

*Chapter 7*

## **METHANOL CONTENT IN BIODIESEL ESTIMATED BY FLASH POINT AND ELECTRICAL PROPERTIES**

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### **ABSTRACT**

International standards for Biodiesel (BD) characterization include two properties that are very important from the standpoint of safety in production, storage and transport of biofuels: Methanol Content (MC) and Flash Point (FP).

This chapter presents a systematic exploration of the direct relation existing between MC and FP, including electrical properties (permittivity and conductivity) that, although at present are not included in international standards for BD, provide relevant information on this subject.

Precisely known amounts of methanol (up to 2.5% V/V) were added to BD, and FP was determined by the well known Pensky-Martens method. An excellent fitting to a potential function was found between MC and FP. Moreover, the maximum allowable MC according to International Standards corresponds precisely to the minimum FP value indicated by the Standards.

Measurements of Electrical Properties (EP) carried out at different temperatures show a clear dependence between MC and the permittivity and conductivity of the samples. The results presented in this chapter show that FP and EP measurements are an interesting alternative for the verification of methanol content in biodiesel.

## INTRODUCTION

Biodiesel (BD) is a liquid biofuel that can replace petroleum-based Diesel fuel (DF) or blended with it, since they can be mixed in any ratio. ASTM (formerly known as the American Society for Testing and Materials) defines biodiesel as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751 [1].

In many countries, including the United States and the European Union, biodiesel in blends with DF in a proportion ranging from 5% (B5) to 20% (B20) is routinely used in Diesel engines without any modification. In consequence, world production and use of biodiesel has significantly increased in recent years, since it is a renewable fuel that offers an alternative to fossil fuels in automotive applications.

Biodiesel [2], [3] is obtained by transesterification of vegetable oils or animal fats with short linear - chain alcohol (methanol or ethanol). The reaction must take place under well defined conditions. Raw materials for BD production may include new or used, edible or non-edible vegetal oils and animal fats. Therefore, biodiesel may be produced from oil from soybean, sunflower, corn, peanut, cotton, palm tung, castor seed, jatropha, rapeseed, micro-algae, and animal fats from cows, pigs, chicken, fish, etc.

As a result of the transesterification process, glycerin and a mixture of esters are obtained. Biodiesel is obtained from this mixture of esters, after a purification process. It must be remarked that although the production process is straightforward, it is not always easy to obtain a final product that qualifies as BD according to the requirements of standards.

Quality control of fuel during production and distribution is essential to ensure the quality of the product delivered to users and the good performance of engines. To establish the good quality of the liquid biofuel, several properties must be measured. Moreover, since biodiesel properties depend on the type and proportion of esters, i.e. from the raw material, standards indicate allowable ranges for the key properties. To qualify as BD, measurement results must fall within these prescribed limits. Acceptance ranges for BD properties vary slightly between standards set by different organizations (ASTM D 6751, EN 14214, IRAM 6515, DIN V 51606, ÖN C 1191, UNI 10635, etc.) [1], [4], [5] but these differences have little technological impact. In some cases standards only establish maximum or minimum allowable values.

Parameters that define BD quality may be classified in two main groups [6]: general properties (including density, viscosity, flash point, cloud point, pour point, cetane number, acid number) and the chemical composition and purity of the mix of esters from fatty acids (alcohol content, ester content, proportion of mono-, di- and tri-glycerides, total and free glycerin content, iodine index, etc.)

Although not all the standardization organizations require the measurement of the same properties, most of the required properties of BD are common to the different standards. The general properties of biodiesel used for characterization are: density, viscosity, lubricity, flash point, acid number, iodine index, cetane number, oxidation stability, carbon residue, sulfated ash, water content, non water soluble impurities and copper strip. The chemical composition and purity parameters include the content of methyl ester of linoleic acid, esters, methanol, monoglyceride, diglyceride and triglyceride, free glycerin, total glycerin, sulfur, alkaline metals and phosphorus.

