Electrochemical Characterization of Biodiesel from Sunflower Oil Produced by Homogeneous Catalysis and Ultrasound

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Keywords: biodiesel; sustainable fuels; conversion; electrochemical; impedance; voltammetry; potential

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1. Introduction

Energy has always been the key driving force facilitating human and societal development; fossil fuels have been humanity's primary energy source in recent decades [1,2]. However, the massive consumption of fossil fuels prompted the exploration of renewable energy for sustainable development, including biofuel production [3–10]. As alternatives to gasoline and diesel, biodiesel and bioethanol are attracting increasing attention due to their advantages as renewable ecological energy sources [11–17]. Fuels stored in tanks undergo an aging process which particularly applies to fuels containing biocomponents. Therefore the ability to quickly assess changes taking place in energy is increasingly critical. Some studies on the application of electrochemistry in biodiesel [18–20]. Electrochemical impedance spectroscopy (EIS) has been tested in this regard; it facilitates a fast, easy, and continuous determination of gasoline and biodiesel quality, comparing results with physicochemical parameters that change rapidly during the ageing process [21]. EIS provides a fast and easy method to determine the water content (moisture) in biodiesel based on sensitivity variation in the medium's resistance to charge transfer (RCT) in the presence of different amounts of water. In certain studies of EIS in biodiesel, antioxidants were added to increase oxidative stability (ensuring fuel quality) electrochemically characterized by cyclic square wave voltammetry (SWV); the precision of the results was verified using high-performance liquid chromatography (HPLC) [22]. Previous studies of electrochemistry in biodiesel to identify tert-butyl hydroquinone (TBHQ) and propyl gallate according to Hoffmann et al. [23] or Cu^{2+}. Freitas et al. [24] used differential pulse voltammetry (VPD). Ultrasound-assisted transesterification was performed in waste cottonseed oil (WCSO) with ethanol; a maximum conversion of 98.7% was observed [25]. The advantages of these methods include a considerable reduction in reaction time and an increase in yield [14,26–28]. A few studies report biodiesel production from soybean oil using the ultrasound method. However, other reports in the literature applied this method to seeds other than cotton [29], Kumar et al. [30] used coconut oil to produce biodiesel and used jatropha cinerea seed oil. Innovative technology coupling emerged as an intelligent alternative to intensify the bioactive compound extraction process of vegetable substrates [31,32]. Ultrasound has been used to improve the heterogeneously catalyzed transesterification reaction for biodiesel production [33]. There are more than 15 parameters to characterize biodiesel, including density, viscosity, lubricity, high heating value, and chemical analysis. The only experiments involving electrochemical techniques are water content and acidity experiments. Generally, techniques such as Fourier transform infrared spectrometry (FT-IR), gas chromatography of fluids, and nuclear magnetic resonance (NMR) are used. There are also reports of dielectric spectroscopy being used to assess the quality of vegetable oils or identify adulteration [34]; in these experiments, vegetable oils are assessed with unique probes and specialized devices, such as electronic LCR meters that measure inductance, capacitance, and resistance. The oils' dielectric constant helps discriminate between different pure oils by estimating Cole-Cole parameters. Relaxation frequency indicates the presence of impurities. According to Man et al. [28], measuring with capacitive techniques in the kHz range can predict water content ranging from 0.03% to 0.13%; they also indicated that the impedance of oil properties is well described by its capacitive reactance, so a simple system that measures voltage and current can be used to predict some of the oil's chemical characteristics. Villarreal-Castellon et al. [20] indicate that an electrical measurement technique is helpful, although more studies are needed. Prevc et al. [35] according to a linear model, the relationship between the dielectric constant and different vegetable oils' conductivities decreases with temperature. Naranjo et al. [36] reviewed the use of bioimpedance methods as quality control systems for fruits and vegetables such as apples, bananas, kiwis, lettuce, tomatoes, and others. According to Salaheldeen et al. [37], it is apparent that bioimpedance spectroscopy is potentially helpful in detecting the electrical characteristics of fruits and vegetables, which can facilitate cleaner control systems. Naranjo et al. [36] reported using electrochemical impedance spectroscopy (EIS) to characterize a variety of vegetable oils. The impedance of their spectra and the equivalent circuit used showed that reactions took place in the system, probably due to salt or water content. However, they concluded that the technique could be applied as an analytical method to identify, monitor, and detect specific properties of biodiesels.

