# ZÁPADOČESKÁ UNIVERZITA V PLZNI FAKULTA ELEKTROTECHNICKÁ

KATEDRA TECHNOLOGIÍ A MĚŘENÍ

# DIPLOMOVÁ PRÁCE

# Závislost permitivity na pracovních podmínkách uvnitř palivové nádrže

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# ZADÁNÍ DIPLOMOVÉ PRÁCE

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Jméno a příjmení:	Bc. Jan BENDA
Osobní číslo:	E14N0117P
Studijní program:	N2612 Elektrotechnika a informatika
Studijní obor:	Elektroenergetika
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#### Zásady pro vypracování:

- 1. Proveďte rozbor vlastností různých paliv a jejich chemického složení.
- 2. Zjistěte vliv chemického složení paliva na jeho permitivitu.
- 3. Ověřte vliv napájecích elektrických parametrů na určení permitivity.
- 4. Analyzujte závislost permitivity paliv s ohledem na teplotu, tlak, vliv nehomogenity, kontaminaci paliva a analyzujte vliv plynné fáze v kapalině na její permitivitu.
- 5. Stanovte závislost tlaku sytých par na teplotě v uzavřeném systému s ohledem na různá paliva.

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- 1. Mentlík, V.: Dielektrické prvky a systémy, BEN Praha, 2006
- 2. Horák, Z., Krupka, F.: Technická fyzika
- 3. Brož a kol: Základy fyzikálních měření
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Vedoucí diplomové práce:

Doc. Ing. Olga Tůmová, CSc. Katedra technologií a měření

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Ing. Jiří Hammerbauer, Ph.D. Doc děkan

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Doc. Ing. Karel Noháč, Ph.D. vedoucí katedry

## Abstrakt

Prezentovaná diplomová práce se zaměřuje na výzkum permitivity uvnitř palivové nádrže. Zkoumá vliv chemického složení, teploty, tlaku a plynné fáze na permitivitu. Dále se zabývá závislostí tlaku sytých par na teplotě v uzavřeném systému s ohledem na různá paliva.

## Klíčová slova

Palivo, kondenzátor, dielektrikum, polarizace, kapacita, permitivita

#### Abstract

Presented master thesis is focused on permittivity investigation of liquids and saturated vapours inside fuel tank. It investigates permittivity dependence on chemical composition, temperature, pressure, and saturated vapour pressure. It also examines temperature dependence of saturated vapour pressure in a closed system with respect to various fuels.

### Key words

Fuel, capacitor, dielectric, polarization, capacity, permittivity

# Prohlášení

Prohlašuji, že jsem tuto diplomovou práci vypracoval samostatně, s použitím odborné literatury a pramenů uvedených v seznamu, který je součástí této diplomové práce.

Dále prohlašuji, že veškerý software, použitý při řešení této diplomové práce, je legální.

.....

podpis

V Plzni dne 13.5.2016

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# Poděkování

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# List of used brands

С	Capacitance	(F)
Q	charge	(C)
U	voltage	(V)
G	conductance	(S)
γ	conductivity	$(S m^{-1})$
f	frequency	(Hz)
Ι	current	(A)
R	resistance	(Ω)
Z	impedance	(Ω)
А	material constant	(-)
a	material constant	(-)
Т	thermodynamic temperature	(°C)
θ	temperature	(°C)
η	dynamic viscosity	$(N \cdot s \cdot m - 2)$
ε <sub>r</sub>	relative permittivity	(-)
n <sub>k</sub>	concentration of colloid particles	$(m^{-3})$
r	radius	(m)
М	macroscopic dipole moment	(C m)
χik	dielectric susceptibility	(F m <sup>-1</sup> )
<b>E</b> 0	permittivity of vacuum (8,854·10 <sup>-12</sup> )	$(F m^{-1})$
Р	polarization	$(C m^{-2})$
Е	intensity of electric field	$(V m^{-1})$
D	displacement vector	$(C m^{-2})$
S	area	$(m^2)$
ξ	electrokinetic potential	(V)
q	ion charge	(C)
k	Boltzmann's constant	(eV K <sup>-1</sup> )
1	distance of layers	(m)
f	frequency of free electrons	(Hz)
W	dissociation activation energy of ions in the fluid	(J/mol)
jd	current density	$(A m^{-1})$
'ع	real part of permittivity	(-)
8"	imaginary part of permittivity	(-)
р	pressure	(Pa)
$\Delta H_{VAP}$	enthalpy of vaporization	$(J m^{-1})$

# List of used acronyms

GE	Mixture of gasoline with ethanol
GM	Mixture of gasoline with methanol
DS	Mixture of diesel with soybean oil
DR	Mixture of diesel with rapeseed oil
FAME	Fatty acid methyl esters
GHG	Greenhouse gas

#### Introduction

Electronic components are increasingly often used in unusual places where this was not possible in the past, or was not required. This master thesis investigates motor fuels from the perspective of dielectric properties with a focus on relative permittivity.

Accurate measurement of relative permittivity is very complicated not only in terms of the required equipment, but also in terms of the measuring method. Finding the best solution was a long process, and tens of experiments and measurements were done to be able to gather accurate data. To confirm the suitability of the method and devices used, reference measurement was done using n-heptane as a calibration liquid.

The first part of this thesis focuses on theoretical analysis, beginning with basics, and continuing to the problematic of polarization. In the next part, fuel properties and chemical composition are investigated. Chemical composition differs not only by the type of fuel, but also by the refinery where it was manufactured; in this work Diesel EN590 and Gasoline EN228 were used and only chemically pure liquids for fuel blending. The following sections are about practical investigations of relative permittivity dependencies. Temperature, frequency and pressure are the three main properties that might influence the relative permittivity of fuels. In addition the influence of the gaseous phase is examined in an experiment. The last part of the thesis deals with saturated vapour pressure for gasoline and gasoline-ethanol fuels.

# 1 Basic terms

#### 1.1 Dielectric

Dielectric is a designation for a material inside of which an electric field can exist and whose critical attribute is the ability to polarize itself in an electric field. This term has therefore a more general meaning. While every insulator is a dielectric, not every dielectric is an insulator. In practice, most dielectrics are good insulators too. Distinguishing among dielectric is shown in figure 1. [1]

Dielectrics in capacitors serve three purposes:

- Higher capacitances thanks to reduced distance allowed by using medium between them.
- Getting the same charge at a lower voltage by reducing electric field strength, which results in an increase in effective capacitance
- Increasing resistance against dielectric breakdown. [2]



Figure 1. Distinguishing of dielectrics [3]

## 1.2 Capacitance

The definition of capacitance is how much charge per volt the capacitor can hold. This means that the amount of charge depends on voltage sourced to the capacitor. Less technically speaking, it means that connecting the capacitor to a higher voltage source will result in an increased number of electrons in comparison to connecting it to lower voltage source. Capacitance is one of the most important parameters in this work, because permittivity is calculated from capacitance. [4]

Definition of Capacitance:

$$C = \frac{Q}{U} \tag{1}$$

where

C ..... capacitance in farads (F),

Q..... the charge on the capacitor in coulombs (C),

U..... voltage difference between the capacitor plates in volts (V). [4]

#### 1.3 Capacitance of cylindrical capacitor



Figure 2. Cylindical capacitor  $R_1$  – inner electrode radius,  $R_2$  – outer electrode radius, I – Length of capacitor; all values are in meters (m).  $\varepsilon$ - Permittivity of dielectric between two electrodes. [5]

In the case of an ideal cylindrical capacitor as seen in Figure 2, assume that the charge on inner electrodes is +Q and on outer electrodes -Q. Also, only for practical purposes, assume that the positive charge on the inner electrode is located on its axis [4]. Electrical intensity can be calculated from:

$$E_x = \frac{Q}{2\pi\varepsilon_0\varepsilon_r x}.$$
 (2)

The potential difference (voltage) between those two electrodes is:

$$U = \int_{-x}^{x} -Edx = \int_{-x}^{x} -\frac{Q}{2\pi\varepsilon_0\varepsilon_r x} dx = -\frac{Q}{2\pi\varepsilon_0\varepsilon_r} \int_{-x}^{x} \frac{dx}{x}.$$
 (3)

Integrating the equation:

$$U = -\frac{Q}{2\pi\varepsilon_0\varepsilon_r} (\log_e R_1 - \log_e R_2) = \frac{Q}{2\pi\varepsilon_0\varepsilon_r} \log_e \left(\frac{R_2}{R_1}\right). \tag{4}$$

Using (1) we can edit (4) into equation (5) for capacitance:

$$C = \frac{2\pi\varepsilon_0\varepsilon_r}{\log_e(\frac{R_2}{R_1})} \quad . \tag{5}$$

For capacitor length L therefore applies (6): [4]

$$C = \frac{2\pi\varepsilon_0\varepsilon_r L}{\log_e(\frac{R_2}{R_1})} \quad . \tag{6}$$

#### 1.4 **Conductance and conductivity**

#### 1.4.1 **Conductance**

Different currents flow through different conductors when attached to the same voltage source. Exactly how much current will flow through defines the parameter conductance. This depends on the specific properties of the conductor. Electrical conductance denoted G ( $S=\Omega^{-1}$ ) determines how easily a current can flow through a conductor.