The transesterification process may be basic, acid or enzymatic. At industrial scale, the basic process is employed, mainly using methanol. To achieve the highest yield, the amount of methanol exceeds the stoichiometric alcohol - oil ratio. Since it is an impurity, standards require that the free methanol content (MC) in BD be lower than 0.2 %. Therefore, the excess of alcohol must be removed from the mix of methyl esters by an adequate purification process. Flash point (FP) is an important parameter concerning the safety in BD distribution and storage, since higher values lead to a safer handling of the fuel. The minimum value required by standards is usually 100°C or higher.

It is very important to take into account that free methanol content and flash point are closely related. Since the FP of pure methanol is 11°C, it is not surprising that FP of biodiesel will be lower than 100°C if the MC exceeds 0.2%.

There are other properties, in addition to those required by the standards, that provide important information about the fuel, such as its heating value and electrical properties.

Specifically, measurement of electric properties is a widely used technique in liquid samples[7], [8]. Among other applications, electrical techniques make possible to characterize mixtures and detect contaminants independently from the color or turbidity of the liquid phases.

## **PREPARATION OF BIODIESEL SAMPLES**

The samples of biodiesel studied in this chapter were prepared at the Grupo de Energías Renovables -GER- (Renewable Energy Group) at the Facultad de Ingeniería (Engineering School) of the University of Buenos Aires (UBA). Biofuel was made by the basic transesterification of new oil from soybeans and methanol, under constant stirring during one hour at a temperature of 60°C [7], [8]. Sodium hydroxide was used as a catalyst, and a 1:4 (in volume) alcohol to oil ratio. The mixture of methyl esters obtained as a product of the reaction was separated from glycerin and then purified by three washing steps. The first washing step was carried out with water acidified with hydrochloric acid and the remaining two with deionized water. Finally, samples were dried, in order to comply with the maximum water content value allowed by the standards [9].

In this chapter, the final product that complies with standards after the purification process is designated as “BD”.

### **Characterization of Biodiesel According to International Standards**

The samples of BD studied in this chapter were characterized by the following properties: viscosity, density, acid number, flash point (FP), cloud point, pour point, copper strip corrosion, free methanol content (MC) , free and total glycerin content and water content. All the measurement results were within the allowable ranges as required by international standards.

## Preparation of Biodiesel Samples with Known Methanol Content

To obtain the value of FP as a function of MC, biodiesel samples prepared by the process described in the previous paragraphs were mixed with known volumes of methanol (analytical grade).

### DETERMINATION OF FLASH POINT

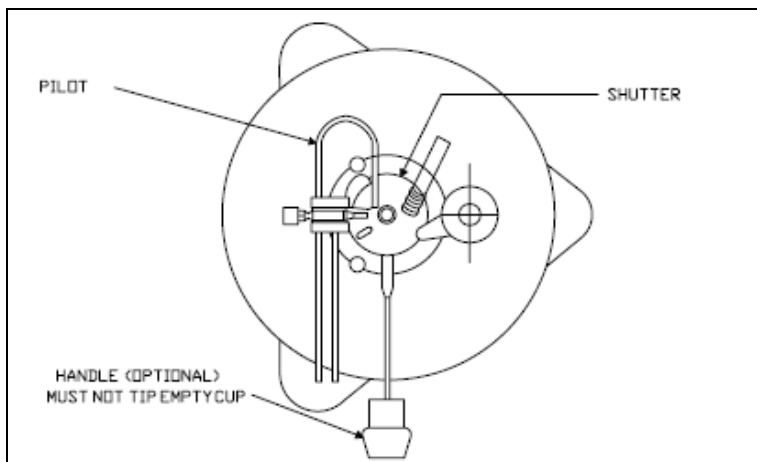
Flash point measurements were carried out using the Pensky-Martens Closed Cup Tester according to ASTM D 93 [10]. An outline of the Pensky-Martens apparatus, in accordance with the design illustrated in ASTM D93, is shown in Figure 1.