As a result of these studies findings, the authors decided to use electrochemical techniques, such as chronoamperometry, to evaluate open circuit potential (OCP), linear sweep voltammetry (LSV) to identify electroactive species, and electrochemical impedance spectroscopy (EIS) to quantify fuel resistance and charge transfer facility. All techniques, together, can characterize homemade synthesized biodiesel and compare it with fossil diesel. According to the literature, these techniques have not been widely used for this purpose. However, other applications have been noted: Sangarunlert et al. [38] used LSV to evaluate the catalytic activity of Pt-M/C to obtain optimum catalysts, used LSV to optimize the effect of temperature and thermal decomposition time concerning methanol oxidation; Ha et al. [39] used LSV for a combined effect of catholyte gap and cell voltage on syngas ratio in continuous CO_2/H_2O co-electrolysis; Garcia [40] chose EIS, among other electrochemical techniques, to study evolution reaction in polycrystalline rhenium; and preferred EIS and other methods to investigate the super capacitive behavior of a symmetrically fabricated nanocomposite electrode setup using aqueous KOH as the electrolyte [41]. This study's objective was to apply the techniques of open circuit potential, linear sweep voltammetry and electrochemical impedance spectroscopy using a potentiostat–galvanostat to characterize biodiesel; together, these measurements could be used as an alternative biodiesel evaluation method. To accomplish this, the transesterification reaction was carried out at two temperatures with sunflower oil and methanol, assisted by ultrasound, and potassium hydroxide as a catalyst for the improved production of biodiesel.

2. Materials and Methods

2.1. Materials and Reagents

Sunflower oil is composed of (wt.%) palmitic (6.2%), stearic (2.95%), palmitoleic (0.05%), oleic (17.35%), and linoleic (73.45%) fatty acids was obtained from a commercial brand. Analytical-grade reagents were used. Aqueous solutions were prepared with MilliQ water of 18.2 MΩ cm resistivity [42]. To roduce biodiesel, sunflower oil was prepared with potassium methoxide (CH_3OK), alcohol (anhydrous methanol) CH_3OH from Merck (Rahway, NJ, USA), max. 0.003% H_2O), and potassium hydroxide (anhydrous KOH from Meyer (Mexico City, Mex), ≥99.97%).

2.2. Biodiesel Production

Potassium hydroxide (KOH) (0.34 g per sample) was weighed and then dissolved in 12.5 mL of methyl alcohol in an Erlenmeyer flask; the resulting potassium methylate was mixed with sunflower oil (37.5 mL) to obtain a 50 mL volume [37]. This mixture was placed in an ultrasonic UP 200S device (Hielscher Ultrasonic Gmblt, Teltow, Germany). The ultrasonic process operated at 200 W and 24 kHz frequency with a Sonotrode S26d14 (Titanium sonotrode, 100 mm long with a 14 mm diameter) for 15, 30, 45, and 60 min each. Each test was carried out in triplicate at room temperature, 22 °C, and 50 °C. Samples were placed in a centrifuge (model IEC centrum CL2, Thermo Brand, (Kunshan, Jiangsu, China) at 3000 revolutions per minute (RPM) for 3 min. Later, the glycerin and biodiesel thus formed were separated and measured. The biodiesel was washed with water in a 1:1 ratio and then separated via centrifuge at 3000 RPM for 2.5 min. The washing process was duplicated. Subsequently, the experimental data for each sample's conversion, performance, and physicochemical analysis were obtained; these were statistically processed in Excel using Microsoft 365 software, getting the arithmetic mean and standard deviation. Figure 1 shows the process for obtaining biodiesel on a small scale using the following equipment: an ultrasonic actuator, which is an ultrasonic device with a positive pressure module to measure probe and flow rate (200 W at a 24 kHz operating frequency); an energy meter and electric power; a 20 L processing tank; a 1.5 kW heating element; a premixed 2 L catalyst tank; a catalyst premix stirrer; a 1.0 HP centrifugal pump with variable speed drive to control the mixture's flow toward the ultrasound; a back pressure valve to adjust the pressure in the flow cell; and a supply pressure gauge. The processing and premix tanks were composed of high-density polyethylene. The setup contained a centrifuge to separate the biodiesel from the glycerin and mix it with water for washing.

