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Note

Electrochemical characterization of Biodiesel by linear voltammetry and electrochemical impedance spectroscopy

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Biodiesel from different sources were synthetized according to transesterification method. Actually, there are different methods to characterize these fuels, but majority are physicochemical techniques, some of they, like water content by Karl-Fischer method are really complex. Because electrochemical techniques offer fast and accurate results, an electrochemical cell was designed and built to measure these biodiesels, in particular electrolytic conductivity, which is an important parameter that characterizes solutions in different fields of research and industry. Biodiesel obtained from castor oil present the lowest electrolytic conductivity from four evaluated.

Keywords: Biodiesel, Electrochemical Characterization, Linear Voltammetry, Electrochemical Impedance Spectroscopy.

1. INTRODUCTION

Considering the continuous increasing in energy demand around the world, environmental problems and shortage of fossil fuel, it is necessary to think about new ways to obtain energy. It is reported that world will need 50 % more energy in 2030 than today, particularly for industrial and transportation sectors, besides, it is expected that 4.1 billion metric tons of carbon dioxide will be released to the atmosphere from 2007 to 2020 [1], fossil or non-renewable fuels emit pollutants in the form of oxides, carbon monoxide, lead, hydrocarbons, and others during both their processing and use [2]. Considering these problems, scientific community is making efforts in different scientific energy fields: solar, eolian, hydrogen, biofuels and others. Even there are reports about energy balances, indicating that these processes need to be improved [3-6], mainly in improving efficiency of the production process, developing cost effective catalyst or making that production have less impact on the environment [7].

Actually, the two most important biofuels are biodiesel and bioethanol, which can be obtained from vegetable oils, seeds and lignocelluloses. Biodiesel can substitute fossil diesel and bioethanol can replace petrol [8]. Bioethanol is synthesized mainly from fermentation of sugarcane, corn, wheat, maize and potatoes [8], biodiesel are produced from plant oils like rapeseed, castor oil, soybean, sunflower, coconut, jatropha, karanja, algae, waste or recycled oil or from animal fats by applying processes like pyrolysis, micro-emulsification or transesterification [1, 2], or even from waste cooking oil [9].

Regarding castor oil, there are some reports about the process to produce biodiesel [10, 11], using mainly tranestererification process. Canoira et.al. [12] reported that fatty acid methyl esters from castor oil are unsuitable in pure state for its direct use in internal combustion engines, indicating that properties like oxidative stability or lubricity are critical properties with different behavior compared with reference diesel, they conclude that in order to meet most of the specifications of the EN 590 standard, up to 40 % in volume must be used.

Concerning to biodiesel characterization techniques, there are more than 15 methods to characterize the product; density, viscosity, lubricity, high heating value and chemical analysis mainly, only water content and acidity are experiments that involve electrochemical techniques, usually, techniques like Fourier-transform infrared spectrometer (FT-IR), gas or liquid chromatography, even nuclear magnetic resonance (NMR) has been reported elsewhere [12-16]. However, there are reports where dielectric spectroscopy has been used to evaluate the quality or identify if there is adulteration of vegetable oils [17-19], in these experiments, vegetable oils are measured with special probes and specialized apparatus like LCR-meters. By estimating Cole-Cole parameters, dielectric constant of oils can be used to discriminate different pure oils, or the relaxation frequency is the parameter that indicates the presence of adulterants. Ragni et.al [20] found that measuring with capacitive techniques at kHz range, water content from 0.03 % to 0.13 % can be predicted, also indicate that results of impedance are well described by the capacitive reactance, so a simple measurement system that measure voltage and current can be used to predict some chemical characteristics. All of these results, according to Cataldo et. Al [17] indicates that this electrical technique is useful, although more studies are needed. Prevc et.al [21] reported the relationship between dielectric constant and conductivities of different vegetable oils with temperature, where it decreased with temperature according to a linear model. El Khaled et.al [22] made a review paper to use bioimpedance methods as a tool for quality control systems for fruits and vegetables like apple, banana, kiwi, lettuce, tomato and others, where it is clear that bioimpedance spectroscopy is a potential technique to detect electrical characteristics in fruits and vegetables that can help for cleaner control systems.