The test sample is placed in a brass test cup of specified dimensions that is fitted with a cover of specified dimensions. The cup is heated and the sample is stirred at a specified rate. At regular intervals, the stirring is interrupted and at the same time an ignition source is directed into the test cup, until a flash is detected. The flash point is defined as the lowest temperature at which application of an ignition source causes the vapors of the test sample to ignite under the specified conditions indicated by the standard. For the purposes of FP determination, it is considered that the test sample has flashed when a flame appears and instantaneously propagates itself over the entire surface.

The following test conditions are set by the Standard:

- The temperature of the sample must increase at a rate of 5 to 6°C/minute.
- The ignition source must be applied at each temperature increase of 2°C, beginning at a temperature of 23 +/- 5°C below the expected flash point.
- The required sample volume is 70 ml.

It should be noted that, according to most standards, FP of biodiesel should be higher than 100°C, and usually it is above 130°C. This is a significant difference with the FP of Diesel fuel, which is above 50°C, and it is one of the advantages for the transport and storage of BD.



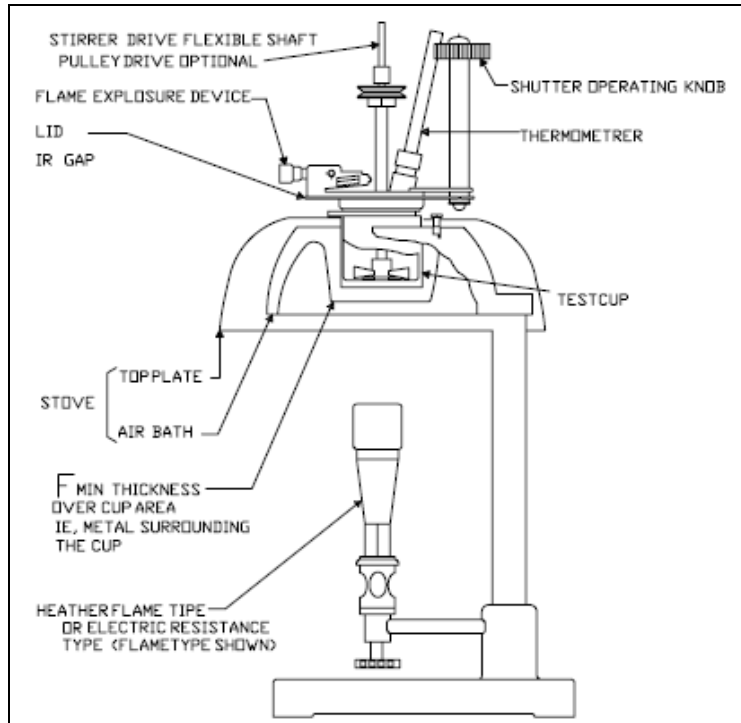


Figure 1. Scheme of Pensky - Martens Closed Flash Tester Equipment.

## MEASUREMENT OF PERMITTIVITY AND CONDUCTIVITY IN LIQUIDS

Broadly speaking, the relative permittivity of a substance characterizes its dielectric polarization, that is, the macroscopic (average) response of the permanent and induced dipole moments at the atomic and molecular scales, when an external electric field is applied. Similarly, conductivity determines the macroscopic current originated by transport processes of free charges (electrons and ions), when the substance is subjected to an external electric field [11].

The conductivity and permittivity of the sample as a function of the excitation angular frequency,  $\omega$ , are usually jointly described by the complex relative permittivity  $\varepsilon_r(\omega)$ , defined as the ratio of the capacitance of the cell containing the sample,  $C_s(\omega)$ , to the capacitance of the empty cell,  $C_0$ .

$$\varepsilon_r(\omega) = \frac{C_s(\omega)}{C_0} \quad (1)$$

where the imaginary part of  $\varepsilon_r(\omega)$  is written with a negative sign:

$$\varepsilon_r(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega) \quad (2)$$

As follows from (1) the real part of  $\varepsilon_r(\omega)$  is proportional to the electrostatic energy stored as dielectric polarization, whereas the imaginary part  $\varepsilon_r''(\omega)$  represents the energy lost through dissipative processes. Usually, the imaginary part of the permittivity is often written as the sum of two terms:

$$\varepsilon_r''(\omega) = \varepsilon_{r,pol}''(\omega) + \frac{\sigma}{\varepsilon_0 \omega} \quad (3)$$

The first term,  $\varepsilon_{r,pol}''(\omega)$  represents the dissipative processes (relaxation) associated to the dielectric polarization. Therefore, it is related to the same molecular and electronic processes that give rise to the dipole moments described by the real part of the permittivity,  $\varepsilon_r'(\omega)$ . The second term describes the energy loss associated to the electrical conduction due to free charge carriers (ions and electrons).

