-B-3** | 24 | 14.3 | 5.6 | 2.8 |
| **A-B-4** | 32 | 14.5 | 4.1 | 3.5 |
| **A-B-5** | 40 | 14.6 | 2.8 | 4.0 |
| **A-B-6** | 48 | 14.9 | 1.3 | 4.3 |
| **A-B-7** | 56 | 15.0 | 0.3 | 4.7 |
| **A-B-8** | 64 | 15.2 | 0.0 | 5.3 |
| **A-B-9** | 72 | 15.5 | 0.0 | 5.9 |

Table 4. Oil samples taken during artificial alteration "biogas" (A-B-0 to A-B-9) including alteration hours and oil properties determined by laboratory analysis

### 2.4 Evaluation in field operation

In order to evaluate the proposed sensor at real conditions, the sensor was integrated in the oil circulation system of a stationary gas engine driven with biogas from a wood gasification facility. The sensor signals were recorded every minute. The operating temperature of the engine oil at the sensor position was approximately 80 °C and hence was significantly lower than the temperature chosen in the laboratory tests (see 2.2 and 2.3).

During the observation period, oil samples were taken every 250 operating hours to carry out reference measurements in the laboratory. The laboratory analyses included KV at 100 °C, TBN and AN. The properties of the oil samples taken are listed in Table 5.

## 3. Results and discussion

### 3.1 Laboratory evaluation at static conditions

In laboratory tests, sensors were immersed in model oils (M1 to M3) containing an acidic component for fundamental evaluation of the behaviour of the novel setup with focus on sensitivity and reproducibility (Table 6). Thereby, a reasonable reproducibility was achieved (M1 - 1 and M1 - 2) as well as a higher corrosion rate and shorter time for complete corrosion, respectively, for higher amounts of acid could be demonstrated. (Dörr et al., 2009)

Based on these results, a series of model oils composed of base oil with selected lubricant additives and/or typical acids was tested under similar conditions. In Table 7, the results of corrosion experiments with model oil containing only one additional component (additive or acid) are listed. As shown, all additives selected (here antioxidant and detergents) as well as the mineral base oil used for these experiment showed no appreciable corrosive attack to the sacrificial layer of the sensor during the entire experiment.

However, model oils containing acidic compounds (here organic acids of different chain lengths) showed immediate corrosive attack to the metal film reflected by complete

| sample no. | operating hours [h] | KV @ 100 °C [mm²/s] | TBN [mg KOH/g] | AN [mg KOH/g] |
|---|---|---|---|---|
| **F-0** | 0 | 13.7 | 8.9 | 1.5 |
| **F-1** | 250 | 14.1 | 8.7 | 1.5 |
| **F-2** | 500 | 14.5 | 8.0 | 1.7 |
| **F-3** | 750 | 14.7 | 7.8 | 2.0 |
| **F-4** | 1000 | 14.9 | 7.3 | 2.0 |
| **F-5** | 1250 | 15.0 | 7.1 | 2.1 |
| **F-6** | 1500 | 14.9 | 7.1 | 2.1 |
| **F-7** | 1750 | 15.0 | 6.8 | 2.1 |
| **F-8** | 2000 | 15.1 | 6.7 | 2.3 |
| **F-9** | 2250 | 15.1 | 6.4 | 2.3 |
| **F-10** | 2500 | 15.2 | 6.7 | 2.4 |
| **F-11** | 2750 | 15.2 | 6.6 | 2.4 |
| **F-12** | 3000 | 15.3 | 5.9 | 2.5 |

Table 5. Properties of used oil samples taken every 250 operating hours during the field test

| sample no. | corrosion rate [nm/h] | time for complete corrosion [h] |
|---|---|---|
| **M1 - 1** | 350 | 1.7 |
| **M1 - 2** | 375 | 1.6 |
| **M2** | 550 | 1.1 |
| **M3** | 750 | 0.8 |

Table 6. Corrosion rates of sensors immersed in model oils (M1 to M3) with different amounts of acid and time for complete corrosion of the sacrificial layer

consumption of the sacrificial layer within few hours. Furthermore, it can be seen that in the model oil containing the organic acid of middle chain length the metal film corrodes faster than that with long chain length. This can be explained by different amounts of effective acidic compound as both model oils contained the same percentage by weight of organic acid. But in the case of shorter chain lengths the number of reactive moieties is higher confirmed by determination of the acid number in Table 2. Eventually, the metal film started to corrode earlier.