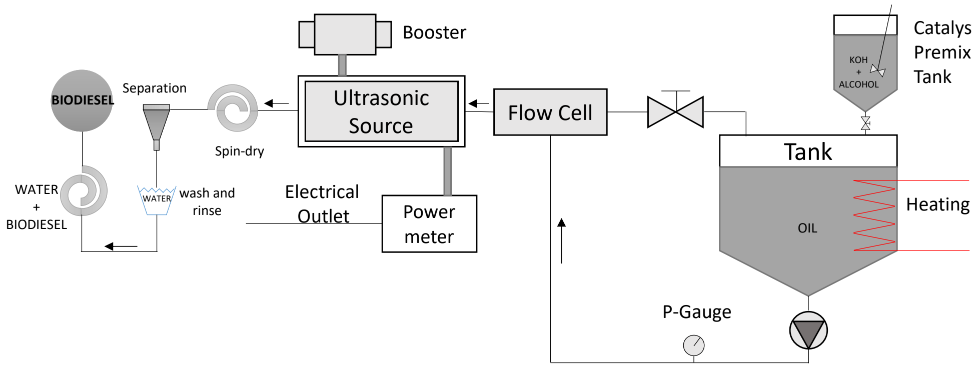

Figure 1. Ultrasound biodiesel generation process.

2.3. Physicochemical Analysis

This study determined biodiesel's acidity index, viscosity, and density following International Organization for Standardization (ISO) standards 660, 3104, and 3675 [43]. The biodiesel density used was evaluated according to the American Society for Testing and Materials (ASTM) D4052 international standard; results are expressed in grams per cubic centimeter. This standard establishes a density range of 0.860–0.900 g cm^{-3} at 15 °C. The kinematic viscosity at 40 °C was based on the ASTM standard D613 and expressed in $mm^2\ s^{-1}$. The acid number was determined using volumetric titration with KOH 0.05 N to identify the KOH quantity necessary to neutralize free fatty acids (defined as oleic acid) in 1 g of sample. The percentage of triglyceride conversion was determined using reversed-phase high-performance liquid chromatography with an ultraviolet (UV) detector at 205 nm. A Zorbax 300 SB C18 4.6 × 150 mm column was used for this analysis, with a 1 mL/min flow rate. The high-performance liquid chromatography test was performed on an Agilent 1100 HPLC system (Germany), which included G1315A DAD, G1316A Col-Comp, G1329A ALS, G1311A QuatPump, and G1322A. A degasser and reservoir tray were required to process the data and a Windows computer with Chemistation version 15 software. To determine the biodiesel's triglyceride profile, 38 μL of biodiesel and 962 μL of hexane mixed with 2 propanols (4 parts hexane and 5 parts of 2 propanols) were added to 1 cc bottles with screw caps explicitly manufactured for use in HPLC equipment. The area difference between triglycerides in oil and biodiesel yields their conversion percentage.

2.4. Electrochemical Tests

Samples obtained at 50 °C were selected to evaluate the stability of the material [44,45] using open circuit potential, linear sweep voltammetry, and electrochemical impedance spectroscopy. For a point of reference and comparison, a commercial fossil diesel (PEMEX brand) obtained from a gasoline station in Queretaro, Mexico, was used. All samples were stabilized to room temperature for 45 min previous to measurement. No additional preparation procedure was used; all experiments were carried out at room temperature in a glass electrochemical cell configured with two electrodes and a 12 mL capacity with a compartment constant of 0.012 cm^{-1}. Because no electrochemical reactions are expected, and trying to built a non-expensive cell, the electrodes used were constructed using 304 stainless steel sheets. The experiments were carried out using a Gamry potentiostat–galvanostat (Reference 3000 model, manufactured in the USA) and using Gamry Framework software.

