Fuel 209 (2017) 224–231

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Novel concepts for onboard determination of fuel quality in plug-in hybrid cars

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ARTICLE INFO

Keywords:
Fuel
Biofuel
Fuel design
Fuel aging
Fuel sensors
Dielectric spectroscopy
Plug-in hybrid vehicle

ABSTRACT

In consideration of the CO2 saving potentials of biofuels, a quota of biodiesel in fossil diesel fuel is established in a number of countries all over the world. However, primary investigations on fossil diesel fuel/biodiesel blends showed a certain tendency to form precipitates, which can be considered as oligomers. They result from aging of biodiesel. However, the tendency of fuel blends to form precipitates during long term storage could jeopardize the operational safety in plug-in hybrid vehicles (PHEV). In PHEV, the combustion engine is only used when the power supply from the battery is too low. On short distance rides, the combustion engine is not necessary, because of frequent battery recharging. Consequently, the storage time of the fuel in the tank is much longer than usual. For this reason the fuel long-term stability in PHEV is of particular importance. A mixture design based on a simplex-lattice design fourth-degree was used to obtain variable fuel composition. Aged samples containing linoeleic acid methyl ester (C18:2) formed precipitates that could sediment at the bottom of the vials. After a waiting period of 30 and 300 s of sedimentation time, samples of the upper phase of the vial were taken and investigated by dielectric- and fourier transform infrared spectroscopy (FTIR) to determine the stability of the suspension. For reasons of comparison size-exclusion chromatography (SEC) was used too. It was shown, that the stability of the suspension is very much dependent on the fuel mixture. The lowest stability was found in the range of 15 to 22.5% C18:2. Finally, a fourth-order regression model for the real part of the permittivity was found, which could estimate the composition of fresh fuels.

1. Introduction

Variable diesel fuel compositions, e.g. through different biodiesel qualities, different biofuel mixing rates and different proportion of aromatics in fossil fuels pose new challenges for commercial vehicle manufacturers. The motor management in vehicles is not designed for such a fuel variability. Diesel fuels for example are highly complex mixtures containing linear alkanes (n-alkane), branched alkanes (iso-alkane) in a carbon range of C_8 to C_{22}, polyaromatic hydrocarbons and cycloalkanes [1]. Investigations with gas chromatography show a normal distribution of n-alkane in the range of n-C_{11} to n-C_{14} [2]. Additionally, different quotas of biodiesel in fossil diesel fuel is established in several countries all over the world [3]. In Germany for example, a proportion of max. 7% v/v biodiesel is added to fossil diesel fuel [4]. Aggravated by the fact that modern fuels like HVO (hydro-treated vegetable oil) and GTL (gas-to-liquid) – a mixture of mainly branched and unbranched alkanes – are becoming more popular as neat fuels or as an addition to fossil fuels [5], also aromatic free fuel are introduced in the market. Furthermore, fuel degradation must be considered: Firstly, aged fuels differ in their emission behavior [6]; secondly, fuel degradation, especially blends, showed a certain tendency to form precipitates which can be considered as oligomers [6–8]. The cause of undesired fuel instability are unsaturated hydrocarbons: They undergo autoxidation forming alkyl and peroxy radicals [9,10] which can react with oxygen to form peroxide or hydroperoxide. In the next reaction step these peroxides and hydroperoxides degrade into low molecular oxidation products such as aldehydes, alcohols, ketones, acids and high molecular oligomers [8,11,12]. Problems due to aged fuels can occur at the fuel pump, injection systems or exhaust after-treatment. Fuel pump and injection system are very sensitive to an increase in viscosity due to oligomerization. The increased viscosity leads to poorer nebulization during injection. This can lead to an increase of soot or unburned fuel due to an incomplete combustion. Enabling factors for fuel aging are oxidative and thermal stress. Since the

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http://dx.doi.org/10.1016/j.fuel.2017.07.102
Received 9 May 2017; Received in revised form 3 July 2017; Accepted 26 July 2017
Available online 31 July 2017
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Table 1
Mixture design of several fuels with upper and lower bounds according to the simplex-lattice design fourth-degree.

Sample Nr.	Design matrix			Response marks	Operational matrix		
	Alkane (X_1)	Aromatics (X_2)	C18:2 (X_3)		Alkane	Aromatics	C18:2
1	1	0	0	y_1	1	0	0
2	0	1	0	y_2	0.7	0.3	0
3	0	0	1	y_3	0.7	0	0.3
4	0.50	0.50	0	y_{12}	0.85	0.15	0
5	0.5	0	0.5	y_{13}	0.85	0	0.15
6	0	0.5	0.5	y_{23}	0.7	0.15	0.15
7	0.75	0.25	0	y_{1112}	0.925	0.075	0
8	0.25	0.75	0.0	y_{1222}	0.775	0.225	0
9	0.75	0	0.25	y_{1113}	0.925	0	0.075
10	0.25	0	0.75	y_{1333}	0.775	0	0.225
11	0	0.75	0.25	y_{2223}	0.7	0.225	0.075
12	0	0.25	0.75	y_{2333}	0.7	0.075	0.225
13	0.5	0.25	0.25	y_{1123}	0.85	0.075	0.075
14	0.25	0.5	0.25	y_{1223}	0.775	0.15	0.075
15	0.25	0.25	0.50	y_{1233}	0.775	0.075	0.15

