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Determining the aging degree of domestic heating oil blended with biodiesel by means of dielectric spectroscopy

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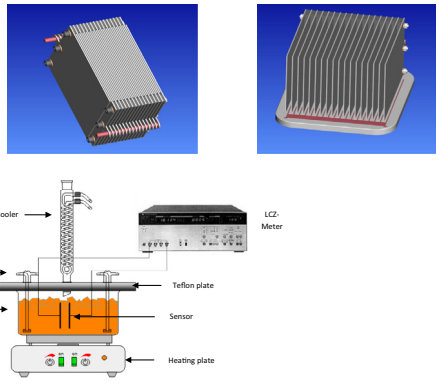
HIGHLIGHTS

- We developed a method for determining the oxidation stability of domestic heating oil blended with biodiesel.
- Oxidation products from heating oil blended with 10% biodiesel were investigated by dielectric spectroscopy.
- The alteration of dielectric parameters during the accelerated aging is used to determine the oxidation stability.

GRAPHICAL ABSTRACT



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ABSTRACT

To raise the share of renewable energies in the domestic heating market, the use of bio heating oil becomes increasingly important and popular. Considering the German heating market, bio heating oil blended with 10% biodiesel is already available. The affinity of biodiesel to forming oxidation products requires fast and reliable measuring methods which cannot be covered with conventional methods such as the Rancimat method according to DIN EN 15751. Therefore, a new measuring technique is introduced in this work, where oxidation products from heating oil blended with 10% biodiesel (HO B10) and for comparative purposes neat heating oil (HO B0) were investigated by dielectric spectroscopy. The results were verified by gel permeation chromatography (GPC) and by measuring of the total acid number (TAN). The alteration of dielectric parameters during the accelerated aging is used to determine the oxidation stability.

1. Introduction

The idea that the supply of fossil energy sources by conventional methods is contradictory to the reality [1]. The use of renewable energy sources is necessary to ensure a safe and an environmental friendly energy supply. For this reason blending fossil diesel fuels with biodiesel has already been successfully introduced by several countries all over the world in their transport sectors. There are several advantages of using biodiesel: conservation of fossil fuels, independence of global energy suppliers – thus strengthening the local economy and the reduction of climate-effecting emissions.

Similar trends are also observed in the domestic heating market. In addition to developing modern and efficient oil burner technology such as cogeneration, the use of regenerative energy

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sources is also focused on [2]. The proportion of biodiesel in fossil diesel fuel has already been established in several countries all over the world. Because of the similarity between diesel fuel and heating oil, both being middle distillates, the latter are also blended with biodiesel. In Germany, heating oil blended with 10% biodiesel is already available in the domestic heating market.

Early investigations on fossil diesel fuel blended with biodiesel showed the tendency to form sedimentation when biodiesel was aged [3]. During long-time storage in heating oil tanks similar problems could be observed. Consequently, it could lead to clogging of nozzles, oil preheaters and filters [4]. Biodiesel consists of methyl esters which include saturated and unsaturated amounts of esters. These unsaturated esters are responsible for the instability in the fuel and thus lead to sedimentation. Generally, unsaturated hydrocarbons undergo autoxidation with the formation of alkyl- and peroxy radicals [5,6] which can react with oxygen to form peroxide or hydroperoxide. These peroxides lead to cyclic products which form acids, aldehydes, alcohols or react with other alkyl- and peroxy radicals to form dimers or oligomers [7].

It is important to offer high quality bio heating oil to ensure protection of the overall heating system. Due to the reduced oxidation stability of biodiesel, e.g. during long-time storage in heating oil tanks or during the injection, a quantification method of determining the quality of heating oil blended with biodiesel is only possible with elaborate laboratory procedures. The determination of oligomers for example, requires GPC. Standard method DIN EN 15751 describes the Rancimat method. This is the measuring of increase in conductivity by acid formation during an accelerated aging process of biodiesel. Further oxidation products (e.g. alcohols, oligomers) cannot be determined by this method. Dittmar et al. [8] showed that a subsequent additive addition in biodiesel can reach the necessary induction time of 6 h according to DIN EN 14214:2003, although biodiesel was already pre-aged. The formation of acids can be avoided by the use of BHT (butylated hydroxytoluene) or δ-tocopherol despite the presence of further oxidation products like oligomers, alcohols etc. Hence, standard techniques, such as the Rancimat method, are not always significant enough as a prediction method for the quality of biodiesel. For this reason the development of new sensor techniques has become necessary.