Electrochemical Techniques

The open circuit potential measurement indicates the electric potential at which the system is stable without any external disturbance; in this condition, oxidation and reduction rates are equal, resulting in zero net currents. This was maintained for five minutes to confirm whether the system was evolving. The linear sweep voltammetry technique was used to identify electroactive species in biodiesel and fossil diesel. Potential sweeps were carried out from the open circuit potential to both anodic and cathodic potentials. These experiments were done to ±1.0 V from the open circuit potential of each sample at a sweep speed of 2 mV s^{-1}. Range of potential was selected considering that 1 V from open circuit potential is enough to observe main reactions in electrochemical systems [33]. Sweep rate was selected to make the results comparable to those of the electrochemical impedance test, which must be carried out in the stationary state. Electrochemical impedance spectroscopy (EIS) measurements were performed from 30 kHz to 1 Hz intervals with 7 points per decade, and applying a sinusoidal disturbance of 200 mV RMS; this disorder allowed experimentation in the steady state and also disturbed the system sufficiently to be observable using the potentiostat. Each system was allowed to stabilize for five minutes before making measurements.

3. Results and Discussion

3.1. Physicochemical Characterization

Table 1 shows the ultrasound transesterification results for 0.34 g potassium hydroxide per sample performed at 22 °C, as described in Section 2.2. The conversion percentage, X (%), represents the region where triglyceride-free glycerin plus bound glycerin is found in the form of monoglycerides and diglycerides that are partial products of the conversion reaction of triglycerides to methyl esters. However, in 15-minute tests, the density percentage was slightly above European Standard (ES) 14214.

Table 1. Results of transesterification at 22 °C.

S. num = Sample Number	**t = Time**	**BD = Biodiesel Density**	**KV = Kinematic Viscosity**	**AI = Acidity Index**	**X = Conversion of Triglycerides**	**POY = Percentage of Oil Yield**
		15 °C (g cm^{-3})	**40 °C (mm^2 s^{-1})**	**(mg KOH g^{-1})**	**(wt.%)**	**(wt.%)**
1	15	0.91 ± 0.01	4.92 ± 0.12	0.42 ± 0.05	97.79 ± 0.05	63.04 ± 0.25
2	30	0.88 ± 0.02	4.64 ± 0.11	0.40 ± 0.02	98.96 ± 0.04	65.32 ± 0.35
3	45	0.87 ± 0.02	4.49 ± 0.10	0.37 ± 0.03	99.12 ± 0.03	66.42 ± 0.73
4	60	0.86 ± 0.02	4.285 ± 0.09	0.35 ± 0.03	99.23 ± 0.03	68.03 ± 0.49

Table 2 shows ultrasound transesterification results at 50 °C. For the first 15-minute test sample, the triglyceride conversion percentage, X(%), was greater than 99%, achieving a 0.89 g cm^{-3} density parameter and 4.17 mm^2 s^{-1} kinematic viscosity; both values are within ES 14214.

Singh et al. [43] demonstrated that using ultrasound transesterification in a batch reactor, a biodiesel yield of more than 99% can be achieved by observing a high decrease in reaction time and remarkable conversion efficiencies in a short reaction time. Furthermore, as the percentage (by volume) of glycerin produced increased as the test time increased, more biodiesel, with increased purity, was generated. The best result was obtained at 60 min, with a 0.85 g cm^{-3} density. Meanwhile, Pukale et al. [46] reported a 92% of biodiesel yield obtained in 90 min of reaction time.

Table 2. Results of transesterification at 50 °C.