M´Peko et.al [23] have reported the use of the technique electrochemical impedance spectroscopy (EIS) to characterize different vegetables oils, however, from their impedance spectra and the equivalent circuit used, it is possible to note that there are reactions in the system, probable because salts or water content, nevertheless, they conclude that the technique can be applied as analytical method for identifying, monitor and/or sensing certain biodiesel properties. Because of those papers, authors decided to apply electrochemical techniques like linear voltammetry (LV) and EIS to characterize biodiesel synthetized *in-house* and compare against fossil diesel, according with our references, these techniques have not been use for this purpose.

2. EXPERIMENTAL

2.1. Biodiesel synthesis.

Biodiesel was synthesized by using transesterification method reported elsewhere [4, 12], where 20 mL of methanol and 1 g of sodium hydroxide were added to 100 ml of oil. After transesterification, glycerin was separated and biodiesel was washed with water and dried at 105 ºC during 5 hours.

Three biodiesel precursors were used: in house made castor oil, commercial soja oil and commercial mix oil. Centrifuge Solbat, model J40 was used to separate biodiesel and Air performance drying oven from Dynamical was used to dry after separation. All reactive are ACS grade.

2.2 Experimental procedure

Biodiesel was successfully synthetized according to transesterification process. In this case, the process for biodiesel obtaining it was implemented for house castor oil, commercial soja oil and commercial mix oil. Viscosity from three biodiesels was measured in order to characterize and assure their quality, in all cases results are according to limits indicated elsewhere [2].

2.3. Electrochemical system.

Because of electrolytic conductivity characteristics of biodiesels, an electrochemical cell was specifically designed and simulated on SolidWorks® software and built in glass; that cell was used for all electrochemical experiments. Two electrodes configuration was used, where SS304 foils were used as electrodes. Nominal cell constant of 0.017 cm^{-1} was obtained by geometrical characteristics [24]; the real cell constant was obtained by using Certified Reference Material (CRM) [25].

Experiments were performed by using a potentiostat/galvanostat Reference 3000 from Gamry®. Linear sweep voltammetry (LSV) was made from open circuit potential in both cathodic and anodic sense at slow scan speed (2 mV/s) to make it comparable with EIS experiments, which need to be made at steady state.

For electrochemical impedance spectroscopy (EIS) experiments, frequency was scanned from 100 kHz to 10 Hz, at an applied potential perturbation of 200 mV and 7 points by decade. The impedance spectra were analyzed by using Z-view® program.

In order to compare the information with a reference, commercial diesel obtained from a gas station was also measured at same experimental conditions.

2.4. Simulation and design of the electrochemical cell

According to biodiesel intrinsic characteristic like water content, salts content or electrolytic conductivity, there are no commercial cells that can be used accurately to measure this very low level of electrolytic conductivity, so an the electrochemical cell was designed and built. It is possible to see design and first prototype in figure 1.

