Concentration measurements of biodiesel in engine oil and in diesel fuel

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Abstract. This work comprised a method for concentration measurements of biodiesel in engine oil as well as biodiesel in diesel fuel by a measurement of the permittivity of the mixture at a frequency range from 100 Hz to 20 kHz. For this purpose a special designed measurement cell with high sensitivity was designed. The results for the concentration measurements of biodiesel in the engine oil and diesel fuel shows linearity to the measurement cell signal for the concentration of biodiesel in the engine oil between 0.5\% Vol. to 10\% Vol. and for biodiesel in the diesel fuel between 0\% Vol. to 100\% Vol. The method to measure the concentration of biodiesel in the engine oil or the concentration of biodiesel in the diesel fuel is very accurate and low concentration of about 0.5\% Vol. biodiesel in engine oil or in diesel fuel can be measured with high accuracy.

Keywords: permittivity, biodiesel, diesel fuel, engine oil, concentration measurement

1. Introduction

Regular oil change intervals are necessary for the maintenance of modern combustion engines. Especially diesel engines equipped with diesel particular filters (DPF) and powered by biodiesel or biodiesel blends need frequent oil change intervals to reduce engine wear. That circumstance is caused by a carry-over of fuel into the engine oil, which can lead to oil dilution and chemical degradation of the engine oil [1]. The oil dilution is caused by the regeneration strategy of the diesel particular filter that uses late post injection to increase the exhaust gas temperature to regenerate the DPF [2]. In that post injection cycle the fuel is moved to the oil pan where it can dilute the engine which on the one hand leads to increased viscosity of the engine oil, and on the other hand it can undergo a variety of chemical reactions in the engine oil which can lead to sludge formation [3].

The common strategy to solve these problems is the decrease of the oil change interval, which means increased engine oil consumption [4]. There have been published some approaches to reduce the oil dilution caused by the DPF. For example to run late injections only in one cylinder [5], or use control procedures as described in [6] to link the concentration of fuel components in the engine oil with the regeneration periods of the DPF. The overall idea of those methods is to prevent the oil dilution by restrain the oil to move in to the oil pan and to estimate the dilution of the engine oil.

However, these evaluations must always be an approximation as the exact amount of biodiesel in the engine oil remains unknown and with it the probability of harm by chemical reaction. As a
consequence, oil change may be carried out earlier as necessary with increased engine oil consumption. With knowledge about the effective composition of the engine oil the oil change intervals could be better defined with that the engine oil consumption can be decreased. This work based on the idea of an online-measurement of the biodiesel content in the engine oil to find the optimal moment for an engine oil change interval. If the concentration of biodiesel in the engine oil exceeds a critical level the onboard diagnostic (OBD) can inform the driver to perform an oil change soon. With this method the overall consumption of engine oil can be decreased by an optimized oil change interval and the diesel engine is prevented from taking damage by oil dilution or oil sludge formation.

We want to introduce a method for concentration measurements of biodiesel in engine oil or diesel fuel. Blends from biodiesel/diesel fuel and biodiesel/engine oil were measured at different frequencies by a special designed capacitive cell (in the following called sensor) and the concentration of biodiesel in the mixture was calculated by the measured permittivity. The method of the concentration measurement and the measurement results will be explained in detail, focused on the concentration measurements of biodiesel in engine oil. Further approaches to use the sensor’s abilities to measure the amount of biodiesel in diesel fuel will also be made and discussed in order to expand the field of application of the sensor.

2. Theoretical background

The measurement cell works on capacitive basis and characterizes different liquids by change of the permittivity. The permittivity describes the macroscopic behaviour such as permanent and induced dipole moments in presence of an electrical field. One opportunity to determine the fuel in engine oil is to assay these dielectric properties like the relative permittivity. Basically there are two options to do the analysis. One is to use the measurement method in the time-domain, where by changing voltage and field intensity abruptly the relaxation of the molecules is measured. Alternatively, there is the possibility of measuring in the frequency-domain. In a range of different frequencies, the dielectric characteristics were measured. In this work we used the method of the frequency domain.