S. num = Sample Number	**t = Time**	**BD = Biodiesel Density**	**KV = Kinematic Viscosity**	**AI = Acidity Index**	**X = Conversion of Triglycerides**	**POY = Percentage of Oil Yield**
		15 °C (g cm^{-3})	**40 °C (mm^2 s^{-1})**	**(mg KOH g^{-1})**	**(wt.%)**	**(wt.%)**
1	15	0.89 ± 0.01	4.17 ± 0.11	0.22 ± 0.05	99.519 ± 0.04	75.70 ± 0.71
2	30	0.87 ± 0.02	4.04 ± 0.08	0.17 ± 0.03	99.61 ± 0.04	84.14 ± 0.65
3	45	0.86 ± 0.02	3.89 ± 0.08	0.16 ± 0.03	99.67 ± 0.02	91.17 ± 0.38
4	60	0.85 ± 0.02	3.79 ± 0.08	0.15 ± 0.05	99.79 ± 0.01	93.40 ± 0.09

Figure 2 shows the percentages of biodiesel generated during the ultrasound transesterifications at 22 °C and 50 °C. Although the percentage of biodiesel indicated by the red line varies, it is always within acceptable parameters according to ES 14214. The highest biodiesel quality obtained by weight was 93.4 wt.% which represents 6.6 wt.% glycerol which is slightly lower than the data reported by Chilakamarry et al. [17].

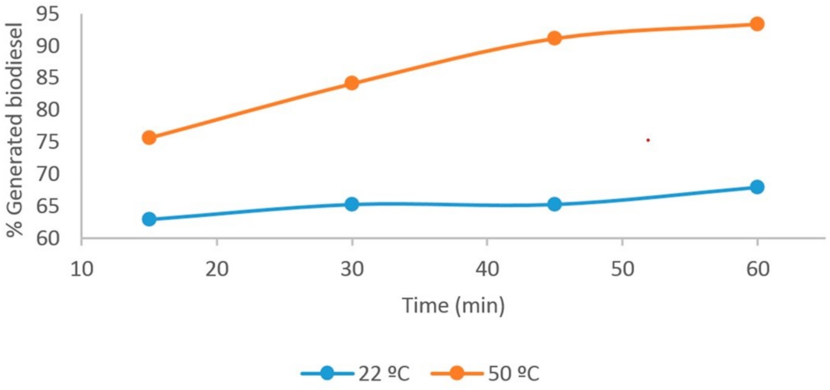

Figure 2. Percentages of biodiesel generated.

The concentration of methyl ester (conversion to biodiesel) and the relative amount of methyl ester concerning oil in biodiesel (yield) during homogeneous transesterification of sunflower oil catalyzed with KOH at 65 °C by Gemma Vicente et al. [37,47] was 99.76 ± 0.05, and 91.67 ± 0.27, respectively [37]. These results are similar to ultrasound results at 50 °C, with a 99.79% conversion and 93.40% yield, as shown in Table 2. Ha et al. [39] used a low-frequency ultrasonic reactor (20 kHz) with 200 W of ultrasound power for 40 min; they obtained an 89.5% conversion to fatty acid methyl esters (FAME) with a methanol/oil molar ratio of 6:1, 1% (by weight) of KOH, and a reaction temperature of 45 °C [37,48], as shown in Table 3.

Table 3. Vegetable oil parameters of the ultrasound-assisted transesterification process at 200 watts.

Vegetable Oil	Ultrasonic Power (W)	Frequency (kHz)	Ultrasound Time (min)	Temperature in °C	Molar Ratio Methanol/Oil	KOH Catalyst (wt.%)	Conversion (%)	Reference
Waste cooking	200	20	40	45	06-ene	1	89.5	[49]
Sunflower	200	24	60	50	06-ene	1	99.79	This study

This study used the same power, methanol/oil molar ratio, and wt.% KOH as Hingu et al. [48]. In this study, frequency, ultrasound time, and temperature were increased by 4 kHz, 15 min, and 5 °C, respectively, resulting in a 99.79% conversion. Homogeneous catalysis studies have been carried out recently [37] using different raw materials. Such is the case of Andreo et al. [1] who used pigfat and methyl alcohol (MeOH) as solvent obtaining a conversion to biodiesel of 99%, on the other hand Yuliana et al. [49] obtained a conversion of 98.9% using ethyl alcohol (EtOH) and leather tranning waste as raw material; these results are slightly lower than those obtained in this study using ultrasound.