The field of application of dielectric spectroscopy is very diverse: Characterization of fuels during the biodiesel production [9,10], the content of methanol in biodiesel [11] as well as the determination of the biodiesel content in diesel fuel during the engine fuel adaption [12] are some examples where dielectric measurements are used. Hence a completely new sensor was developed based on a parallel-plate capacitor which is capable of measuring dielectric parameters in biodiesel or heating oil blended with biodiesel in real-time during an accelerated aging to determine its aging degree. A particular highlight of the sensor is its ability to measure the dielectric parameters in low frequency ranges where polar oxidation products like alcohols, acids and especially oligomers can be detected.

2. Theoretical background

Measurements of dielectric parameters in the frequency-domain, relative permittivity ε_r' and dissipation factor tan δ were measured by applying an alternating voltage between the plates of a parallel-plate capacitor at different frequencies. Inserting a dielectric material (e.g. liquid, solid) between these electrodes leads to a decrease of the primary electrical field because of polarization mechanisms like displacement polarization or orientation polarization [13].

2.1. Displacement polarization

In atoms or nonpolar molecules exposed to an electrical field, the displacement of the positive charge and negative charge concentrations respectively lead to an intramolecular electrical field which is opposed to the primary electrical field. Consequently the displacement polarization leads to an attenuation of the primary electrical field.

2.2. Orientation polarization

Orientation polarization describes the alignment of polar molecules in an electrical field. In the frequency domain, while an alternating electrical field is applied, the mobility of these molecules is highly dependent on the frequency. Polar and high molecular compounds show at higher frequencies less mobility because of inertia. It is also clear that the orientation polarization is strongly dependent on the temperature which also influences the mobility of these molecules. Afterwards, similar as in the displacement polarization, adjusted molecules attenuate the primary electrical field.

2.3. Interfacial polarization

The interfacial polarization is noticeable at low frequencies. In this case, polar molecules acting as free charge carrier in the mixture are able to migrate to the capacitor plates and therefore attenuate the primary electrical field.

The polarization mechanism and thus the decrease of the primary electrical field leads to an increase of the capacitance in a parallel plate capacitor. Generally, the relative permittivity ε_r' is defined as the quotient of the capacitance with a dielectric $C(\omega,T)$ and the capacitance of the empty cell $C(\omega,T)$, where ω is the angular frequency and T the temperature [14]:

$$\varepsilon_r'(\omega,T)=\frac{C(\omega,T)}{C_0(\omega,T)} \tag{1}$$

Commonly, permittivity can be described by a complex valued function:

$$\varepsilon_r(\omega,T)=\varepsilon_r'(\omega,T)-i\varepsilon_r''(\omega,T) \tag{2}$$

The meaning of the real part is already mentioned in (1). However, the imaginary part describes the dissipation caused by polarization mechanism and conductivity. Both the alignment of polar molecules and motion of free charges in dielectrics lead to friction with vicinal molecules and thus to losses which is described by the dissipation factor tan δ:

$$\tan\delta=\frac{\varepsilon_r''(\omega,T)}{\varepsilon_r'(\omega,T)} \tag{3}$$

According to Eq. (4) tan δ can be further subdivided into conductivity losses tan δ_L and polarization losses tan δ_P.

$$\tan\delta=\tan\delta_L+\tan\delta_P \tag{4}$$

The easiest way to describe a real capacitor with losses is the parallel equivalent circuit of a capacitor C_P and a resistor R_P (see Fig. 1 (left)). Hence, the dissipation factor can be calculated from the quotient of the power factor in the resistor and the reactive power in the capacitive cell [15]:

$$\tan\delta=\frac{\frac{U^2}{R_P}}{\omega C_P U^2}=\omega C_P R_P \tag{5}$$

In an ideal capacitor, current $\underline{I}$ and voltage $\underline{U}$ are out of phase by 90°. If losses occur in the dielectric, they can be detected by the resistor R_P. As a result, $\underline{I}$ deviates by a loss angle δ from $\underline{U}$ (see Fig. 1 (right)).