The capacity of the measurement cell \( C_0 \) can written as equation (1),

\[
C_0 = K_0 \times \varepsilon_0
\]

where \( K_0 \) is a constant that depends on the geometrical properties of the measurement cell and \( \varepsilon_0 \) is the permittivity of free space. Commonly the permittivity can be described as a complex-valued function shown in equation (2),

\[
\varepsilon_r(\omega, T) = \varepsilon_r^\prime(\omega, T) - i \varepsilon_r^\prime\prime(\omega, T)
\]

where \( \varepsilon_r^\prime(\omega, T) \) is the real part of the permittivity that depends on the temperature \( T \), the angular frequency \( \omega = 2\pi f \), and the frequency \( f \). \( \varepsilon_r^\prime(\omega, T) \) express the polarization of the molecules in a liquid and \( \varepsilon_r^\prime\prime(\omega, T) \) describes the imaginary part of the permittivity that are linked to the losses associated with conductivity by the presence of free charge carriers and polarizations, where adjustment of polar molecules redound to friction. \( \varepsilon_r^\prime(\omega, T) \) can be written as equation (3),

\[
\varepsilon_r^\prime(\omega, T) = \frac{C(\omega, T)}{C_0}
\]

where \( C(\omega, T) \) is the measured capacity of the cell filled with a sample and \( C_0 \) is the capacity of the unfilled cell. Further there are three kinds of polarization that influence \( \varepsilon_r(\omega, T) \). The displacement polarization, the orientation polarization and the interfacial polarization. The displacement polarization occurs for non-polar molecules with no dipole moment. In this case the electric field cause a displacement of the electric charges in the atoms and a dipole moment is induced. The orientation polarization causes an alignment of already present dipole moments along an electric field [7]. Therefore molecules with large mass or no dipole moment, for example biodiesel or diesel fuel, have a
low orientation polarization at high frequencies according to their inability to follow the alternating electrical field. In this case equation (3) is independent from frequency. Also the orientation polarization is strongly influenced by temperature according to the thermal forces that counter the assortative forces of the electrical field [8]. The interfacial polarization can occur for polar substances in the mixture. These polar molecules can act as free charge carrier in the mixture and are able to migrate to the capacitor plates. This causes an increase of \(\varepsilon_r' (\omega, T)\) at low frequencies in presence of polar substances [9].

3. Methods and Materials
For sample preparation we used biodiesel according to [10] and diesel fuel according to [11] as well as 15W40 engine oil supplied by Concept Tech. We used a sample volume of 5 litres that is typical amount of engine oil used in passenger car. In order to avoid errors in the sample preparation the amount of biodiesel in the samples were checked prior the measurement by gas chromatography with mass spectrometry (GC/MS). For this task we used a 7890 Agilent gas chromatograph with a 5975C mass selective detector. Table 1 shows the used samples for the concentration measurements of biodiesel (BD) in engine oil (EO).

| Sample | Amount of BD [% Vol.] | Amount of EO [% Vol.] |
|--------|------------------------|-----------------------|
| BE0    | 0                      | 100                   |
| BE0.5  | 0.5                    | 99.5                  |
| BE1    | 1                      | 99                    |
| BE2    | 2                      | 98                    |
| BE3    | 3                      | 97                    |
| BE5    | 5                      | 95                    |
| BE10   | 10                     | 90                    |

Analogue to Table 1 we prepared samples of biodiesel and diesel fuel (DF) according to Table 2.

| Sample | Amount of BD [% Vol.] | Amount of DF [% Vol.] |
|--------|-----------------------|-----------------------|
| B0     | 0                     | 100                   |
| B5     | 5                     | 95                    |
| B10    | 10                    | 90                    |
| B15    | 15                    | 85                    |
| B20    | 20                    | 80                    |
| B25    | 25                    | 75                    |
| B50    | 50                    | 50                    |
| B100   | 100                   | 0                     |

To test reproducibility and accuracy of our sensor we compared measurements of the permittivity according to equation (3) of pure biodiesel in a range of 23±0.1 °C to 100±0.1 °C with literature and checked \(\varepsilon_r' (\omega, T)\) for linearity in a frequency range from 100 Hz to 20 kHz. Figure 1 depicts the measurements of pure biodiesel at 100 Hz and 20 kHz for example. The nonlinearity at higher temperatures is caused by the strong temperature dependency of the orientation polarization as mentioned in [8] and is equal for all measured frequencies. The deviation in \(\varepsilon_r' (\omega, T)\) between the
frequencies is very small and the other measured frequencies show the same low deviation. Further, in [12] and [13] permittivity measurements of pure biodiesel at different temperatures were performed and compared to our measurements we find very good correlations regarding to the different biodiesel charges we used. Therefore our measurement setup can produce comparable results with high reproducibility.

![Figure 1](image.png)

Figure 1. Measurement of $\varepsilon_r'(T)$ for pure biodiesel at different temperatures for 1000 Hz and 20 kHz. The sensor shows low deviation for measurement of $\varepsilon_r'(T)$ between 100Hz and 20kHz. The nonlinearity at higher temperatures is caused by the temperature dependency of the orientation polarization [8].