3.2. *Electrochemical Characterization*

3.2.1. Open Circuit Potential

Figure 3 shows the behavior of the open circuit potential for all systems. It is possible to see that in all conditions, the system is rapidly stabilized; before approximately 120 s, the system achieved equilibrium for all samples. This indicates that there are no complex electrochemical reactions that require more time, nor complex mechanisms with difficult rearrangement of loads in the double layer. It is reported that a more complex system needs a longer time to stabilize the system. It is possible that even days after, the system is still evolving [50]. In this case, because of the short time required to stabilize, it can be inferred that no reactions occurred at the interfaces but must be demonstrated by linear sweep voltammetry, regarding electrical. Potential stabilized, values of approximately −30 mV for sample 1, −250 mV for sample 2, −790 mV for sample 3, −690 mV for sample 4, and −2000 mV for the commercial sample were obtained. These results indicate a relatively high potential drop for samples 2, 3, and 4. Theoretically, when using two electrodes of the same nature, there should be no potential difference between electrodes, as occurred in sample 1. For sample 1, it is possible to assume that it contains species that contribute to electrolytic conductivity. However, for samples; 2, 3, and 4, it is possible to infer that they contained fewer electroactive species, which increased the charge resistivity step. Regarding commercial samples of fossil diesel, it is possible to indicate that they contain ever lower electroactive species, leading to almost three times the drop potential. Despite not a significant number of studies reported, these results are significantly different than those obtained for commercial diesel and are probably due to hydrocarbon components that provide higher electrolyte resistances. These results were expected; the literature [51,52] reports hundreds of mV of difference and a few minutes required to stabilize the system.

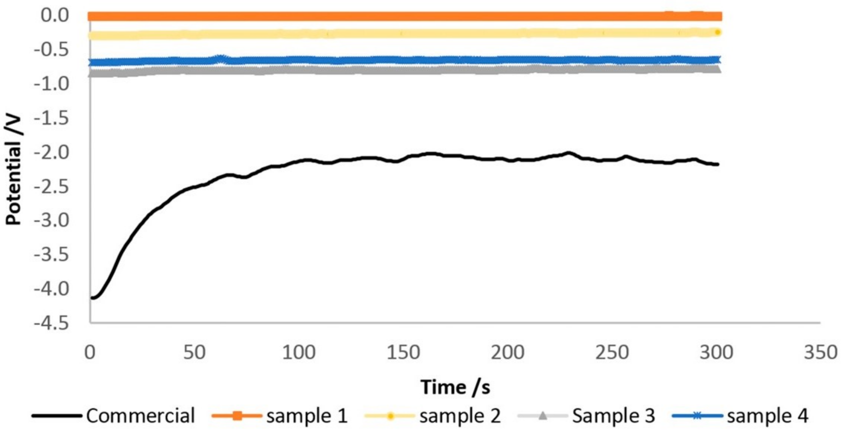

Figure 3. Open circuit potential was observed in the system.

3.2.2. Linear Sweep Voltammetry

Figure 4 shows linear sweep voltammetry results. Both anodic and cathodic scans were studied up to 1.0 V, and the current was in the order of the nano Ampere; this can be attributed to impurities or electroactive elements that remained after the synthesis process. This result was expected, as it has been reported that fuels, such as biodiesel, do not present characteristic reaction peaks in similar potential windows [51,52]. For sample 1, is it possible to see the highest values, as expected, because in the open circuit potential experiment, very low resistance was observed. Voltammograms for samples 2, 3 and 4 are very similar, with very low currents densities. Voltammograms of the commercial sample indicate even smaller current values, which is in line with expectations, as this sample contains substances that are even more inert or less electroactive.