For the investigation of the interaction of additives and acids, models oils containing both types of components were prepared (Figure 4). The results from static corrosion experiments clearly showed that the model oil containing antioxidant and acids corrodes similarly than the model oil containing only the acidic component (see Table 7). It can be concluded that the antioxidant does not influence the corrosion process which was only determined by the acidic component. Furthermore, the antioxidant is not able to prevent the metal film from corrosion and consequently it can not neutralise the acid in the oil.

| oil type | corrosive attack |
|---|---|
| **BO** | no corrosion |
| **AO** | no corrosion |
| **DET1** | no corrosion |
| **DET2** | no corrosion |
| **S1** | corrosion after 2 h |
| **S2** | corrosion after 4 h |

Table 7. Results of corrosion experiments at static conditions with selected model oils

The experiments with detergent and a low amount of acid (0.1 %) showed no significant corrosive attack to the metal film during the entire experiment. In this case, the detergent was possible to neutralise the acidic component and therefore prevent the corrosion of the metal film. The experiment with large amount of acid (0.5 %) showed a negligible corrosive attack to the metal film for about 50 hours then followed by a slow steady increase of the sensors signal. The observed behaviour showed that the detergent was not able to neutralise the total amount of acidic component and therefore a small quantity of reactive substances left induced slight corrosion of the sacrificial layer.

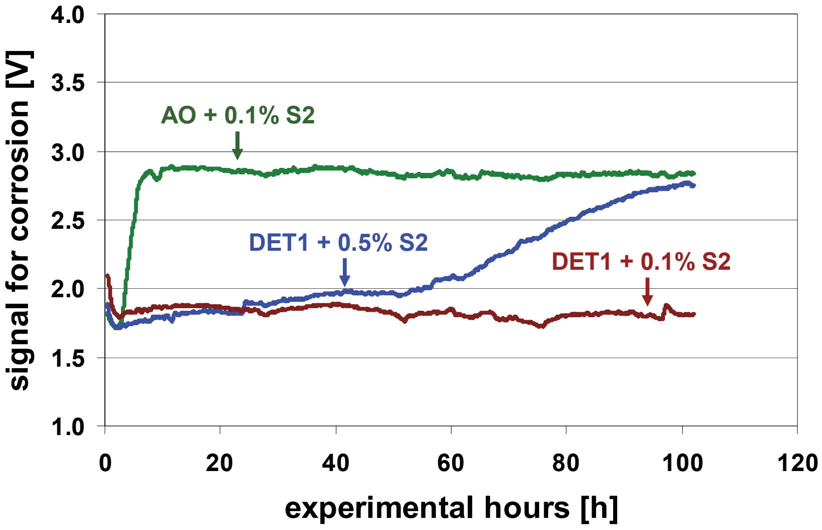

Fig. 4. Corrosion experiments performed at static conditions with model oils containing both additives and acidic compounds

The static conditions chosen – constant temperature and constant oil condition – showed good response and repeatability and hence allowed the pre-selection of elements of the proposed sensor. The results clearly showed that the metal film mainly corroded due to the acidic components dissolved in the model oils. Additives selected for these experiments (antioxidant and detergents) showed no significant corrosion. The knowledge about the ability of additives to neutralise acids and their interaction with surfaces is of essential importance for the understanding of the corrosion process and the behaviour of the sensor.