It is proportional to the conductivity parameter,  $\sigma$ , and inversely proportional to the angular frequency of the excitation,  $\omega$ . Clearly, at low frequencies ( $\omega \rightarrow 0$ ) conductivity often is the most important dissipative process and therefore dominates the imaginary part of complex permittivity. The constant  $\varepsilon_0$  is the permittivity of free space ( $8.854 \cdot 10^{-12}$  F/m).

The phase angle (with a minus sign) of the complex permittivity as a function of  $\omega$  is customarily designated as  $\delta(\omega)$ . It is also usual in technological applications to define the dissipation factor  $D_f(\omega)$  as the tangent of  $\delta(\omega)$ , that is, as the ratio (with a minus sign) of the imaginary to the real part of the complex permittivity  $\varepsilon_r(\omega)$ :

$$D_f(\omega) = \operatorname{tg} \delta(\omega) = \frac{\varepsilon_r''(\omega)}{\varepsilon_r'(\omega)} \quad (4)$$

It is easy to see from equations. (1) and (2) that, under steady - state time - harmonic excitation, the dissipation factor is proportional to the ratio of the energy dissipated to the energy stored per cycle in the dielectric.

The results of complex permittivity measurements are usually presented as plots of the real and imaginary parts,  $\varepsilon_r'(\omega)$  and  $\varepsilon_r''(\omega)$ . The dissipation factor  $D_f(\omega)$  is often given, since in the frequency range where free charge transport is the predominant dissipative process,  $D_f(\omega) \sim \omega^{-1}$ , which is easily recognized in a log-log graph of  $D_f(\omega)$ .

Measurements of permittivity and conductivity are based in the interaction of the substance under study with a time-varying electric field. The liquid sample is introduced in a cell kept at constant temperature, usually by means of a thermostatic system. Inside the cell, a set of electrodes connected to the measuring circuit are submerged in the liquid. In the measuring range of interest in this chapter (20 Hz to 2 MHz), the measuring circuit provides a constant-amplitude, time-harmonic excitation to the cell. The response signal is processed and compared the excitation signal, in order to determine the capacitance of the cell, as a function of frequency. Measurement of capacitance may be carried out using stand-alone instruments made by different manufacturers, such as RCL Meters, Impedance Analyzers and Dielectric Analyzers [12], [13], [14].

As an alternative, other dielectric measuring systems use separate instruments: a Signal Generator to provide the excitation, a Dielectric Measuring Interface connected to the sample cell, and to compare the response signal with the excitation, a Phase-Amplitude Analyzer, a Lock-in Amplifier or a Digital Oscilloscope controlled by a Personal Computer (PC) with Fourier Analysis (FFT) software.

In the authors experience, sample cells with platinized platinum electrodes (of the usual type used for electrochemical work), are quite adequate for the measurements described in this chapter.

Measurements presented in this chapter were carried out by an automated dielectric system [15], [16] consisting of a GW - 830 Signal Generator, a custom - design Dielectric Measuring Interface and a Tektronix TDS - 210 Digital Oscilloscope. The temperature of the sample cell was controlled by a Lauda thermostat.