#### 1.4.2 Ion conductivity and electrolysis

When talking about conductivity, it is important to mention the phenomenon of electrolysis. It is a chemical phenomenon caused by the passage of electric current in liquid in which chemical changes occur on the electrodes. An electrically conductive fluid contains a mixture of positive and negative ions formed by dissociation in the liquid. The passage of electric current leads to a movement of positive ions to negative electrode and the negative ions to the positive electrode. Positively charged ions move to the negative electrode during electrolysis. They receive electrons and are reduced. Negatively charged ions move to the positive electrode during electrolysis. They lose electrons and are oxidized.

#### 1.4.3 Electrophoretic conductivity

Electrophoretic conductivity is not significantly different from ionic electrical conductivity. Electrophoretic conductivity occurs in colloidal systems, which are characterized by the fact that they consist of two phases. The first phase appears in the form of fine particles. It is called the disperse phase and is dispersed in a second phase, called the dispersion medium. In liquid materials there exists suspension and emulsion. Due to the force effects of the electric charges, the two phases will not separate.

According to empirical rules, the colloidal particles are positively charged if their relative permittivity is higher than the relative permittivity of the dispersion medium and negatively charged if their permittivity is lower than the relative permittivity of the dispersion medium. However, there are also some exceptions. Colloidal particles generally absorb free ions and with it they retake their charge. As a result, each such particle has a certain potential, which we can designate  $\xi$ . It is called electrokinetic potential and its value is from 0.05 to 0.07 V.

Final equation for electrophoretic conductivity is:

$$\gamma_k = \frac{n_k r \xi^2 \varepsilon^2}{6\pi\eta},\tag{7}$$

where

 $\gamma_k$  ..... is electrophoretic conductivity (S),

 $\eta$ ..... is dynamic viscosity (N·s·m-2),

 $\epsilon$  ..... is permittivity of liquid insulator,

 $\xi$  ..... electrokinetic potential (V),

nk ..... is concentration of colloidal particles,

r .....is a radius.

#### 1.4.4 Temperature dependency of conductivity

The movement of free charge carriers is highly temperature dependent. It is also closely associated with dynamic liquid viscosity and its temperature dependency. The relation between conductivity, liquid viscosity and temperature is theoretically proven by the Walden equation:

$$\gamma \cdot \eta = \frac{n \cdot q^2}{l_2} \cdot \frac{l_1^2 \cdot f_{01}}{l_2^2 \cdot f_{02}} \cdot e^{-\frac{W_1 - W_2}{kT}}.$$
(8)

By index 1, parameters for ions are marked, index 2 is for molecular parameters. During the analysis, three possibilities can occur

 $W_1>W_2$  - Ions are bound to the molecules tighter than molecules between each other. Occurs even when with the raising temperature the concentration of free charge carriers is increasing- Dissociation occurs.

 $W_1 < W_2$  - Bound between molecules are stronger than bonds ion-molecule. Product  $\gamma \cdot \eta$  is lowering with raising temperature – drop of viscosity s faster than conductivity increasing.

 $W_1=W_2$  – Both bounds are similar. If  $f_{01}=f_{02}$  and  $l_1=l_2$ , rise of conductivity  $\gamma$  and drop of dynamic viscosity  $\eta$  have identical character. With these circumstances, conditions of Walden rules are met in the form:

$$\gamma \cdot \eta = \frac{n \cdot q^2}{l_2} = constant.$$
<sup>(9)</sup>

This chapter was written using [3], [6], [7], [8].

#### 1.5 Polarization

When a dielectric sample is placed in an external electric field E, it acquires a nonzero macroscopic dipole moment indicating that the dielectric is polarized under the influence of the field. There are two ways to describe polarization: macroscopic and microscopic. In this thesis only the macroscopic point of view will be discussed.

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In this case, interest is in the result of polarization, which is the creation of a bound electrical charge on the surface of a polarized dielectric. That means that the whole dielectric gains a dipole moment. Moreover, based on this principle, it is possible define a vector of polarization  $\vec{P}[C \cdot m^{-2}]$ , which characterizes a polarized dielectric. [3], [6], [7], [8]

$$P = \frac{\langle M \rangle}{V} \tag{10}$$

 $\langle M \rangle$  is the macroscopic dipole moment of the whole sample volume V, which is comprised of permanent microdipoles (i.e. coupled pairs of opposite dielectric relaxation phenomena in complex materials) as well as dipoles that are not coupled pairs of microcharges within the electroneutral dielectric sample. The brackets  $\langle \rangle$  denote the ensemble average. In the linear approximation, the macroscopic polarization of the dielectric sample is proportional to the strength of the applied external electric field E:

$$P_i = \varepsilon_0 \chi_{ik} E_k \,. \tag{11}$$

Where  $\chi_{ik}$  is the tensor of the dielectric susceptibility of the material and  $\varepsilon_0 = 8,854 \cdot 10^{-12}$  is the dielectric permittivity of the vacuum. If the dielectric is isotropic and uniform, w is a scalar and Eq. (5) will be reduced to the more simple form:

$$P = \varepsilon_0 \chi_{ik} E . \tag{12}$$

According to the macroscopic Maxwell approach, matter is treated as a continuum, and the field in the matter in this case is the direct result of the electric displacement (electric induction) vector D, which is the electric field corrected for polarization:

$$D = \varepsilon_0 E + P \,. \tag{13}$$

For a uniform isotropic dielectric medium, the vectors D, E, P have the same direction, and the susceptibility is coordinate-independent. Therefore:

$$D = \varepsilon_0 (1 + \chi) E = \varepsilon_0 \varepsilon_r E. \qquad (14)$$

Where  $\varepsilon_r = 1 + \chi$  is the relative permittivity. Traditionally, it is also called the dielectric constant, because in the linear regime it is independent of the field strength. However, it can be a function of many other variables. For example, for time variable fields it is dependent on the frequency of the applied electric field, sample temperature, sample density (or pressure applied to the sample), sample chemical composition, and so on. [9]

#### 1.5.1 Mechanisms of polarization

#### Electronic (Atomic) polarization

This is a polarization that occurs in atoms that are affected by an external electrical field. The electrical field leads to the disposition of electron. (see (a) in Figure 2). By the disposition of electrons, an internal atomic electrical field is created, in the opposite direction from that of the external field.





#### Ionic polarization

When an electric field is applied to an ionic material, cations and anions get displaced in opposite directions, which leads to a net dipole moment (see (b) in Figure 2).

Dipole (Orientation) polarization

All molecules have a dipole moment. It is the position of their charge. The basic molecules are not

*Figure 3. Polarization* position of their charge. The basic molecules are not oriented without being affected by an external electric field. There are also exists permanent dipoles that are polarized even without any electric field affecting them (see (c) in Figure 3).

Interface or Space change polarization

Space charge polarization occurs due to the diffusion of ions, along the field direction, thereby giving rise to redistribution of charges in dielectrics. [10], [11]

All polarization mechanisms respond to an electrical field by shifting masses around. This means that masses must be accelerated and de-accelerated, and this will always take some time. So we must expect that the (mechanical) response to a field will depend on the frequency f of the electrical field; on how often per second it changes its sign. If the frequency is very large, no mechanical system will be able to follow. We thus expect that at very large frequencies all polarization mechanisms will "die out", i.e. there is no response to an extremely high frequency field. This means that the dielectric constant  $\varepsilon_r$  will approach 1 for  $f \Rightarrow \infty$ . [12]



Figure 4. Permittivity characteristics of a polar dielectric versus frequency [13]

#### 1.6 Permittivity

Permittivity (also called the dielectric constant) is the measure of a material's influence on an electric field. The net capacitance will increase or decrease depending on the type of dielectric material. Permittivity relates to a material's ability to transmit an electric field. In capacitors, an increased permittivity allows the same charge to be stored with a smaller electric field, leading to an increased capacitance.

The capacitance is proportional to the amount of the dielectric constant. As the dielectric constant between the capacitive plates of a capacitor rises, the capacitance will also increase accordingly. The capacitance can be stated in terms of the dielectric constant, as in:

$$C = \varepsilon_r \frac{\varepsilon_0 S}{r},\tag{15}$$

$$C = \varepsilon_r \cdot C_0 , \qquad (16)$$

#### where

С	capacitance in farads (F),
8	relative static permittivity of the material between plates,
	permittivity of free space, which is equal to 8,854 10-12 (F/m),
S	area of each plate, in square meters,
r	separation distance (in meters) of the two plates [14].

Complex permittivity

Using complex numbers for impedance is very useful. It is also useful to use complex numbers while the describing parameters of loss dielectrics of the material variables. Connecting a dielectric to an electric field with sinusoidal waveform

$$E(t) = E_0 \cdot e^{j\omega t} , \qquad (17)$$

where  $E_0$  is amplitude,  $\omega$  is angular frequency and j is an imaginary unit for which it stays  $j^2 = -1$ . From Maxwell's equations it is possible to express current density by the equation:

$$j_d = \frac{dD}{dt},\tag{18}$$

where

 $j_d$  ..... current density (A/m).