### 3.2 Laboratory evaluation at dynamic conditions – artificial alteration

As shown in Table 3 and Table 4, the lubricant deteriorated significantly faster when exposed to the alteration method "biogas". This is particularly expressed by significantly higher acidification determined as higher AN and lower TBN, respectively. Generally, an increase of viscosity can be observed when lubricants alter upon application. In the field of stationary gas engines, the oxidation stress results in the formation of acids (expressed as AN) from the blow-by gas, base oils but also from additives. Acidification by artificial alteration with "air" (simulating combustion with purified natural gas) increased up to 3.0 mg KOH/g after 144 hours. In comparison, artificial alteration with "biogas" (simulating combustion with unpurified biogas) reaches a value of 5.9 mg KOH/g within 72 hours. That is why a considerable base reserve (expressed as TBN) is indispensable to enhance the lifetime of the engine oil. As stated above, the stress is even higher when biogas is burnt as fuel: the base reserve is completely consumed after 64 hours of artificial alteration whereas an gas engine oil altered by "air" still has more than the half of the base reserve after 144 hours. So, it can be concluded that sensors giving information about the degree of acidification are more useful than sensors measuring viscosity as viscosity did not change considerably until the end of artificial alteration or the field test, respectively.

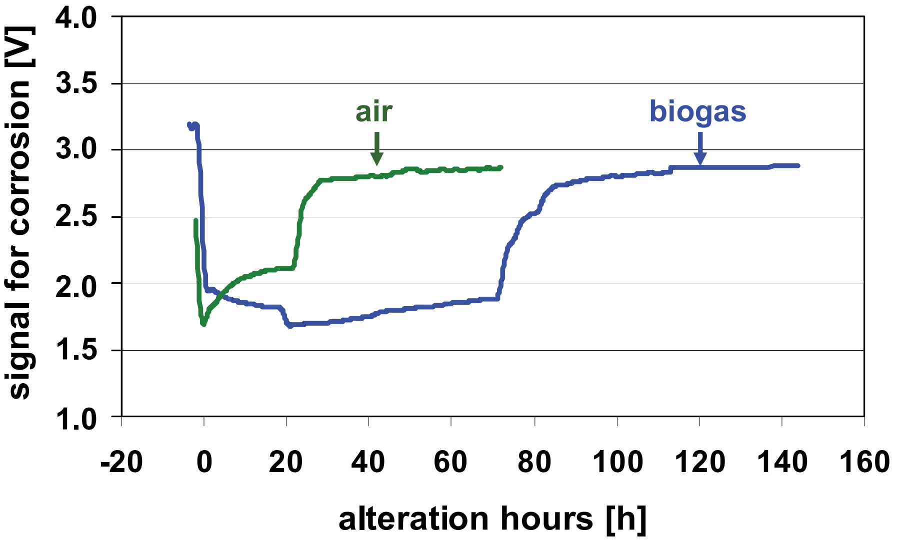

Fig. 5. Sensor signal during artificial alteration using both alteration methods

By looking at the sensor signals recorded during artificial alteration of the lubricant, an obvious shorter initial time for corrosion of about 20 hours with "biogas" can be seen in comparison to "air" causing an initial time for corrosion of about 70 hours (see Figure 5). The trend of the sensor signals shows a sharp decrease of the signal at the beginning of the alteration. This is due to the adaptation of temperatures to the alteration temperature of 160 °C. This period is followed by a relatively constant signal till the initial point for corrosion is observed. In this constant phase, no significant corrosion is noticeable. After the initial point of corrosion, the signal increases very fast due to corrosive attack of the sacrificial layer of the sensor till the whole metal film is corroded and the end signal of about 3 V is reached.

As it can be seen in Table 3 and Table 4, both oils had an acidification (AN) of 2 to 2.5 mg KOH/g and a base reserve (TBN) of about 7 mg KOH/g at the initial point of the corrosion. A similar initial point for corrosion was also reported in (Schneidhofer et al., 2009) using a resistive readout method. These results give evidence that the sensor is sensitive to a certain oil condition reached after a certain "amount" of stress independent from the time needed to achieve this condition. In other words, the sensor is capable of condition monitoring of engine oils run with different fuel qualities. An additional correlation with data from laboratory analysis is demonstrated in chapter 3.4.