### **DETERMINATION OF THE TEMPERATURE DEPENDENCE OF ELECTRICAL PROPERTIES OF BIODIESEL**

In the frequency range of interest in this chapter, from about 20 Hz to 2 MHz, no dielectric relaxation processes are observed in biodiesel; therefore,  $\varepsilon_r'$  may be considered as independent of  $\omega$  and  $\varepsilon_r \text{ pol}''$  is negligible. On the other hand, the presence of free charge carriers due to the presence of contaminants and thermal effects in BD originate dissipative effects and the conductivity term  $\sigma/\omega$  must be included in the imaginary part of the complex permittivity. Moreover, since thermal agitation tends to oppose the polarization associated to molecular orientation,  $\varepsilon_r'$  may be expected to decrease with temperature.

In summary, in this chapter the dependence of electrical properties of BD with the absolute temperature T and the angular frequency of the excitation,  $\omega$ , will be fitted to the following expression:

$$\varepsilon_r(\omega, T) = \varepsilon_r'(T) - i \frac{\sigma(T)}{\varepsilon_0 \omega} \quad (5)$$

The real part  $\varepsilon_r'(T)$  will be assumed to have a linear dependence on temperature

$$\varepsilon_r'(T) = a - b T \quad (6)$$

where the parameters  $a$  and  $b$  depend on the BD composition and also are affected by the presence of contaminants.

On the contrary, the conductivity of pure BD is very low but increases exponentially with temperature [8]; moreover, the presence of contaminants changes significantly the room temperature value of conductivity and its dependence with the temperature.

## CORRELATION BETWEEN FLASH POINT AND METHANOL CONTENT IN BIODIESEL

Measurements show that there is a strong correlation between flash point and methanol content (Figure 2). The following expression fits very well the experimental data, with a correlation coefficient ( $R^2$ ) greater than 0.99:

$$y = 38 x^{-0.6} \quad (7)$$

where  $x$  is the methanol content in biodiesel (% V/V) and  $y$  is the flash point of the sample ( $^{\circ}\text{C}$ ), with  $x \geq 0.2$ . FP of BD samples with no methanol added always exceeded the maximum FP value that could be measured with the equipment available at the GER ( $> 180^{\circ}\text{C}$ ).

All the FP measurements were double-checked.

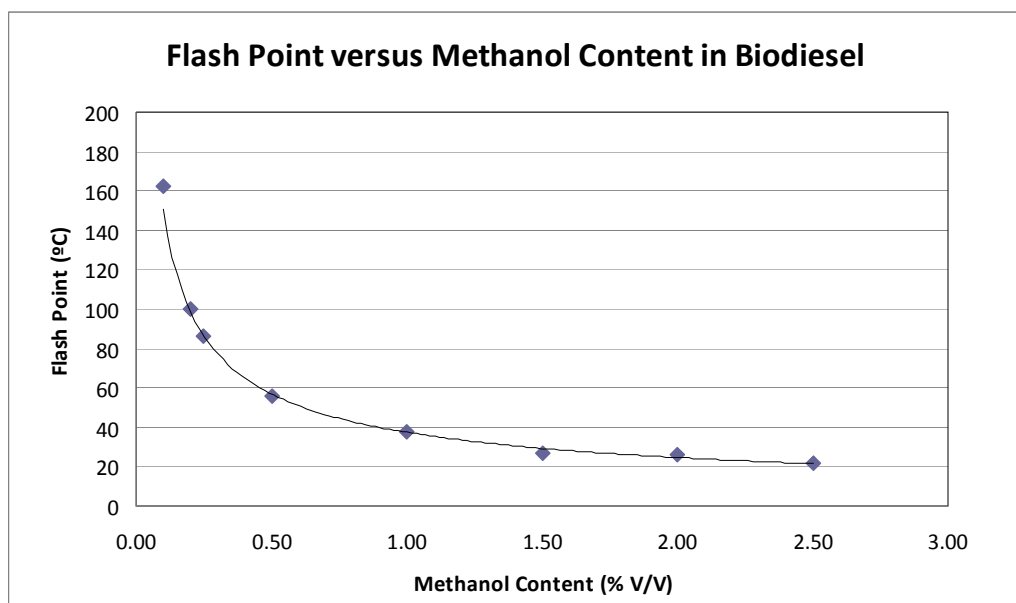


Figure 2. Flash Point versus Methanol Content in Biodiesel.