While dielectric induction after introducing complex permittivity:

$$D = \varepsilon_0 \cdot \varepsilon_r^* \cdot E \,. \tag{19}$$

And after Eq. (17) is used in (19) and then in (18), an equation for ideal and loss current density is gained.

$$j_d = j_i + j_z = j\omega\varepsilon_0 \cdot (\varepsilon' - i\varepsilon'')E = j\varepsilon_0\varepsilon'\omega E - \varepsilon_0\varepsilon''\omega E , \qquad (20)$$

where  $\varepsilon$ ' is the real part and  $\varepsilon$ '' is the imaginary part of permittivity. The imaginary part of the equation on the right side expresses the ideal (polarization) part and the real part expresses the loss part of current density inside the dielectric. [1]

#### 1.7 Representation of a circuit

For better understanding of what is happening when a source is connected to a capacitor, it is useful to imagine a scheme with AC connected in series to a capacitor with an air dielectric. The capacity of the capacitor is

$$C_0 = \frac{Q}{U} , \qquad (21)$$

where

- $C_0$  ..... capacity,
- Q ..... charge,
- U ..... voltage.

The capacitor is being charged by a current

$$I_{C_0} = \frac{dQ}{dt} = C_0 \frac{d}{dt} \left( Re(U_0 e^{j\omega t}) \right).$$
<sup>(22)</sup>

The imaginary part j means that current outruns applied voltage by 90° and this can be written as  $e^{j\frac{\pi}{2}}$ . Knowing that we can use

$$I_{C_0} = I_0 Re\left(e^{j\left(\omega t + \frac{\pi}{2}\right)}\right),\tag{23}$$

where  $I_0 = C_0 U_0 \omega$ .

When taking into consideration other dielectrics than air, capacitance will be increased by  $\varepsilon_r$ . The charging current for the capacitor is defined by

$$I_C = j\omega C_0 \varepsilon_r U . (24)$$

That is for an ideal insulator. Because there is no such thing as an ideal insulator, it is necessary to rely on conductance through a dielectric. Therefore, a real capacitor will have two current components,  $I_C$  which is classic capacitor current and  $I_L$ , which is loss current or conduction current.

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Figure 5. Equivalent circuit representation of the capacitor with dielectric between plates a) Parallel b) Series

Current I<sub>L</sub> is can be defined by using Ohm's law:

$$I_L = \frac{U}{R} = UG , \qquad (25)$$

where

G ..... conductivity of dielectric,

R ..... equivalent resistance,

U ..... voltage.

The total current in a real capacitor is the sum of current  $I_L$  and  $I_C$ . And using C instead of C<sub>0</sub>, the equation modifies to:

$$I = j\omega C_0 \varepsilon_r U + UG . aga{26}$$

The current now does not have 90°; it has 90- $\delta$ ° because it has both a real and an imaginary part. [15]

#### 1.8 Dielectric loss and dissipation factor tan δ

It is important to consider the losses in AC capacitors. All dielectrics (except vacuum) have two types of losses. One is a conduction loss, representing the flow of an actual charge through the dielectric. The other is a dielectric loss due to movement or rotation of the atoms or molecules in an alternating electric field.

One way of describing dielectric losses is to consider the permittivity as a complex number that was used before, more comprehensibly written as:

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$$\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon e^{-j\delta} , \qquad (27)$$

where

- ε'..... permittivity of ac capacitance,
- ε"..... dielectric loss factor,
- $\delta$  ..... dielectric loss angle.

Loss factor tan  $\delta$  can be expressed as

$$tg\delta = \frac{\varepsilon''}{\varepsilon'}.$$
(28)

In this thesis a real dielectric is being worked with, so it is important to take into account the existence of free charge carriers (conductivity), which means working with a current density in an electrostatic field  $(j_s)$  is a necessity required. [1], [3]

#### 1.9 Dielectric absorption

Dielectric absorption involves complicated nonstationary processes occurring in a technical dielectric that has been inserted between a capacitor's electrodes after its connection to the source of DC voltage. [3]

"A capacitor which has been charged for a long time and then been completely discharged, has a small voltage on its terminal wires again, within seconds or minutes." [16] That means the capacitor does not charge immediately, but with some delay. It will also discharge with a similar delay. The reason for this is dielectric relaxation - a delayed response of a dielectric t the effects of an electric field caused by slow polarization. [16]

## 2 Fuel properties and chemical composition

#### 2.1 Gasoline, diesel fuel and their production

Gasoline and diesel are both petroleum products. Petroleum is a mixture found in the earth, composed of crude oil and natural gas. While the products that are derived from petroleum power the modern world, raw petroleum is of little use until it is refined. It is the refining process that converts crude oil into gasoline, fuel oil, and diesel fuel. [17]

Crude oil contains hundreds of different types of hydrocarbons all mixed together and, depending on the source of the crude oil, different impurities. In order to produce gasoline, diesel or any other oil-based products, the hydrocarbons have to be separated, by refining of one type or another.

Gasoline and diesel are both products of a fractional distillation process which is used on petroleum. At different temperatures, different products are created. Gasoline is produced first in this process because it is formed at temperatures between 35 and 200 degrees Celsius. Diesel needs at least 250 °C, up to 350 °C. The next step is blending with other elements to fulfil the requirements.

"Diesel is composed of about 75 % saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25 % aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is C12H23, ranging from approx. C10H20 to C15H28. Gasoline consists of hydrocarbons with between 5 and 12 carbon atoms per molecule but then it is blended for various uses. Overall a typical gasoline sample is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), aromatics and olefins (alkenes). The ratios vary based on a variety of factors." [18]

	Diesel	Gasoline
Uses	In diesel engines, heating systems	In gasoline engines
Made from	Petroleum/ Crude oil	Petroleum/ Crude Oil
Made by	Fractional distillation	Fractional distillation
Torque (for 10L engine)	1000 Nm @ 2000 rpm	300Nm @ 4000 rpm
Power (for 10L engine)	490Hp @ 3500 rpm	600Hp @ 5500 rpm
Power = torque*RPM	More torque at low speeds	Runs at higher RPM
Auto-ignition temperature	210 °C	246 °C
CO2 emission	Diesel fuel produces approximately 13 % more CO2 gas per gallon of fuel burned, compared to gasoline engines.	Lower than diesel.
Viscosity	increase at lower temperatures	No change
US Consumption (2006)	50 Billion gallons	148 Billion gallons
Types of ignition	Direct ( by compression )	Spark

Table 1. Difference between diesel and gasoline [18]

#### 2.2 Biofuels

Fuel	Heat of combustion (MJ/l)
Gasoline	34.2
Diesel	38.6
Ethanol	24
Methanol	17.9
Biofuel	33.5

Table 2. Heat of combustion offuels and biofuels [19]

There are several different biofuels in the fuel industry. The main ones are ethanol and methanol for gasoline fuels and FAME (Fatty Acid Methyl Esters) and HVO (Hydrotreated Vegetable Oils) for mixing with diesel. HVO is a new product only introduced as this work was being finished. It will not be discussed or measured here, due to its unavailability.

The energy per mass of ethanol is only about half that of gasoline. Car engines have to be manufactured or modified to be able to run on ethanol. Moreover it produces more ozone than gasoline and comparing the smog contribution, they are very similar. Those are negatives, but ethanol is a high octane fuel, its burning creates less carbon monoxide and thus it is cleaner than gasoline. A major advantage is that ethanol is easy to produce from renewable sources. The heat of combustion of ethanol is 24 MJ/l, in comparison to that of gasoline, at 34.2 MJ/l this is low. Methanol has similar parameters to those of ethanol, and has a lower heat of combustion, 17.9 MJ/l.