### 3.3 Field operation

The usefulness of the proposed sensor concept is also illustrated by results determined by online condition monitoring in stationary gas engines. Figure 6 shows the trend of the sensor signal of a sensor system implemented into a gas engine driven with wood gas. The bright line signifies the moving average to smooth out the short-term fluctuations of the sensor signal. It is to note that the trend depicted includes only periods with running engine. Non-operating periods are not considered for better recognition.

After about 1300 operating hours, a significant increase in the sensor signal due to corrosion of the sacrificial layer was observed till the whole metal film was corroded after about 2200 operating hours followed by the constant end signal of the sensor. Before the onset of corrosion after 1300 operating hours, the sensor showed an almost constant signal (base signal) due to no significant corrosive attack to the sacrificial layer. As shown in Table 5, the oil was characterised by an acidification of about 2 mg KOH/g and a TBN of about 7 mg KOH/g at the initial point of corrosion. This critical oil condition was also detected during artificial alteration (see 3.2).

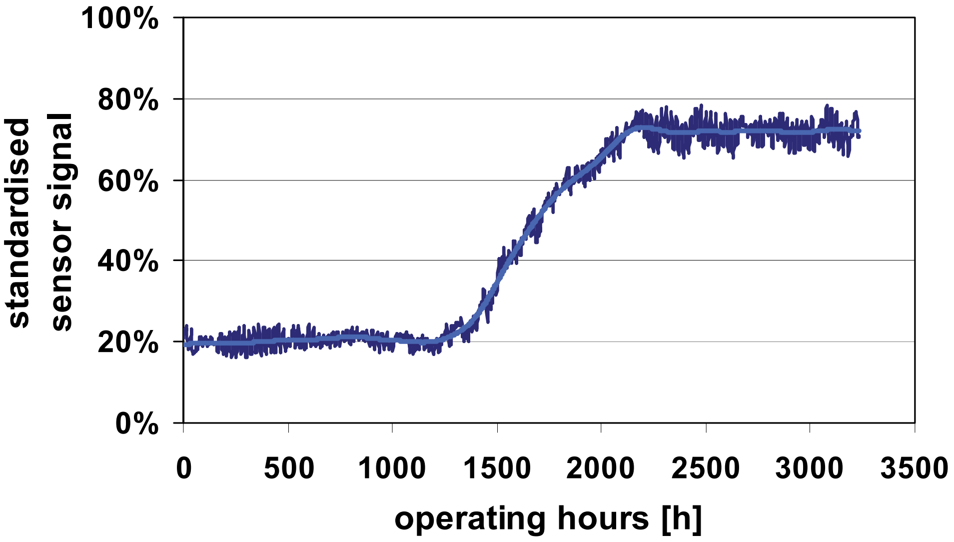

Fig. 6. Trend of the sensor signal during an entire oil interval of a stationary gas engine driven with wood gas; moving average of the sensor signal is highlighted

### 3.4 Correlation of sensor signal with data from laboratory analysis

The results from the experiments at static conditions (see 3.1) clearly showed that the metal film of the sensor is sensitive to the acidic components in the oil. If there are free reactive molecules which cannot be neutralised by the oil, the sacrificial layer is corroded according to the rule of thumb: the higher the amount of acid the faster the corrosion process.

The results obtained from the artificial alteration and field operation suggest that an initial point exists where a critical amount of acid is in the oil. For the correlation with data from laboratory analysis, the sensor signals at the time of sampling were extracted and compared with the conventional oil parameter AN determined in the laboratory. It can be seen in Figure 7 that the critical amount of acid equals AN of about 2 mg KOH/g for the used gas engine oil and the conditions applied. This value is equivalent to an increase of about 0.5 mg KOH/g in comparison to the acid number of the fresh oil (samples A-A-0 in Table 3, A-B-0 in Table 4 and sample F-0 in Table 5).