We measured the permittivity $\varepsilon_r'(\omega, T)$ according to equation (3) of the samples of biodiesel/diesel fuel and biodiesel/engine oil in a frequency range of 100 Hz to 20 kHz. For this purpose we used a Hewlett Packard function analyzer 4276A LCZ. The prototype of the sensor was designed for easy and accurate use especially at low frequencies and optimized for high accuracy. In order to test the essential functional principle all samples were measured at constant room temperature of about 25±0.5 °C to rule out deviations of the permittivity, according to [8].

4. Results and Discussion

Figure 2 depicts the measurement results of the diesel/engine oil blends for the frequency range from 100 Hz to 20 kHz. The results show a nonlinear behaviour of $\varepsilon_r'$ at low frequencies. Engine oil contents different additives for example for wear protection or cleaning properties [14]. These additives cause interfacial polarization and also orientation polarization and are the reason for the behaviour of $\varepsilon_r'$ at low frequencies. Further, the results shows that raising concentration of biodiesel in the engine oil (BE0 to BE10) causes $\varepsilon_r'$ to increase.
Figure 2. Measurements of different blends of biodiesel/engine oil at frequencies from 100 Hz to 20 KHz. The graph shows nonlinearities at low frequencies caused by polar molecules in the engine oil by interfacial polarization and orientation polarization.

Figure 3 depicts the dependency of $\varepsilon_r'$ at constant frequency at 1000 Hz with increasing biodiesel concentration (BE0 to BE10, Table 1). The linear function fits very accurate and the fitting factor is $R^2=0.99817$. The fitting factors for the remaining frequencies are better than $R^2 > 0.998$.

Figure 4 shows the measurements results of biodiesel/diesel fuel blends at frequencies from 100 Hz to 20 KHz. Compared to Figure 2 $\varepsilon_r'$ shows a linearity over the complete frequency range. This can be explained with a low amount of polar substances in the diesel fuel. Therefore the measurement is low influenced by the interfacial polarization, and the displacement polarization that is independent from frequency in our frequency range [15]. Analogue to biodiesel in engine oil a raising amount of biodiesel (B0 to B100, Table 2) causes $\varepsilon_r'$ to increase. Figure 5 shows the linear dependency of the increasing amount of biodiesel in the diesel fuel and the increase of the permittivity at a frequency at 1000 Hz. The linear function fits very accurate and the fitting factor is $R^2=0.99934$. The fitting factors for the remaining frequencies are better than $R^2 > 0.999$. 

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Figure 3. Measurement results for the amount of biodiesel in the engine oil at a frequency of 1000 Hz.

Figure 4. Measurement results for the amount of biodiesel in the engine oil at a frequency of 1000 Hz.
Figure 4. Measurements of different blends of biodiesel/diesel fuel at frequencies from 100 Hz to 20 KHz. The most absence of polar substances in diesel fuel is the reason for the linear shape of the graph at low frequencies according to low interfacial polarization [9].

Figure 5. Measurement results for the amount of biodiesel in diesel fuel at a frequency of 1000 Hz.

5. Conclusion

The knowledge about the concentration of biodiesel in the engine oil can help to find the optimal time for an oil change interval of modern diesel combustion engines. For this purpose we tested a method to measure the concentration of biodiesel in the engine oil and in diesel fuel with high accuracy.

The results showed a nonlinear behavior of $\varepsilon_r^\prime$ at low frequencies for measurements in engine oil (Figure 2). This can be explained by the presence of polar substances in the engine oil that cause interfacial polarization as well as orientation polarization. The linear behavior of $\varepsilon_r^\prime$ at the measurements of biodiesel in diesel fuel (Figure 4) leads to the conclusion of a lower amount of polar substances in the diesel fuel and therefore to lower polarization effects. It is possible to use the information about these polarization effects of a sample for a prediction about the content of polar substances or large molecules, for example for degeneration products of engine oil or biodiesel. In our research group we started efforts to research this field of application of the sensor.

Overall, the ability of our sensor to determine the amount of biodiesel in the engine oil even at low concentrations of about 0.5 % Vol. is very accurate (Figure 3). Further the sensor is capable to measure low concentrations of about 0.5% Vol. of biodiesel in diesel fuel too (Figure 5). It must be considered that the additive composition of engine oil can differ among engine oil suppliers and
therefore the permittivity measurements can be applied in the first instance strictly to the engine oil used in the experiments. Further the measurement temperature should be kept constant during the measurement otherwise the result of the permittivity will drift according to the temperature dependency of equation (3). The full potential of the method explained in this work is still not fully utilized and further elaborated experiments will be done to optimize the method and to expand the range of application.

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