Biodiesel reduces emissions and increases fuel lubricity. Their heat of combustion is high, 34.2 MJ/l. There are already problems with diesel engines in winter; biodiesel will increase these problems if it is not modified by additives to withstand lower temperatures. [19], [20]

There are many sources for producing FAMEs: rapeseed, sunflower seed, soybeans, palm oils and animal fats are the most common. The final product is biodegradable and non-toxic. FAME's physical properties are similar to those of conventional diesel. The disadvantages of this fuel type are high production cost and its possible corrosive effects in fuel system. [21]

	FAME	Diesel
Density at 20 °C (kg/l)	0,88	0,83
Lower heating value (MJ/kg)	37,1	43,1
Viscosity at 20 °C (mm2 / s)	7,5	5
Cetane number	56	50
Fuel equivalence	0,91	1
GHG (gCO2eq/MJ)	Rape seed: 46	
	Palm oil: 54	

Table 3. Comparison of Fuel Properties [21]

Greenhouse gases trap heat in the atmosphere, which makes the Earth warmer. "The greenhouse gas (GHG) intensity for fuels and energy is expressed in terms of grams of carbon dioxide equivalent per Mega Joule of fuel (gCO2eq/MJ). The GHGs taken into account are carbon dioxide (CO2), nitrous oxide (N2O) and methane (CH4)." [22]

#### 2.3 Chemical composition

"Diesel is composed of about 75 % saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25 % aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is C12H23, ranging from approx. C10H20 to C15H28. Gasoline consists of hydrocarbons with between 5 and 12 carbon atoms per molecule but then it is blended for various uses. Overall a typical gasoline sample is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), aromatics and olefins (alkenes). The ratios vary based on a variety of factors." [18]

Examples of problems caused by unwanted components

- Water: Low dissolving power in corrosion protection for conductive materials
- Elemental sulphur: Reaction with Cu leads to creating insulating layers
- Acids (from alcohol): Corrosion
- Dust particles, particles: Abrasive wear and tear
- Sodium chlorides (NaCl): Corrosion [23]

### 2.4 Chemical composition of fuels according to the standards

Table 4. Gasoline EN 228 [24]

	Limits (%)
Content of oxygen-	
containing organic	Max
compounds	
Methanol	3
Ethanol	10
Isopropylalkohol	12
Isobutylalkohol	15
Tert-Butylalkohol	15
Ether (5 or more C-Atom)	22
Other oxygenates	15

Table 5. Diesel EN 590 [25]		Limits	
	Unit	Min	Max
Polycyclic aromatic	%		8
hydrocarbons	(m/m)	-	0
Sulphur	mg/kg	-	10
Manganese	mg/l	-	2
Carbon residue(on 10 % distillation residue)	%		0,3
Ash content	%	-	0,01
Water content	mg/kg	-	200
Fatty acid methyl ester (FAME) content	% (V/V)	-	7

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Table 6. FAME (RME / PME / SME) EN 14214 [26]

	Unit	Min	Max
Fatty acid methyl ester content	%	6,5	-
Content of linolenic acid methyl ester	%	-	2
Content of polyunsaturated fatty acid methyl esters with the double bonds $\geq 4$	%	-	1
Methanol- Content	%	_	0,2
Monoglycerid- Content	%	-	0,7
Diglyceride- Content	%	-	0,2
Triglyceride- Content	%	-	0,2
Acid value	mg KOH/g	-	0,5
Water content	mg/kg	-	500
Total pollution	mg/kg	-	24
Ash content (sulphate ash)	%	-	0,02
Sulphur content	mg/kg	-	0
Content of alkali metals (Na + K)	mg/kg	-	5
Content of alkaline earth metals (Ca+Mg)	mg/kg	_	5
Phosphorus content	mg/kg	-	4

#### 2.5 Additives

The composition of gasoline can vary widely depending on the blending specifications required for different regions based on climate and environmental regulations. The trick, as one source puts it, is to formulate a gasoline that "does not cause engines to knock apart, does not cause vapour lock in summer but is easy to start in winter, does not form gums and deposits, burns cleanly without forming soot or residues, and does not dissolve or poison the car catalyst or owner." [27]

- Anti-knock additives Increase of the octane number (anti-knock index)
- Antioxidants Improvement of shelf life
- Detergents Pollution prevention (suction, fuel induction)
- Corrosion protection Fuel system protection
- Anti-icer Reduction of icing during fuel induction
- Lubricative additive Wear protection
- Dyes Used to identify fuel, because of taxes, octane number, usage, etc. Different countries have different uses for dyes [27]

#### 2.6 Parameters of materials contained in fuels

Table 7. Permittivity of materials contained in fuels at 20°C [28], [29]

	Relative permittivity $\varepsilon_r$
Vacuum	1
Metals	infinite
Gassess	1.00XX (at one atmosphere)
Hexane	1.8865 (20 °C)
Cyclohexane	2.0243 (20 °C)
Benzene	2.285 (20 °C)
Gasoline	2
Ethanol	23,72
Methanol	33,1
Water	87,9 (0 °C) to 55,5 (100 °C)
Diesel	2,14
RME	3,1

#### 2.7 Process of fuel dilution

For better understanding of ethanol fuels, it is important to examine concentrations that are commonly produced. To get these concentrations, 100 % ethanol, with less than 100 ppm of water and GE98, with about 550 ppm of water, were used to blend with. Using volume blending, however, is very inaccurate. This is caused by the fact that blending two materials with the same volume, but different densities results in a final liquid with a density that cannot be simply calculated and also the final volume ratio may not be the same. It can be better understood using an example. Blending 700 millilitres of gasoline with 300 millilitres of ethanol does not lead to GE30. Though the concentrations are given in volume units, a more accurate way to blend liquids to get the final concentration is by calculation of the weight of the fuel from the concentration required and the density. This way, the weight ratio is acquired. All blending required was prepared by using Kern EW 2200-2NM scales.

# 3 Influence of frequency

#### 3.1 Measuring method

This measurement was done at room temperature, using a Hioki IM3536 LCR meter, thermometer and electrode system LCM-8716. The bottom of the electrode system was sealed, and the electrode was fully filled by fuel, the top open for the thermometer probe. The frequency range examined was from 100Hz to 1MHz with 41 measuring points. The temperature was recorded for every fuel. While working with ethanol, it is important to minimize the time it is in contact with air, because it absorbs water from air humidity.

#### 3.2 Measured fuels

Diesel fuels	Gasoline fuels
Diesel EN590	Gasoline EN228
ArcticD	Ethanol
R100	GE10
S100	GE30
DR30	GE55
DS20	GE85
DS30	GE98
	Methanol
	GM5
	GM15
	GM45

Table 8. List of measured fuels for frequency dependence investigation

- ArcticD- Arctic diesel
- DR- Diesel- rapeseed oil blend
- DS- Diesel- soybean oil blend
- GE- Gasoline- ethanol blend
- GM- Gasoline- methanol blend

#### 3.3 Measuring corrections

For these measurements, LCR meter Hioki IM3536 was used. Several options for reducing the measuring error were tested. A few experiments were done to investigate the influence of open, short and load correction. It was found that open correction can be avoided by using shielded connectors. It is important to measure with short and load corrections.

#### 3.4 Results

In this measurement all fuels were measured by the same method and for each one of them, the temperature was recorded. Permittivity of nonpolar liquids is mainly dependent on the viscosity of the material. Therefore, in the range of these frequency measurements no changes can be seen. For polar liquids, the permittivity measurement is much more complicated due to polarization which affects capacitance. Interface polarization can be seen for all polar fuels, its effect is decreases with increasing frequency, fully negating its effect at tens of thousands Hz. In the figures below, there are examples of a several measurements. Full measurement data and graphs can be found in the technical report Frequency Dependence of Permittivity [37].



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## 4 Influence of temperature

#### 4.1 Measuring method

For this measurement the test cell is filled with the fuel and connected to a barometer using Teflon tubes attached to the top entry of the test cell. The bottom input is used for attaching a thermometer probe connected to an Alhborn thermometer.

The first examined liquid, sample A, was chosen because the measured temperature range was the widest. Therefore, it was the best to test the equipment used.

It is important to take into account the volume expansion of liquids caused by changing temperature. Not leaving enough space for expansion may lead to an enormous increase in pressure. Fully filling the test cell and leaving just a bit of air in tubes leads to increasing pressure. At 60 °C the pressure was about 4 bars, increasing up to 15 bars when heated to 80 °C.

On the other hand, having more fuel than needed will help avoid creating empty space in the test cell when decreasing temperature lowers the volume. To reduce the surface where fuel is in contact with air, a long narrow tube that led to the thermometer and barometer was used as a reservoir.

#### 4.2 Cables

Coaxial cables (RG316/U) were used for connecting the cell and Hioki LCR meter by BNC connectors. Results were corrected to cable length 1.8 m. Capacitance temperature dependency is approximately 0.05 pF/ °C and it was not considered.

A decision to test cable connectors at temperature 130 °C for 1 hour was made, to be sure it could withstand the measuring temperature in the thermal chamber. This was done mainly because of the unknown behaviour of the dielectric part of the connectors, which was made from a material called delrin. After heating the connectors for one hour, we tested mechanical and electrical parameters were tested. Observed parameters did not change.

#### 4.3 **Temperature controlling**

Measuring at different temperatures was done using the CTS (Climatic Temperature System) TS-50/530. This machine uses nitrogen as an atmosphere as a safety precaution, because spontaneous ignition can occur at higher temperatures for all fuels. Even though this system is sealed, any small leak might cause problems without the atmosphere. The CTS is able to control temperature and keep it constant in a range from -60 °C to +180 °C.

#### 4.4 Results

All results with data can be found in [38].

#### 4.4.1 Sample A

The relative permittivity of this fuel decreases with increasing temperature. Most of this liquids substances are non-polar. Therefore, influence of interface polarization cannot be seen.



Figure 12. Sample A relative permittivity dependence on temperature

#### 4.4.2 Sample B

Sample B acts very similar to sample A. The only difference is in the temperature range, which was decreased because of its lower boiling point. To increase the boiling point and negate the negative effects of the gaseous phase, the pressure of the fuel was increased.