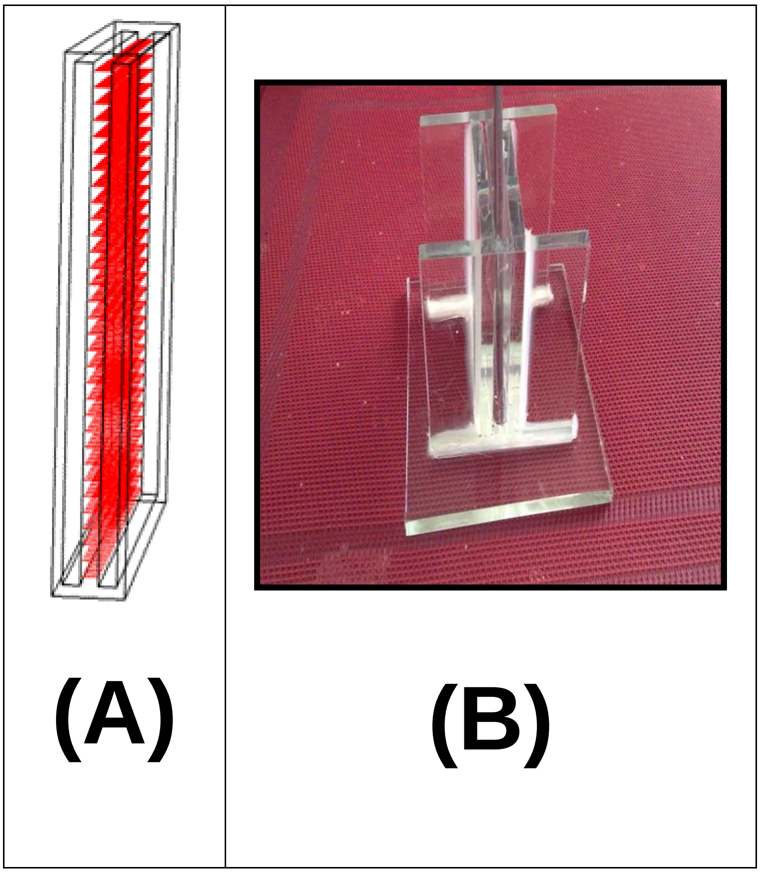


Figure 1. Electrochemical cell designed (A) and built (B) *ex professo* to measure electrolytic conductivity in solutions with values lower than 1 uS/cm.

In figure 1A it can be observed the results of simulation with Comsol Multiphysics® of primary current distribution across the cell. Lines are parallel in all electrodes area, which is necessary for electrolytic conductivity measurements. On the other hand, in figure 2B the built cell is shown.

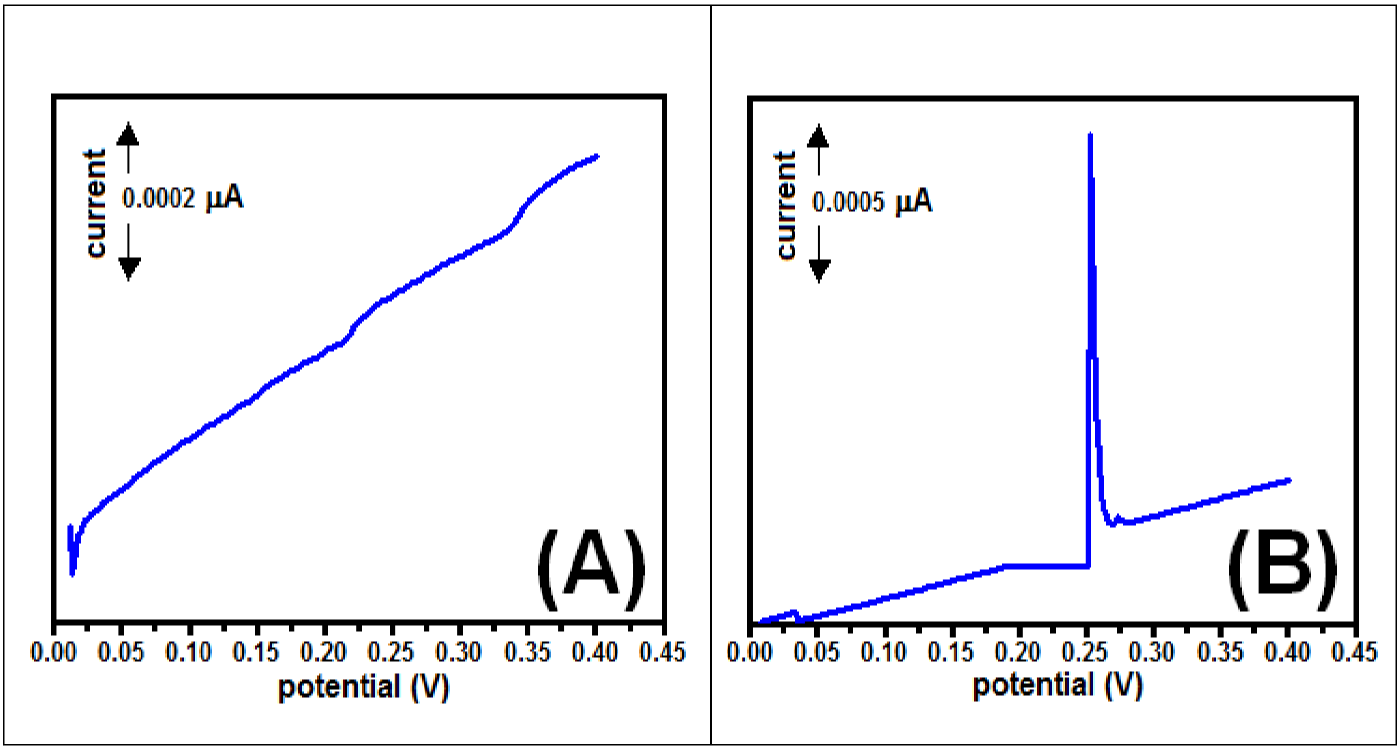
This cell can be used also for different liquids, always bearing in mind that it was designed for solutions with EC lower than 1 μS/cm. By using CRM, the constant cell obtained is 0.012 cm^{-1}, according to references [26] this cell is useful to measure EC in the range 0.05 to 10 μS/cm. It is important to note that electrodes are made of stainess steel, which is a not expensive material, and it is important to know the behavior whit this kind of fuels, particularly about possible corrosion effects.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization

3.1.1. Linear Voltammetry

A typical linear sweep voltammetry is shown in figure 2. It is possible to see that in all cases the electrochemical behavior is comparable, which indicate that biodiesels have similar behavior compared with fossil fuel. As expected, in all potential range studied for all cases, there is no current that could indicate that reactions occur, this result could indicate that biodiesel produced are pure materials, without electroactive species [27] and also means that stainless steel can be used to perform that kind of measurements, where no corrosion occur. Even if for castor oil biodiesel there is an increase in current of three magnitude orders, these values are related with no electrochemical reactions. Those results cannot be compared against references, because according to authors, this kind of experiments has not been reported. This result is an option to perform fast and accuracy test to know the diesel quality, in this, related to electroactive species.



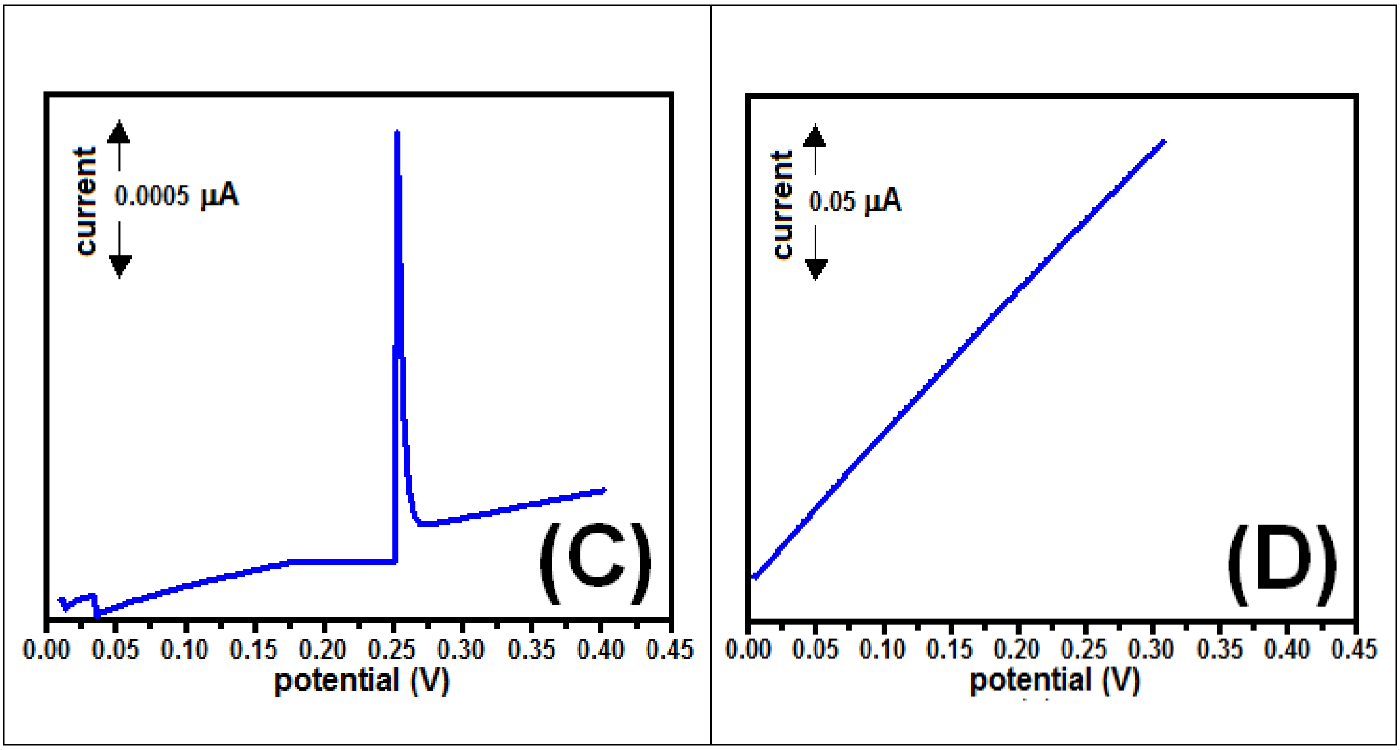


Figure 2. Linear sweep voltammetry. *(a) Comercial diesel; (b)Soya Biodiesel; (c) comercial mix Biodiesel; (d) Castor oil Biodiesel.*

From figure 2, it is also possible to estimate that even 0.3 V as amplitude perturbation in electrochemical impedance experiments can be used and system will be in steady state, which is a premise in this technique.

Linear voltammetry technique is important because it is possible to evaluate the electrochemical behavior of biodiesels, and to establish the potential range where we can operate the system and get better spectra, in only a few seconds and accurately.

3.1.2. Electrochemical Impedance Spectroscopy

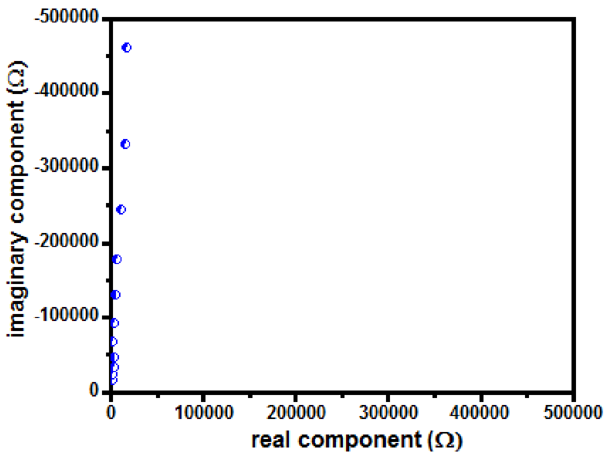


Figure 3. EIS results for biodiesel obtained from castor oil.

In figure 3 is shown EIS results for biodiesel obtained from castor oil. This spectra shape is typical for all samples, with values of impedance associated to each sample. The spectra are really different from reported by M´Peko et.al. [23], where well-defined semicircles were observed, authors consider that experimental conditions at present work are better because only the resistance of the biodiesel is observed; there is no influence of a second resistance associated to resistance to charge transfer.