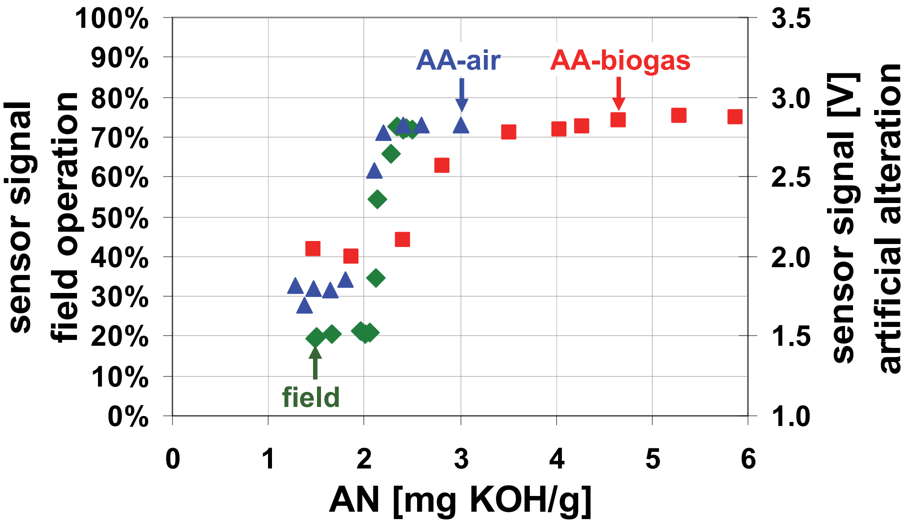

Fig. 7. Correlation of the sensor signal with AN of artificially altered oils series (AA-air and AA-biogas) as well as field samples (field)

The correlation of the sensor signal with the base reserve (Figure 8) showed a similar behaviour as identified for acidification: a critical value of about 7 mg KOH/g was observed for the gas engine oil selected which is equivalent to a decrease of TBN of approximately 2 mg KOH/g.

It has to be pointed out that a dependence of the critical values for acidification and base reserve on the composition of the engine oil (base oil and additives) may occur. That is why the initial point for the corrosion process of the sacrificial layer could vary. Consequently, it is important to know the critical initial point for a correct interpretation of the sensor signal for a proper decision on the optimal time for an oil change. The method of artificial alteration described has proven to be a valuable tool for a rapid but close-to-reality evaluation of the initial time as the same critical values for AN and TBN for both artificial alteration methods as well as at the field operation was observed.

The knowledge of the initial point of corrosion can be used as pre-warning for a critical amount of oil acidification reached. The period after initiation of corrosion can also be exploited for continuous oil condition monitoring till the whole metal film has been removed by corrosion. The time of the oil change can be adjusted to the end point of the corrosion of the metal film when following aspects are considered: proper adaptation of the thickness of the sacrificial layer, operating temperature and knowledge about engine behaviour.

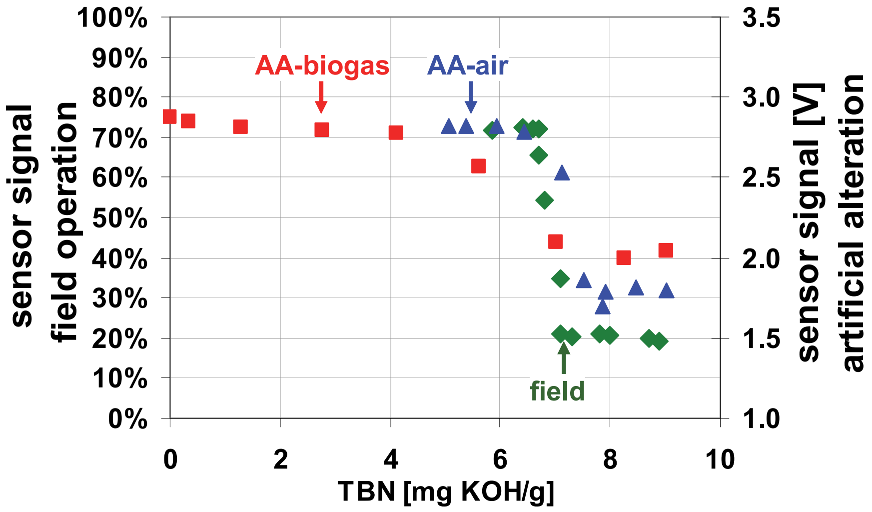

Fig. 8. Correlation of the sensor signal with TBN of artificially altered oils series (AA-air and AA-biogas) as well as field samples (field)