Figure 13. Sample B relative permittivity dependence on temperature

#### 4.4.3 Sample G

The figure below shows the decrease of permittivity at higher temperatures. At low temperatures there is also a trend, when permittivity is decreases with increasing frequencies.



Figure 14. Sample G relative permittivity dependence on temperature

#### 4.4.4 Sample H

While measuring sample H interesting behaviour was noticed. At very low frequencies, the calculated capacitance increases significantly. This is caused by interface polarization. The best range for these measurements, where permittivity measurement is most precise, is from 100 kHz up to 1 MHz max.



Figure 15. Sample H permittivity dependence on temperature

#### 4.4.5 Gasoline-ethanol blends

Blends of gasoline with ethanol with concentrations of 10, 30, 55, 85 and 98 were measured. These blends were chosen to cover the range of concentrations. Using the results in the technical report Temperature Dependence of Permittivity [38], it is possible to predict the permittivity of all other concentrations at required temperatures and frequencies.

## **5** Influence of pressure

#### 5.1 Method

From a theory it is known that very high pressure will influence the permittivity measurement due to the increased number of molecules in the same volume. The focus of these measurements was to explore the influence at lower pressures. The measurement was done for sample A at atmospheric pressure and at 15 bar and temperature 80 °C. The pressure was modified by increasing temperature for two volumes of air where the fuel can expand. The etalon of the barometer used was 0.025 % of R + 0.01 % FS.

#### 5.2 Results

The difference between the two measurements at different pressures was approximately 0.005 (-) in relative permittivity, which is approximately a 0.25 % difference. Using data for density increase with pressure, a 0.115 % difference was calculated. As the permittivity reduces with increasing temperature, taking into account that the temperature is a little higher for results for higher pressure measurement, it is possible to assume that the increase in permittivity caused by a pressure increase is even a bit higher. A full list of measured data and figures can be found in [39].

### 6 Influence of power level

Using different power levels may lead to increasing parasitic inductions. Also too low voltage may lead to decrease in measurement accuracy. These experiments consisted of three parts.

In the first part measurements for an empty cell were taken. The hardware allowed the examination of a range from 0.01 V to 5 V. For higher frequencies, the measurement results are very accurate at all used power levels. But for lower frequencies, as can be seen in the graphs below, there is a high influence of power level on accuracy. Increasing the voltage up to 1 V leads to significant accuracy improvement for low frequencies. The difference between 1 V and 2 V is negligible and there is almost no difference between 2 V and 5 V.

The second part is focused on examining the power level influence on capacitance for an electrode system filled with methanol. It was done for 0.1 V, 1 V and 5 V power levels.

In last part Rapeseed oil is measured for power level 0.01 V, 0.1 V, 1 V, 2 V and 5 V.

Full report with data and graphs can be found in [40]

Measuring at low power level leads to an increase of interference and measuring error. Depending on the circuit, it is necessary to give enough power output to negate these effects. From the results, it was decided that 1V is accurate for the circuit used in this paper. Also, higher voltage would disable the option to measure at higher frequencies above 1 MHz because of LCR meter limits. From the methanol measurement results it was found that the lower voltage increases in capacitance is caused by interface polarization. Measurement for R100 showed that using low voltage for less conductive fuels may cause huge errors. Using the highest available voltage is recommended for most accurate results.



Figure 16. Measurement for empty cell with power level from 0.01V to 0.5V

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Figure 17. Measurement for empty cell with power level from 0.1V to 5V



Figure 18. Measurement for empty cell with power level from 1V to 5V

## 7 Influence of nonhomogeneous fuel

For fuel blends there is a possibility that their blending will not be ideal. Due to different densities of ethanol and gasoline, there may occur that parts of the fuel separate. Density of ethanol is 785.1 (kg/m<sup>3</sup>) and density of gasoline is from 719 to 778.8 (kg/m<sup>3</sup>) [29]. These densities are quite similar, but may cause that the ethanol, with its higher density, may settle on the bottom.

An experiment was performed to test if this is possible. One litre of fresh blended GE65 fuel was left in a graduated cylinder for three days at constant temperature. The graduated cylinder was covered to prevent evaporation. After three days the two samples were withdrawn, one from the bottom of graduated cylinder and one from the top. Measuring both samples showed no difference in relative permittivity. Nonhomogeneous medium may also occur by contamination of fuel by dust particles, however, these particles are small and will have negligible effect on relative permittivity of the volume.

## 8 Influence of a gaseous phase

Gasoline consists of many substances, some of which have a very low boiling point. Boiling these substances creates a gaseous phase that may influence the capacitance measurements. To analyse this, an experiment was done using water, because of its high permittivity, a plate capacitor, and a system for nitrogen injection, which substitutes for the gaseous phase.

Two coplanar capacitors (Figure 19 and 20) were fixed to each other to create a plate capacitor. The measuring device was a Hioki LCR meter, used to measure capacitance. The final results are shown in the figure below. The flow rate of nitrogen was controlled in the range of 0-30 litres per minute with a step of 5, while waiting few seconds after each increase of flow. After reaching 30 litres per minute, the flow was reduced to zero. At the end of the measurement there were a few bubbles attached to the electrodes, decreasing the capacity measured. There was no option to use shielding for the electrodes, nor the cables, so the influence of jamming has to be considered.

These results confirmed assumptions that the gaseous phase will reduce the number of molecules of higher permittivity material between electrodes. Therefore, the capacitance is decreased with an increasing flow rate.



Figure 19. Support part of capacitor

Figure 20. Electrodes



Figure 21. Percentage change in capacity while changing flow rate of nitrogen

"Vapour pressure is used as a classification criterion for the safe handling and carriage of petroleum products, feedstock and components; it has a relationship to the potential for hydrocarbon emissions, under uncontrolled conditions, and thus is the subject of environmental scrutiny." [30]

DVPE

• Dry vapour pressure equivalent, also called RVP (Reid vapour pressure), is measured for 37,8 °C (100 °F) with the presence of air

TVP

• True (Absolute) vapour pressure is measured for any temperature without the presence of air or other gases.

Vapour pressure is affected by temperature and the chemical composition of a fuel. Blending ethanol with gasoline increases the pressure significantly, with its peak up to about 10 % ethanol. Further blending decreases the RVP.



Reid Vapour Pressure  $\blacksquare$  Furey and Jackson, 1977;  $\blacklozenge$ US Department of energy, 1991; X Ethanol RVP;  $\varDelta$  gasoline RVP; \*gasoline/ethanol blend of ideal solution, as a function of the mole fraction of ethanol ( $\chi_{eth}$ ) blended in gasoline. [31]

Figure 23. Gasoline-ethanol blends: vapour pressure increase vs ethanol content [32]

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Exact values are difficult to obtain due to different compositions of gasoline. Gasoline fuel is produced differently in summer and winter. This is caused by requirements for different temperatures. In winter, the temperature causes gasoline to evaporate less and that causes difficulties with starting a gasoline car, and it also runs rough. In summer, the temperature is high and the gasoline evaporates too much, which is a reason for using gasoline with a lower RVP. It decreases emissions and prevents drivability problems such as vapour lock. For future investigations using the procedures from DIN EN 13016-1 standard is recommended.

Paramatar	Unit	Limits		
I diameter	Unit	Minimum	Maximum	
Research octane number		95	_	
Motor octane number		85	_	
Vapour pressure, summer period	kPa	_	60	
Distillation:				
— percentage evapourated at 100 °C	% v/v	46		
— percentage evapourated at 150 °C	% v/v	75		
Hydrocarbon analysis:				
— olefins	% v/v		18	
— aromatics	% v/v		35	
— benzene	% v/v		1	
Oxygen content	% m/m		3,7	
Oxygenates				
— Methanol	% v/v		3	
Ethanol (stabilising agents may be necessary)	% v/v		10	
— Iso-propyl alcohol	% v/v	—	12	
— Tert-butyl alcohol	% v/v		15	
— Iso-butyl alcohol	% v/v	_	15	
Ethers containing five or more	0/ 1/1		$\gamma\gamma$	
carbon atoms per molecule	70 V/V			
— Other oxygenates	% v/v	—	15	
Sulphur content	mg/kg		10	
Lead content	g/l		0,005	

Table 9. Environmental specifications for market fuels to be used for vehiclesequipped with positive-ignition engines [34]

A standard modifies the vapour pressure specification for regular grade gasoline for countries with low ambient summer temperatures to 70 kPa, for gasoline containing ethanol the vapour pressure limit is 60 kPa, increased by a value corresponding to the ethanol content from the table below. [34]





Figure 24. True vapour pressure of gasoline for different temperature [33]

Bioethanol	Vapour pressure waiver
content (% v/v)	permitted (kPa)
0	0
1	3,65
2	5,95
3	7,2
4	7,8
5	8
6	8
7	7,94
8	7,88
9	7,82
10	7,76

Table 10. Vapour pressure waiver permitted for gasoline containing bioethanol [34]

Vapour pressure for different temperatures can be computed using the Clausius-Clapeyron equation (29). For this calculation, data used are pressure  $p_1$  (kPa) at temperature  $T_1$  (K), constant R=8.3145 (J·K<sup>-1</sup>·mol<sup>-1</sup>), and also enthalpy of vaporization  $\Delta H_{VAP}$  (J·mol<sup>-1</sup>) for the substance and temperature examined.

$$\ln\frac{p_1}{p_2} = \frac{\Delta H_{VAP}}{R} \cdot (\frac{1}{T_2} - \frac{1}{T_1})$$
(29)

Using data collected by the Dortmund Data Bank (DDB) for ethanol  $\Delta H_{VAP}$ , it is possible to calculate its vapour pressure. However, for gasoline vapour pressure it is much more complicated due to its complexity and variety of its composition.