As was awaited [22] and according to voltammetry results where no reactions were observed, impedances are too high, as big as 4 X 10^5 Ω for the low frequency range, and the spectra showed a predominant capacitive behavior in the Nyquist diagram. At the highest frequencies the resistance of the solution is contributing mainly to the total impedance, from these highest frequencies, considering real part at 20 kHz, resistance solution was estimated and used to calculate electrolytic conductivity for all samples.

Table 1. Electrolytic conductivity values obtained for different biodiesels.

Source of biodiesel	Electrolytic Conductivity (µS/cm)
Soja	3.87
Commercial oil, mix of several plants	3.53
Castor Oil	0.40
Fossil	5.00

These values are shown in table 1, where it is possible to note that biodiesel obtained from castor oil has the lowest electrolytic conductivity, which can be related with highest quality, in the sense of no salts or water content, materials that increase electrolytic conductivity. Regarding others biodiesels, electrolytic conductivity results indicate that they have good quality, specially if we compare against fossil diesel, probably because fossil fuel has metallic impurities that can be quantify with impedance.

Even more fundamental studied are needed, for example changes on water or salts content in biofuels and evaluate the electrochemical behavior, both linear sweep voltammetry and electrochemical impedance results indicate that electrochemical techniques can be useful to characterize biofuels, in a fast and accurate way.

4. CONCLUSIONS

An electrochemical cell was designed and built in order to measure electrolytic conductivity of different biodiesels that were synthetized *in-house* by following transesterification method.

Electrochemical techniques as LV and EIS can be used to characterize biodiesels. Biodiesel synthetized from castor oil is who obtained lower electrolytic conductivity, at least from biodiesels studied in this project.

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