introduction of plug-in hybrid vehicles (PHEV), an additional factor could be added – the long-term stability of fuels. In PHEV, the combustion engine is only used when the power supply from the battery is too low. On short distance rides, which are the majority of all driven kilometres (about 80% below 50 km) [13] the combustion engine is not necessary, because of frequent battery recharging. Consequently, the storage time of the fuel in the tank is much longer than usual. For this reason the fuel long-term stability in PHEV is of particular importance.

In the long term, an onboard sensor system must be able to determine the fuel composition as well as the degradation degree in fuels. Series-production PHEV equipped with diesel engines are already available in the market or planned for the future (Volvo V60, Audi Q7 e-tron quattro, Peugeot 508 RXH Hybrid4, Range Rover SDV6 Hybrid Diesel).

In these investigations, therefore, we introduce a direct measuring technique based on dielectric spectroscopy, focusing the in situ determination of degradation products in fossil diesel fuels. Besides a sensor in lab scale, a smart micro sensor was developed in a laboratory test setup, too. In principle it is suited for mass production and could be applied e.g. as fuel tank sensor in PHEV. In this case the fuel must be monitored regarding the most undesired aging products that lead to filter blocking and injector fouling. To fulfill the variety of fuels, a mixture experiment based on the simplex-lattice design fourth-degree was used [14].

2. Theoretical background

2.1. Theory of dielectric spectroscopy

Dielectric parameters were performed by applying an alternating voltage between the electrodes at different frequencies. A change in the liquid composition (e.g. a fuel during its aging) between electrodes leads to a change in its primary dielectric parameters. These changes can be described by several polarization effects like displacement polarization, orientation polarization or interfacial polarization [15].

The most important polarization effect in the low frequency region can be described by the interfacial polarization. In this case, free charge carrier in the mixture can migrate to the electrode surface which influences the permittivity.

The relative permittivity $\varepsilon_r'(\omega,T)$ is defined as the quotient of the capacitance with a dielectric $C(\omega,T)$ and the empty capacity $C_0(\omega,T)$ (Eq. (1)), where ω is the angular frequeny and T the temperature: [16]

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

Furthermore, the permittivity is a complex valued function (Eq. (2))

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

Losses in the dielectric caused by polarization and conductivity effects were described with the imaginary part of Eq. (2). The imaginary part can be subdivided into two terms as shown in Eq. (3). There is a strong dependence of the losses with the frequency as shown in Eq. (3): [17]

$$\varepsilon_r''(\omega,T) = \varepsilon_{r,pol}''(\omega,T) + \frac{\sigma}{\omega\varepsilon_0} \tag{3}$$

$\varepsilon_{r,pol}''(\omega,T)$ is associated with losses due to polarization, whereas the second term is directly proportional to conductivity σ. When frequency is low enough, the second part of the term in Eq. (3) is dominating and conductivity is measureable. ε_0 is the permittivity constant of free space ($8.854^{*}10^{-12}$ F/m).

3. Methods and materials

3.1. Sample preparation

A basic solution of n-Alkanes containing n-undecane, n-dodecane, n-pentadacane and n-hexadacane (volumetric ratio of 0.98/1/0.79/0.63) was mixed. This basic solution was mixed with Shellsol® T, a neat iso-alkane mixture of branched alkanes (carbon chain length 11 and 12). The ratio of iso-/n-Alkane was 0.3/0.7 (degree of branching 30%). In the following these solution is called alkane. As aromatics Shellsol®-A was used, a mixture auf several aromatics (carbon chain length 9). Representative for biodiesel linoeleic acid methyl ester was used, which is in many biodiesel feedstocks contained. It has two double bounds with a bis-allylic position and a carbon chain length of 18. In the following it is called C18:2.

Table 1 shows the matrix for the mixture design based on a simplex-lattice design fourth-degree [14,18–20]. As the resulting mixtures from the design matrix are not all reasonable for real fuel blends, limitations have been implemented (alkane: 70 to 100%; aromatics: 0 to 30%; C18:2: 0 to 30%) thus making the operational matrix. All samples were accelerated aged by using the Rancimat setup described in DIN EN 15751 (110 °C and 10 L/h air supply, 10 mL sample volume). The aging duration was 10 h. To accelerate the aging procedure, no stabilizing additives were used.

3.2. Mathematical model for the determination of permittivity in the simplex

The response function of the mixture model was explained by using following fourth-degree regression model (Eq. (4)) and its coefficients (Eq. (5)) [21]. X_i is the variable and X_iX_j represents the interaction between the variables. The coefficient from eq. 5 are the regression

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