There is a very good study on this topic called "Vapor Pressures of Alcohol-Gasoline Blends" [35] by V. F. Andersen, J. E. Anderson, T. J. Wallington, S. A. Mueller, and O. J. Nielsen. The gasoline they used for this work is also used for the U.S. Federal Test Procedure and its composition is accurately known. Also the alcohols used have a very low and controlled amount of water contamination. Using this gasoline, they did several experiments on Reid vapour pressure.

# **10 Measuring devices**

- Thermometer ALMEMO 2590 Connected to a measuring probe that is interposed in the electrode system. Temperature accuracy of this device is ± 0.0276 °C.
- Thermometer probe GREISINGER Pt100.
- Barometer Used for investigating of pressure influence on permittivity. But it was always attached to the fuel system to check if everything was set and connected right during temperature measurements. In case of leakage the pressure did not increase.
- Climatic chamber CTS (Climatic temperature system) TS-50/530 Used for heating the cell. Its temperature range is from -60 to +180 °C.
- LCR Hioki IM 3536 Device used for impedance and phase measurements, working in ranges from 4 Hz to 8 MHz.
- LCM-8716-CF Electrode system, manufactured by ALFF engineering, it conforms to the IEC 61620 and IEC 60247 standards.
- Kern EW 2200-2NM Weight machine used for fuel dilution.

# 11 Results accuracy and measurement uncertainty

#### 11.1 Basic accuracy by manual

The Hioki has multiple rates of speed of measurement. The difference between them is the number of waves per set of data given. In this work, the slowest and most accurate, slow2 option was set.

Frequenc	y range (Hz)	Number	Frequenc	y range (Hz)	Number
from	to	of waves	from	to	of waves
4,00	10,00	4,00	100010	140000	2400
10,01	39.99	10,00	140010	200000	2400
40,00	99.99	40,00	200010	300000	960
100,00	300,00	50,00	300010	400000	1600
300.01	500	200	400010	500000	1600
500.01	1000	300	500010	700000	2400
1000.1	2000	600	700010	1000000	2400
2000.1	3000	1200	1000100	1400000	960
3000.1	5000	2000	1400100	2000000	960
5000.1	10000	3000	2000100	3000000	1440
10000.1	20000	1200	3000100	4000000	2400
20000.1	30000	480	4000100	5000000	2400
30000.1	50000	800	5000100	600000	4000
50000.1	100000	1200	6000100	8000000	4000

Table 11. Number of waves for each measured data at different frequencies [36]

Basic accuracy given by the manufacturer in its data sheet is:

Z: ±0.05 % rdg.

 $\theta$ :  $\pm 0.03^{\circ}$  (Representative value).

Basic accuracy for measurements of temperature and frequency dependencies of permittivity are calculated using the Hioki IM3536 manual.

Basic accuracy is calculated based on coefficients A and B from the table below, using equations (29) for range 1k $\Omega$  and higher and (30) for range 100  $\Omega$  and lower.

$$Basic\ accuracy = \pm (A + B \cdot \left| \frac{10 \cdot Zx}{Range} - 1 \right|)$$
(30)

$$Basic\ accuracy = \pm (A + B \cdot \left| \frac{Range}{Zx} - 1 \right|) \tag{31}$$

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			Fe	or AC me	asurer	nent (r	neasurer	nent fre	equency	(Hz))	)	
Range	4	99,99	10 <sup>2</sup>	999,99	10 <sup>3</sup>	104	10001	105	100001	106	1000001	8·10 <sup>6</sup>
	Α	В	Α	В	Α	В	Α	В	Α	В	Α	В
100 (MO)	6	5	3	2	3	2	-	-	-	-	-	-
100 (10152)	5	3	2	2	2	2	-	-	-	-	-	-
10 (MO)	0,8	1	0,5	0,3	0,5	0,3	2	1	-	-	-	-
10 (14122)	0,8	0,5	0,1	0,2	0,4	0,2	2	1	-	-	-	-
1(MO)	0,4	0,08	0,3	0,05	0,3	0,05	0,5	0,1	3	0,5	-	-
1 (1V122)	0,3	0,08	0,2	0,02	0,2	0,02	0,6	0,1	3	0,5	-	-
100 (b0)	0,3	0,03	0,2	0,03	0,2	0,03	0,25	0,04	1	0,3	2	0,5
100 (KSZ)	0,2	0,02	0,1	0,02	0,1	0,02	0,2	0,02	1	0,3	2	0,3
10(kO)	0,3	0,03	0,2	0,02	0,05	0,02	0,3	0,02	0,5	0,05	2	0,5
10 (KSZ)	0,2	0,02	0,1	0,02	0,03	0,02	0,2	0,02	0,5	0,05	1,5	0,3
1(k0)	0,3	0,02	0,2	0,02	0,2	0,02	0,2	0,02	0,4	0,02	1,5	0,2
1 (KS2)	0,2	0,01	0,1	0,02	0,1	0,02	0,15	0,02	0,4	0,02	1,5	0,2
100 (0)	0,3	0,02	0,2	0,02	0,2	0,02	0,2	0,02	0,5	0,03	1,5	0,2
100 (22)	0,2	0,01	0,15	0,01	0,1	0,01	0,15	0,02	0,5	0,03	1,5	0,2
10(0)	0,5	0,1	0,4	0,05	0,4	0,05	0,4	0,05	0,8	0,1	2	1,5
10 (22)	0,3	0,1	0,3	0,03	0,3	0,03	0,3	0,03	0,5	0,05	2	1
1(0)	1,5	1	1	0,3	1	0,3	1	0,3	1,5	1	3	3
1 (52)	0,8	0,5	0,5	0,2	0,5	0,2	0,5	0,2	0,7	0,5	3	2
100 (mO)	8	8	5	4	3	2	2	2	4	3	-	-
100 (11122)	5	4	3	2	2	1,5	2	1,5	3	4	-	-

Table 12. Accuracy chart coefficients A, B. (First row is for Z, second for  $\Phi$ )[36]

Measuring the sample gives Z and  $\Phi$ . Inserting the data in Equations (30) and (31) from above, Z accuracy and  $\Phi$  accuracy are calculated. Using Equations (32) and (33), Z<sub>min</sub> and Z<sub>max</sub> are calculated. The same principle applies for  $\Phi_{min}$  and  $\Phi_{max}$  see (34) and (35).

$$Z_{min} = Z \cdot \left(1 - \frac{0.05}{100}\right) \quad (\% \, rdg.) \tag{32}$$

$$Z_{max} = Z \cdot \left(1 + \frac{0.05}{100}\right) \quad (\% \, rdg.) \tag{33}$$

$$\Phi_{min} = \Phi \cdot \left(1 - \frac{0.05}{100}\right) \tag{34}$$

$$\Phi_{max} = \Phi \cdot \left(1 + \frac{0.05}{100}\right) \tag{35}$$

$$C_{pmin} = \frac{\sin \Phi_{max}}{\omega \cdot |Z_{max}|} \tag{36}$$

$$C_{pmax} = \frac{\sin \Phi_{min}}{\omega \cdot |Z_{min}|} \tag{37}$$

Basic accuracy = 
$$\pm \frac{(C_s - C_{min}) \cdot 100}{Cs} (\% rdg.)$$
 (38)

#### 11.2 Basic accuracy by law of error propagation

Using the error propagation law (43), SCP is acquired and C<sub>pmin</sub> and C<sub>pmax</sub> calculated.

$$S(C_P) = \sqrt{\frac{\cos^2 \Phi}{Z^2 \omega^2} \cdot S(\Phi)^2 + \frac{\sin^2 \Phi}{Z^4 \omega^2} \cdot S(Z)^2},$$
(39)

where:

 $S(C_p)$  is difference between minimal (or maximal) and measured data. See next formula:

$$C_{pmin} = C_p - S(C_p), \tag{40}$$

$$C_{pmax} = C_p + S(C_p). \tag{41}$$

Results for this basic accuracy are included in each measurement report.

#### 11.3 **Design of experiment and analysis of variance**

The results for the gasoline-ethanol fuels were analysed using a design of experiment (DOE) and an analysis of variance (ANOVA). These methods were used twice, first for all data measured, including frequencies bellow 5 kHz. This model summary fits the data only in 8,14 %. Data from the DOE shows that there is another parameter which is not specified in the calculations. This parameter is an interface polarization and occurs at low frequencies for conductive liquids. Due to the difficulty of describing the polarization, data affected was excluded. By excluding all data for frequencies lower than 5 kHz, much better DOE results were achieved. Model fits in 99,2 %, and the results give very useful results, showing that main parameters influencing relative permittivity are concentration and temperature.