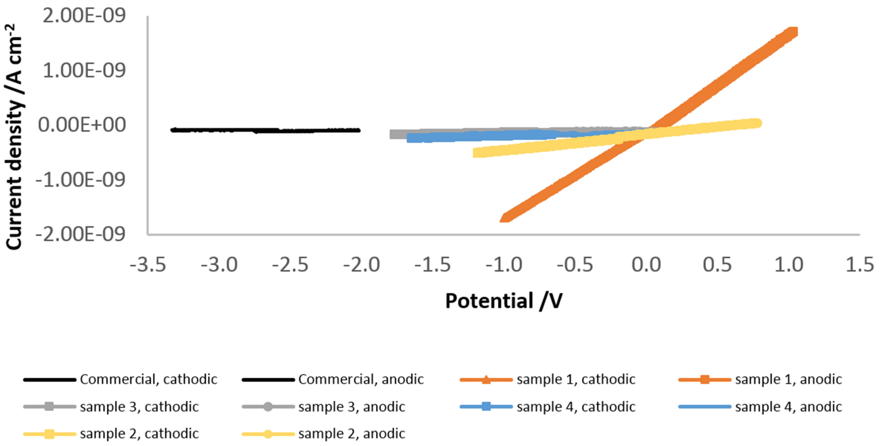

Figure 4. Voltammetry of biodiesel and fossil diesel systems. Sweep speed 2 mV s^{-1}.

It has been reported that for some natural oils, current density are in the order of μA/cm^2, which is three orders of magnitude higher than our systems [53,54]. This result is significant because it can help characterize biofuels, fuels, or oils obtained from natural and artificial sources. NanoAmpere can be used as a reference level in current density for this kind of material.

3.2.3. Electrochemical Impedance Spectroscopy

Nyquist diagrams for each synthesized biodiesel and commercial fossil diesel are shown in Figure 5.

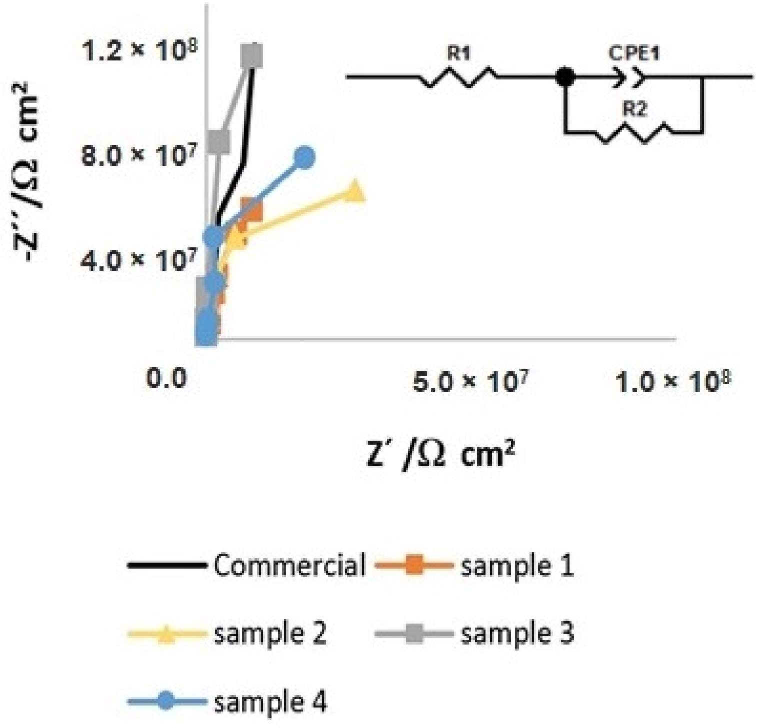

Figure 5. Electrochemical impedance spectrum and equivalent circuit used to fit experimental data.