It is important to remark that the measured flash point value at the maximum methanol content set by international standards (0.2%) corresponds to the minimum allowable flash point ( $100^{\circ}\text{C}$ ) according to the standards. Therefore, compliance with the flash point requirement is also a good indicator of compliance with maximum methanol content. As it is easy to see in Figure 2, a small excess in methanol content originates a sharp decline in flash point of biodiesel.



## PERMITTIVITY AND CONDUCTIVITY IN BIODIESEL CONTAINING METHANOL

Regarding electrical properties, experimental data show that biodiesel containing methanol has a higher permittivity at room temperature than pure BD [7], [8]. As indicated in equation (6), the dependence of the real part of the complex permittivity,  $\epsilon_r'(T)$ , may be fitted to a linear function, where the parameters  $a$  and  $b$  depend on methanol concentration.

From the measurement results plotted in Figure 3, the fitting parameters are summarized in Table I.

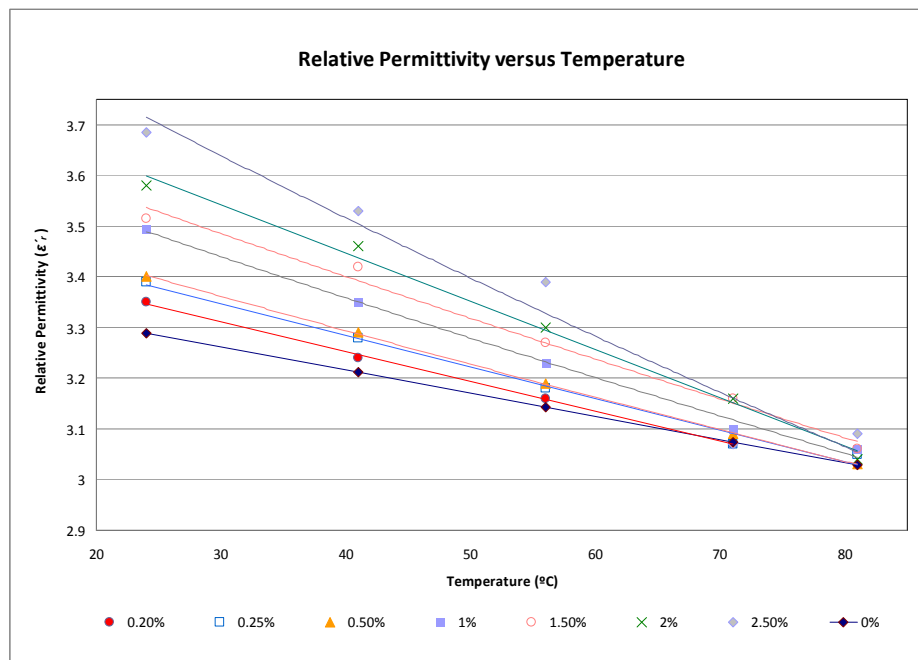


Figure 3. Relative Permittivity versus Temperature as a function of methanol content in Biodiesel.

**Table I. Parameters of the linear fit and correlation coefficient for permittivity versus temperature at different values of methanol content in biodiesel**

Methanol concentration in Biodiesel (%V/V)	a	b	R <sup>2</sup>
0.00	3.398	0,0046	0,999
0.20	3.490	0,0059	0,998
0.25	3.534	0,0062	0,988
0.50	3.544	0,0061	0,998
1.00	3.645	0,0074	0,994
1.50	3.747	0,0084	0,996
2.00	3.828	0,0095	0,993
2.50	3.997	0,0117	0,949

From Figure 3 it may be seen that the rate of decrease of permittivity with temperature increases with methanol content. Also, the fitting of permittivity data as a linear function of temperature is better at lower methanol concentrations (c.f. Table I). At higher temperatures  $\epsilon_r'(T)$  tends to the value of pure BD. This is not surprising since methanol evaporates at 65°C.

From figure 4, below 65°C the conductivity of biodiesel increases with higher methanol content.