# 11.3.1 Results for DOE and ANOVA including data affected by interface polarization

Figures 25 and 26 below shows that relative permittivity is mostly dependent on frequency and concentration. These results were given due to the fact that interface polarization is caused by ethanol molecules, and it occurs on low frequencies.



Figure 25. Pareto Chart of Standardized Effects (response is Rel. Permittivity; $\alpha$ =0,05)



Figure 26. Interaction Plot for Rel Permittivity (-) Data means

In Figure 27 there can be seen the mean for each parameter. The first graph shows that the relative permittivity increases with the concentration. The second graph shows that there is a huge decrease in the relative permittivity when increasing the frequency up to about 5 kHz, however, further increasing the frequency has a negligible effect. The temperature graph is not so clear to read, that is because low concentration fuels are not that temperature dependent. Points with increased mean are for fuels with higher ethanol content.





# 11.3.2 Results for DOE and ANOVA excluding data affected by interface polarization

After excluding the data affected by interface polarization, a model fitting in 99,2% was achieved. The Pareto Chart of the Standardized Effects below shows that the frequency has truly negligible effect and concentration and temperature have the main influence.



Figure 28. Pareto Chart of the Standardized Effects (response is Rel. Permittivity (-);  $\alpha$ = 0,05)



Figure 29. Interaction Plot for Rel.Permittivity (-) Data Means

The temperature dependence is increased with increasing concentration as can be seen in Figure 29. The Main Effects Plot for Rel. Permittivity below describes the characteristics of each parameter. There is still a very low increase in the frequency graph at frequency 5 kHz, meaning that for some concentrations there is still the interface polarization in process. Also notice that the temperature mean is reversed, showing that the relative permittivity is decreasing with increasing temperature. These results prove conclusions made for measurements.



Figure 30. Main Effects Plot for Rel.Permittivity (-) Data Means

## **12 Conclusion**

From the biofuel point of view, it is possible to divide fuels into two groups, gasoline and diesel fuels. Gasoline is mixed with ethanol or methanol to create biofuel blends. The second type, diesel, is mixed with biofuel FAME or the new biofuel type HVO.

The conclusion from the first part of this thesis is that gasoline and diesel fuels have low permittivity, and adding even low concentrations of biofuels may affect the final permittivity. Ethanol and methanol both have permittivity more than ten times greater than gasoline has. Similar changes will occur for blending diesel with FAME. However, its permittivity is much lower, and the difference will not be so significant. Therefore the determination of the concentration of a bio-component is more accurate for gasoline biofuels due to their wide range of permittivity. For diesel biofuels, it will require a much more accurate method and devices to get the accurate percentage value of the concentration. It is also worth mentioning that this work do not take into account any special additives that are added to fuel by distributers, which improve the quality and also the parameters.

To inspect the accuracy of the measuring method and devices, n-heptane liquid was used. Its table permittivity is 1,209. Fifty measurements were done at one frequency and at constant temperature, giving an average value of 1,2075 with the greatest variance of a 0,000044. This gave enough confidence in the measuring method and devices.

Frequency dependence is highly affected by the type of fuel, its parameters, and also by the measuring method. Using a method with low capacity increases the influence of parasite inductance and external jamming. For accurate results, electrode shielding and corrections for inductance are recommended. For conductive fuels, for example ethanol fuels, at low frequencies the interface polarization increases capacitance significantly. There is also confirmed by measurement that the presence of water in the ethanol has great influence on results. Using ethanol with 3000 ppm and 550 ppm of water gives very different results.

The relative permittivity of fuels decreases with increasing temperature. This is caused by fuel volume expansion, which results in less molecules are between the electrodes. Moreover for polar fuels, temperature affects dipole movement and therefore the relative permittivity too. The relative permittivity of polar fuels is decreasing more than nonpolar.

The influence of modifying voltage while measuring was also examined. Low voltage leads to reducing the effect of parasite inductance in the measuring system. However, it increases disturbance at low frequencies. Therefore, the power level should be chosen depending on the measured frequency range and to the measuring method. For frequency and temperature measurements the power level of 1 V was chosen.

The experiment done to investigate the influence of pressure showed that increasing pressure up to 15 bars results in a negligible increase of permittivity, due to the low compressibility of liquids. The influence of pressure might be noticeable at much higher pressures or when using gases instead of liquids. Another experiment was performed to confirm the assumption that a gaseous phase decreases capacitance. The results confirmed the assumption, a gaseous phase reduces the number of molecules of higher permittivity material (fuel) between electrodes therefore the capacitance is decreased with increasing flow rate.

In the last part of this thesis, saturated vapour pressure was investigated. For this part, all data required was found in professional articles and other literature, using this data it was concluded that the highest Reid vapour pressure occurs when gasoline contains approximately 10 % of ethanol. Problems with vapour pressure occur only for lower concentrations of ethanol and increasing the ethanol concentration reduces vapour pressure. Gasoline vapour pressure for the winter season is increased in refineries, and blending with ethanol further increases the pressure. Using fuel like that at higher temperatures may cause vapour lock due to increased vaporization.

Design of experiment and analyse of variants were used to analyse the data for gasoline fuels. These methods showed that the concentration and temperature are the main two aspects influencing the relative permittivity. The frequency influence is very low for frequencies not affected by polarizations. For accurate measuring of the relative permittivity dependencies, defining the range affected by polarizations and working only with the data that is not affected is crucial. The results from DOE and ANOVA confirm findings by measurements.

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# ΗΙΟΚΙ

 No.
 2014H040350

 Date
 2014-12-12

 (YYYY-MM-DD)
 1 / 1

# **CALIBRATION CERTIFICATE**

#### Customer .

HIOKI E.E. CORPORATION

masayshi Jakaki

Inspector Quality Assurance Department

Model Name	:	LCR METER
Model Number	:	IM3536
Serial No.	:	141221343
Customer Record No.	•	
Calibration Date	:	2014-12-12

The above listed product(s) is/are calibrated in accordance with the HIOKI standards. This also certifies that all reference instruments used in the calibration process can be traced back to all or some of the official standards laboratories of the nations affiliated with the International Committee for Weights and Measures (CIPM), such as the National Institute of Advanced Industrial Science and Technology, the National Institute of Information and Communications Technology, and NIST (National Institute of Standards and Technology).

#### Instruments used

Model Name	Model Number	Serial No.	Control No.	Cal. Period
RMS VOLTMETER	URE3	861773/017	512-20-073	2015-03
STANDARD CAPACITOR	WCS010A(1pF)	1408204	000-22-426	2015-03
STANDARD CAPACITOR	WCS100A(10pF)	1408205	000-22-427	2015-03
STANDARD CAPACITOR	WCS101A(100pF)	1408206	000-22-428	2015-03
STANDARD CAPACITOR	WCS102A(1nF)	1408207	000-22-429	2015-03
STANDARD CAPACITOR	WCS103A(10nF)	1408208	000-22-430	2015-03
STANDARD CAPACITOR	WCS104A(100nF)	1408209	000-22-431	2015-03
STANDARD CAPACITOR	WCS105A(1µF)	1408210	000-22-432	2015-03
FREQUENCY COUNTER	53181A	MY40004877	000-44-029	2014-12
RESISTOR FOR IM3536(50mΩ)			000-22-449	2015-01
RESISTOR FOR IM3536(500mΩ)			000-22-450	2015-01
RESISTOR FOR IM3536(5Ω)			000-22-451	2015-01
RESISTOR FOR IM3536(50kΩ)			000-22-452	2015-01

Kalibracní list C. kalibracního listu: ETC-Q-Bj - KL - 83 Kód pozice: JTT100/CB Nr. 159

Pozice			Prístroj			
Název pozice	JTT100/CB Nr. 159		Kód prístroje	JTT100/CB Nr. 159 -	M3	
Císlo zakázky údržby			Výrobní císlo	JTT100/CB Nr. 159 -	M3	
Umístení			Výrobce	AHLBORN ALMEMO	2590	
Podnik	ETC/JTT100_CB/		Zmena rozpetí			
			Provozní teplota		Provozní vlhkost	
Funkce			Kalibrace			
Název	Funkce (ud)		Cas kalibrace	9.3.2015 11:26:00		
Prevodní funkce	Lineární		Príští kalibrace	8.3.2017		
Rozsah	-40 140 °C	-40 140 °C	Teplota okolí	24 °C	Vlhkost okolí	19 %
Kalibracní postup			Kalibrátory			
Datum príští kalibrace	8.3.2017	Kalibracní Ihuta 730 dní	Kalibrátor na vstupu	MC5 : 25519309	Datum	príští kalibrace: 17.2.2016
Mez chyby pro zamítnutí 3	> 0,1 °C		Modul na vstupu	ET : 59910	Datum	príští kalibrace: 17.2.2016
Mez chyby po serízení	% meze pro zamítr	utí Klasifikace	Kalibrátor na výstupu		Datum	príští kalibrace:
Kalibracní strategie			Modul na výstupu		Datum	príští kalibrace:



Jmenovitý vstup [°C]	Aktuální Vstup [°C]	Jmenovitý výstup [°C]	Aktuální Výstup [°C]	Nalezeno Chyba [°C]
-40,00	-40,00	-40,00	-40,000	0,0
0,00	0,00	0,00	0,000	0,0
60,00	60,00	60,00	60,000	0,0
100,00	100,00	100,00	100,000	0,0
140,00	140,00	140,00	140,000	0,0
100,00	100,00	100,00	100,000	0,0
60,00	60,00	60,00	60,000	0,0
0,00	0,00	0,00	0,000	0,0
-40,00	-40,00	-40,00	-40,000	0,0

Poznámka ke kal.::

ProvedI:

Kalibracní list C. kalibracního listu: ETC-Q-Bj - KL - 217 Kód pozice: JTT100/CB Nr. 250

Tisk: 8.4.2016 12:11:31 Vytiskl: Josef Dlabik CMX Verze: 2.7.444.0 (2.7)

Pozice			Prístroj			
Název pozice	PT100		Kód prístroje	JTT100/CB Nr. 250		
Císlo zakázky údržby			Výrobní císlo	JTT100/CB Nr. 250		
Umístení			Výrobce	<b>GREISINGER Pt100</b>		
Podnik	ETC/JTT100_CB/		Zmena rozpetí			
			Provozní teplota		Provozní vlhkost	
Funkce			Kalibrace			
Název	Funkce (ud)		Cas kalibrace	8.4.2016 8:25:00		
Prevodní funkce	Lineární		Príští kalibrace	8.4.2017		
Rozsah	-40 140 °C	-40 140 °C	Teplota okolí	24 °C	Vlhkost okolí	29 %
Kalibracní postup			Kalibrátory			
Datum príští kalibrace	16.3.2016	Kalibracní lhuta 1 roku	Kalibrátor na vstupu	MB140 : 3	Dat	um príští kalibrace:
Mez chyby pro zamítnutí >	> 1 °C		Modul na vstupu		Dat	um príští kalibrace:
Mez chyby po serízení	% meze pro zamítr	utí Klasifikace	Kalibrátor na výstupu	MC5 : 25519309	Datu	m príští kalibrace: 17.2.2016
Kalibracní strategie			Modul na výstupu	ET : 59910	Datu	ım príští kalibrace: 17.2.2016



1. Pred ser.			١	/YHOVUJE
Maximální chyba::	: 0,1630 °C			
Jmenovitý vstup [°C]	Aktuální Vstup [°C]	Jmenovitý výstup [°C]	Aktuální Výstup [°C]	Nalezeno Chyba [°C]
-40,0000	-40,082	-40,0000	-40,13	-0,05
0,0000	-0,013	0,0000	0,07	0,08
60,0000	60,007	60,0000	60,17	0,16
100,0000	100,012	100,0000	100,15	0,14
140,0000	140,051	140,0000	140,08	0,03
100,0000	99,990	100,0000	100,12	0,13
60,0000	59,997	60,0000	60,15	0,15
0,0000	-0,021	0,0000	0,05	0,07
-40,0000	-40,086	-40,0000	-40,13	-0,04

Poznámka ke kal.::





tel. +420 545 555 111, fax +420 545 222 728, www.cmi.cz

Kalibrační laboratoř č. 2202 akreditovaná Českým institutem pro akreditaci, o.p.s.
 Pracoviště: Oblastní inspektorát České Budějovice, U Sirkárny 33, 370 04 České Budějovice
 Oddělení měr a vah, tel. 387 423 624, fax 387 319 071

# KALIBRAČNÍ LIST

# 2051-KL-R0020-15

Datum vystavení: 16. únor 2015

Zákazník: Robert Bosch, spol. s r.o. Roberta Bosche 2678 370 04 České Budějovice

Uživatel: Viz. zákazník

Měřidlo:Váhy s neautomatickou činnostíMax = 2200 gd = 0.01 g

Výrobce: KERN & Sohn, GmbH

Typ: EW2200-2NM

Výrobní číslo: 077770128

Evidenční číslo: JMG200N1/2200CB Nr.4

Výsledky kalibrace byly získány za podmínek a s použitím postupů uvedených v tomto kalibračním listě a vztahují se pouze k době a místu provedení kalibrace.

Datum kalibrace: 10. únor 2015

Kalibraci provedl:



Ratajin'

Ing. Marie Ratajová

Ředitelka oblastního inspektorátu:

Rakym Ing. Marie Ratajová

Tento dokument nesmí být bez písemného souhlasu provádějící laboratoře rozmnožován jinak než v celkovém počtu listů.

List I ze 2 listů

#### KALIBRAČNÍ LIST

2051-KL-R0020-15

#### Použité etalony:

Etalonová závaží tř.F1 1 g - 5 kg, kalibrační list č. 2051-KL-E0012-15, kalibrovány CMI OI České Budějovice dne 23.1.2015

Kalibrační postup:	612-MP-C132
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Přípravna zkušebních stavů Místo kalibrace:

Podmínky prostředí:	Teplota:	$(20,2 \pm 0,4)$ °C
	Vlhkost	$(25.25 \pm 2.65)$ %

#### Výsledky kalibrace:

Opakovatelnost:

Směrodatná odchylka byla stanovena při: jmenovitém zatížení 2000 g a má hodnotu 0,0 g.

Excentricita:

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	$\leq :$	CXX	
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6		
3		
6	100	

Jmenovité zatížení (g)	Sektor	Indikace I (g)	_
	1	1 000,00	
	2	1 000,01	
1000	3	1 000,01	Ì
	4	1 000,00	-
	5	1 000,00	

Správnost:

Tára (g)	Jmenovité zatížení (g)	Chyba (g)	Nejistota U (g)
0	0	0,000	0,006
0	10	0,000	0,009
0	100	0,000	0,009
0	200	0,000	0,009
0	500	-0,001	0,009
0	700	-0,001	0,010
0	1000	-0,001	0,011
0	2200	-0,003	0,017

Standardní nejistota měření byla určena v souladu s dokumentem EA-4/02. Uvedená rozšířená nejistota měření je součinem standardní nejistoty měření a koeficientu k, který odpovídá pravděpodobnosti pokrytí přibližně 95 %, což pro normální rozdělení odpovídá koeficientu rozšíření k = 2.

Vyjádření o plnění specifikace: Chyba linearity deklarovaná výrobcem je  $\pm 0,02$  g v celém rozsahu vážení. Chyby zkoušky správnosti rozšířené o nejistoty měření jsou v souladu s uvedenou specifikací.

Konec kalibračního listu

Tento dokument nesmí být bez písemného souhlasu provádějící laboratoře rozmnožován jinak než v celkovém počtu listů.

Kalibracní list C. kalibracního listu: ETC-Q-Bj - KL - 77 Kód pozice: JMM100/2CB Nr. 9

Pozice			Prístroj			
Název pozice	HONEYWELL		Kód prístroje	JMM100/2CB Nr. 9		
Císlo zakázky údržby			Výrobní císlo	JMM100/2CB Nr. 9		
Umístení			Výrobce			
Podnik	ETC/JMM100_2CI	Β/	Zmena rozpetí			
			Provozní teplota		Provozní vlhkost	
Funkce			Kalibrace			
Název	Pressure Indicator	(pi)	Cas kalibrace	25.2.2015 15:03:00		
Prevodní funkce	Lineární		Príští kalibrace	25.2.2017		
Rozsah	0 20 bar (P)	0 20 bar (P)	Teplota okolí	23,5 °C	Vlhkost okolí	23 %
Kalibracní postup			Kalibrátory			
Datum príští kalibrace	25.2.2017	Kalibracní Ihuta 2 roku	Kalibrátor na vstupu	MC5 : 25519309	Datum	príští kalibrace: 17.2.2016
Mez chyby pro zamítnutí	> 0,2 % rozpetí		Modul na vstupu	INT20C : 46924	Datum	príští kalibrace: 17.2.2016
Mez chyby po serízení	% meze pro zamít	nutí Klasifikace	Kalibrátor na výstupu		Datum	príští kalibrace:
Kalibracní strategie			Modul na výstupu		Datum	príští kalibrace:



Jmenovitý vstup [bar]	Aktuální Vstup [bar]	Jmenovitý výstup [bar]	Aktuální Výstup [bar]	Nalezeno Chyba [% rozpetí]
0,0000	0,0001	0,0000	0,006	0,030
5,000	5,0236	5,000	5,004	-0,098
10,00	10,0226	10,00	10,01	-0,063
15,00	15,0052	15,00	15,01	0,024
20,000	20,0020	20,000	20,00	-0,010
15,00	15,0021	15,00	15,01	0,039
10,00	9,9948	10,00	10,00	0,026
5,000	4,9966	5,000	5,004	0,037
0,0000	0,0003	0,0000	0,034	0,168

Poznámka ke kal.::