Regarding spectra, the equivalent circuit shown in Figure 5 was used to develop fitting by using the Levenberg–Marquardt algorithm, which reached a chi-squared of 0.08 at the worst condition, indicating a good fit Figure 5 depicts a capacitive system for all cases, with very high impedances in the order of MΩ cm^2 at a low-frequency range. Using impedance spectroscopy allows us to distinguish between biodiesel, diesel, and their pseudo-binary combinations in the low-frequency range [55]. At the high-frequency range, diesel resistance is the most significant contributor to impedance, which is of interest regarding biodiesel characterization. In the intermediate frequency range, capacitive impedance is the most important contributor to the whole system; that information is useful for evaluating the capacitive capacity of the material. Finally, at the lowest studied frequencies, charge transfer resistance can be estimated, and get information about how easy is for the system to perform electrochemical reactions. In the circuit, this diesel resistance (R1) is in series with resistance to charge transfer related to electrochemical reactions (R2) and paralleled with the constant phase element (CPE1), representing non-ideal double-layer capacitance. The solution resistance attributed to diesel resistance (R1) and the charge transfer resistance related to electrochemical reactions (R2) obtained from fitting in all conditions is shown in Figure 6.

Figure 6 illustrates that the diesel solution was at a 10^5 Ω cm^2 order of magnitude in all cases. This indicates that all samples were highly resistive, without conductive species. Additionally, the secondary axis shows that charge transfer resistance was very high in all cases; values of 10^8 Ω cm^2 confirm voltammetry results where electroactive substances were not identified. Systems with electroactive species are reported to have charge transfer resistance in the order of 10^3 Ω cm^2 [36]; under different measurement conditions, such as changing exposure time, it can be as high as 10^9 Ω cm^2 [19,51]. That information can also help characterize biofuels and other similar materials. Even measuring at one single frequency can give an idea about the electrochemical composition of materials, similar to electrolytic conductivity meters.

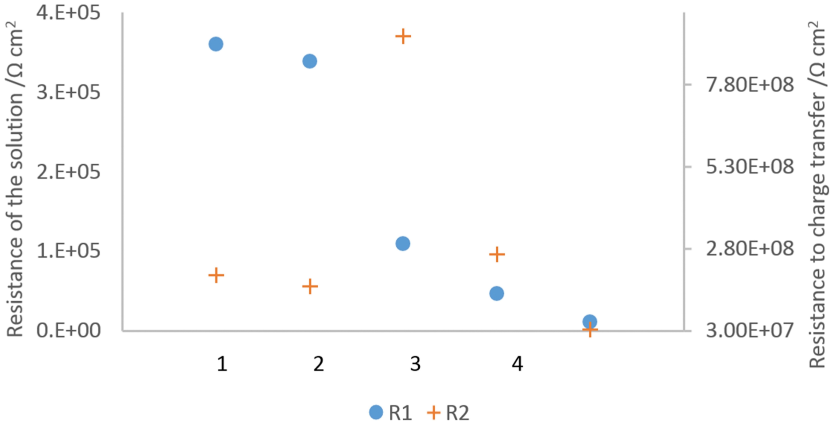

Figure 6. Sample resistance Diesel and charge transfer resistance for samples 1–4 and commercial (5) were obtained from fitting.

4. Conclusions

The results of this study indicate that biodiesel's efficiency and physicochemical characteristics change due to exposure time and temperature when the energy source is assisted by ultrasound, maintaining constant electrical power and frequency. However, if we keep the system at room temperature and increase the exposure time to more than 60 min with ultrasound, we could obtain the conversion of triglycerides to biodiesel with a similar efficiency to when the temperature was increased to 50 °C in 15 min. For industrial biodiesel production, where what is sought is greater production in less time, one could think of increasing the reaction temperature using clean energy. In the techniques used OCP, LSV, and EIS techniques to evaluate the characteristics of biodiesel, it is evident that stabilization time is lower to two minutes, which indicates that the electrochemical double layer is quickly organized. Also, it was observed that at least at the potential range analyzed. There are no electrochemical reactions, which are confirmed by impedance results, with high resistance values in solution and charge transfer, in the order of 10^5 and 10^8 Ω cm^2, respectively.

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