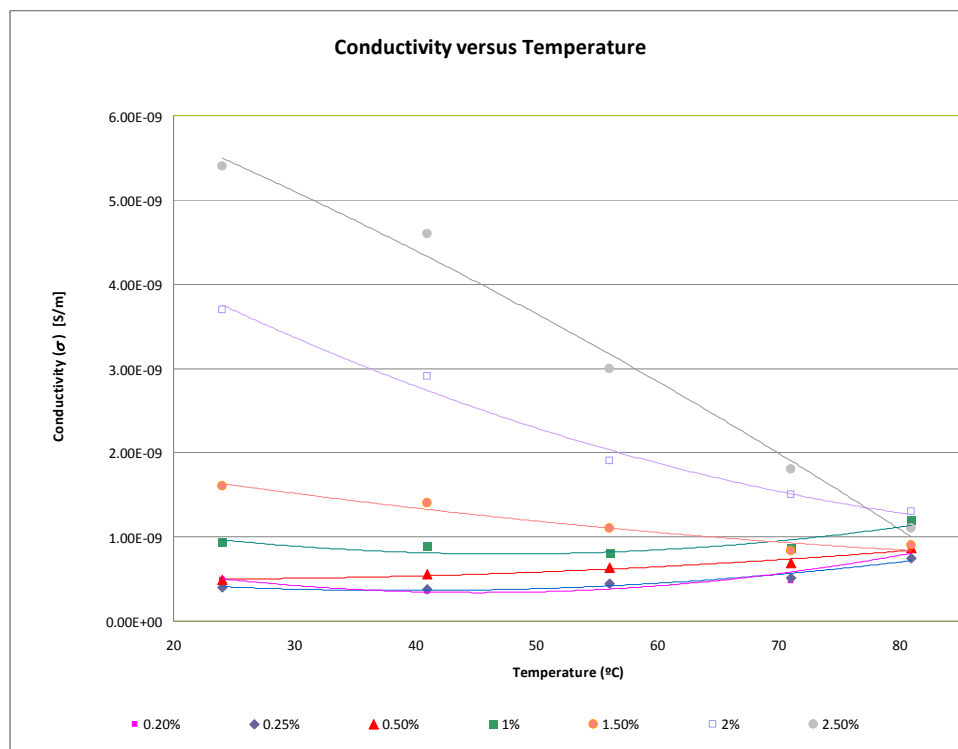


Figure 4. Conductivity versus Temperature as a function of methanol content in Biodiesel.

## CONCLUSION

Measurement data of flash point as a function of methanol content show clearly that small increases of alcohol concentration originate a steep decline in FP. This result is important for production, distribution and utilization of BD. In particular, excess of methanol must be eliminated with an adequate purification process.

From the strong correlation between MC and FP, it is possible to use FP measurements for the preliminary verification (prior to certification) of the compliance with the methanol content requirements of BD standards. This is relevant since FP measurements are much simpler and use less expensive equipment than the procedure for determination of methanol content recommended by standards (chromatographic analysis) [17].

The linear fit of permittivity measurements as a function of temperature makes possible to determine accurately MC in biodiesel within a wide range of concentrations, including the

maximum value set by the standards (0.2%). Methanol content may be obtained from the value of  $\epsilon_r'(T)$  extrapolated to 0°C, that is, the parameter  $a$  in equation (6), given in Table I.

Measurements of biodiesel conductivity at room temperature (25°C) may be used for a preliminary check of methanol concentrations above 0.5%, as shown in Figure 4. This is very convenient since the equipment for conductivity measurement at room temperature is widely available and easier to use than systems for permittivity measurements as function of temperature, particularly in industrial applications.

## ACKNOWLEDGEMENTS

One of the authors (Buesa Pueyo) thanks Universidad Politécnica de Valencia (Spain) for a PROMOE scholarship to carry out his Graduation Project in Agricultural Engineering at the Renewable Energy Group (GER) of the University of Buenos Aires.

The work in this chapter was funded by Project UBACYT I409 of the University of Buenos Aires: “Optimization of process variables for biodiesel production in an automated pilot plant, from different alternative raw materials”.

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