## 4. Summary and conclusions

Online oil condition sensors for the monitoring of the corrosiveness of lubricants are based on a metal film deposited on an inert substrate. Thereby, the material loss due to corrosion is recorded by measuring the capacitive coupling to readout electrodes. The focus of the application of the proposed sensor are gas engines driven with biogas because of the high amount of aggressive compounds formed during the combustion process which potentially lead to severe corrosion of engine parts.

The fundamental applicability of such a sensor system has been investigated with experiments at static conditions in the laboratory using defined model oils which were composed of base oil and selected additives and/or acidic components. The results clearly showed that the metal film of the sensor is sensitive to acidic compounds in the oil: the higher the amount of acid the faster the corrosion process. Selected additives (antioxidant and detergent) used for these experiments showed no significant attack to the sacrificial layer. In the case of model oils containing both additives and acids, the interaction between these components is essential for the corrosive attack. Here, it is essential whether the additive can neutralise the acidic compound or not.

Furthermore, the sensor was evaluated with different procedures of artificial alteration. In detail, two different methods were applied for the simulation of mild conditions ("air") in a gas engine (e.g., driven with natural gas) and harsh conditions caused by an unpurified biogas ("biogas"). The results from the sensor signals reported on higher corrosiveness (shorter initial time for the corrosion process) of the oil deteriorated with "biogas" in comparison to the artificial alteration "air". Artificial alteration is characterised by a significantly shorter experimental time enabling a rapid but close-to-reality evaluation of the sensor.

These results were confirmed by laboratory analyses of oil samples taken during artificial alteration. The correlation of the sensor signal with laboratory analytical data revealed that the initial point of corrosion is equivalent to an oil acidification (expressed as acid number) of about 2 mg KOH/g and a base reserve (expressed as total base number) of 7 mg KOH/g, respectively. In comparison to the values of the fresh oil, the onset of corrosion was observed at an increase of the acid number of 0.5 mg KOH/g and a consumption of the base reserve of 2 mg KOH/g, respectively. Below the initial point detected, the metal film exposed to corrosion remained almost unchanged. After the critical point, the metal film is corroded till the whole sacrificial layer is consumed.

In field operation, the sensor showed the usefulness and applicability of the proposed sensor concept. The results confirmed the initial point for the onset of corrosion already elucidated during artificial alteration.

This research work demonstrates that the proposed sensor for oil corrosiveness is characterized by a sufficient and reproducible sensitivity useful for online oil condition monitoring in engines as pre-warning system. The choice of the sacrificial material and thickness of the metal layer mainly depends on the application determined by fuel quality and the type of engine oil.

The oil condition sensor proposed is suitable for the indication of the impact of biofuel quality on the engine oil condition as successfully demonstrated on the example of a stationary gas engine run with biogas from wood gasification. Concluding, the sensor can be used for online oil condition monitoring in engines as pre-warning system for the indication of critical amounts of acids formed upon combustion of biofuel.

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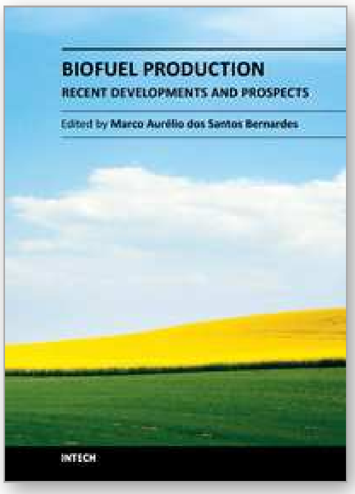

**Biofuel Production-Recent Developments and Prospects**
Edited by Dr. Marco Aurelio Dos Santos Bernardes

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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