Jurnal
Teknologi

Full Paper

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR PALM COOKING OIL DISCRIMINATOR USING PLANAR ELECTROMAGNETIC SENSOR ARRAY

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Received
15 December 2015
Received in revised form
30 March 2016
Accepted
30 May 2016

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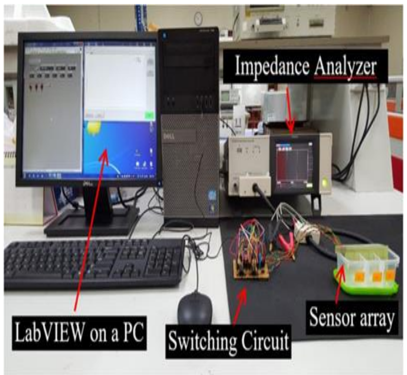
Graphical abstract



Abstract

Cooking oil is an important product in the Malaysia food industries. Most of the cooking oil products is based on palm oil. However, there are activities in selling cheaper cooking oil by labelling as high quality in cooking oil product. Traditional methods have been developed to measure the quality of the cooking oil product such as the chromatography technique but the cost for the system setup is expensive and requires a large amount of time to analyse the sample. Thus, a suitable and reliable system with less analysis time is needed for widespread industrial uses. This paper has presented a discriminative technique for palm cooking oil using Electrochemical Impedance Spectroscopy (EIS) with planar electromagnetic sensor array. The sensor consists of a meander sensor and an interdigital sensors which interact with the test samples. Three types of palm cooking oil such as double refined palm oil, refined and deodorized palm oil with peanut and sesame oil, and filtered palm oil were prepared. The results obtained showed that the presented technique was able to differentiate the samples between 20 kHz to 1 Mhz. The results obtained correlate with the theories on EIS technique and planar electromagnetic sensor which are presented in this paper.

Keywords: Palm cooking oil, EIS technique, discrimination, planar electromagnetic sensor

1.0 INTRODUCTION

Palm oil is the major cooking oil in Malaysia. Various kind of palm cooking oil products have been produced by the industries. However, some of them are prone to sell a low quality of palm cooking oil in order to gain profit [1]. Therefore, a discriminator is needed to prevent this negative activity from affecting the consumers.

Most of the classical techniques that have been developed by the researches for measuring the cooking oil quality is based on the ion concentrations of a solution such as Gas Chromatography (GC) [2] and High Performance Liquid Chromatography (HPLC) techniques [3]. These techniques separate the ions in the solution using pressurization by injecting the solution samples into a column pipe and adding a specific chemical reagent to interact with the ions in the sample [4]. Then, the concentration of the ions are determined using the retention time measured by chromatograms.

Although the chromatography techniques give a sufficient information regarding the concentration of ion but the cost for the system setup is expensive and complex [5]. Furthermore, a professional machine handler is needed to handle the instruments [6] plus a strict laboratory environment to conduct the experiments [7]. Thus, a reliable and high sensitivity system with less amount of time for analyzing the samples is important.

This paper presents a system to discriminate three types of palm cooking oil products in Malaysia using Electrochemical Impedance Spectroscopy (EIS) technique and planar electromagnetic sensor with parallel configuration as the sensor tool. The theories about EIS technique and planar electromagnetic sensor will be covered.

2.0 IMPEDANCE SPECTROSCOPY

Electrochemical Impedance Spectroscopy (EIS) is a technique that utilized a fringing built sensor to determine the conductive profile from the material sample using the output response from the impedance spectrum as a result of applying an external electrical and magnetic field that circulates through the sample [5], [8]. EIS technique are applied in several applications such as non-destructive testing [9], and phthalates detection [10] because of its advantages. For example, it used a single side access sensor for detection tool and provides on-site measurements which reduces analysis time [5], [9].

Theoretically, EIS provides information regarding the changes of the parameters in the electrochemical properties of the material by analyzing the impedance spectrum based on Randall's circuit which contains resistances, capacitances and inductance. Typically, the equivalent circuits are differ to the geometry of the sensor. Subsequently, the permittivity and conductivity of the material sample can be calculated by relating the impedance equation from the equivalent circuit with equations (1) and (2) which are defined as [11]:

$$R_E = d/\sigma A \qquad (1)$$

where R_E is the resistance of the material sample, d is the thickness of the sample between electrodes, A is the electrode geometry of the area A in which current is carried, and σ is the conductivity of the cooking oil sample. The capacitance of the material sample, C_E, is expressed as:

$$C_E=\varepsilon_r\varepsilon_o A/d \qquad (2)$$

where ε_r is the relative permittivity of the sample, and ε_o is the constant permittivity of a vacuum. Moreover, the complex terms of impedance obtained are represented in Bode or Nyquist plots [5] in terms of real and imaginary values with respect to the applied frequencies as shown in Figure 1.

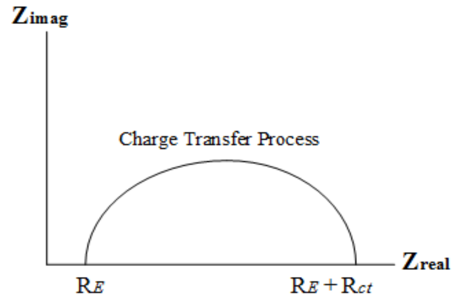


Figure 1 The example of Nyquist plot using the impedance complex terms

3.0 PLANAR ELECTROMAGNETIC SENSOR

A planar electromagnetic sensor is a device for detecting the dielectric properties such as conductivity and permittivity of material under test. It also known as an impedance characteristic sensor which can be categorized as three different types of sensing such as capacitive sensing, inductive sensing, and passive sensing [11]. Normally, a planar electromagnetic sensors are built using dielectric or magnetic materials and interacts with the material samples to provide information regarding dielectric properties of the samples based on the response in the impedance spectrum.

Several investigation have been carried out using planar electromagnetic sensors as detecting mechanism such as water contamination detection [12]–[15], and biological cell detection [16] since the cost of fabrication these sensors is inexpensive. However, the understanding about the behavior of planar electromagnetic sensor were not fully explained. Therefore, the following subsections describe the planar electromagnetic sensors detection mechanism:

3.1 Structure of Planar Electrodes

The planar electromagnetic sensor was designed as a passive type sensing structure where the top surface of the planar sensor is a combination of a meander sensor and an interdigital sensor with series-connected, printed on a FR-4 substrate [15] as illustrated in Figure 2. There are five square meander loops in the planar sensor with a size of 20 mm × 20 mm. The outer loop and the inner loop are placed with a distance of 0.5 mm between each other. Moreover, the planar sensor had five positive electrodes and four negative electrodes on the interdigital sensor parts with the width of both working and references electrodes were set at 0.5 mm and 1.0 mm, respectively.

The width of the negative electrodes are wider than the positive electrodes which improved the overall response of the sensor [15]. On the other hand, the ground plate of the sensor is placed at the bottom surface of the planar sensor under the interdigital sensor with a dimension of 8 mm × 10mm.

The value of inductance L for the planar electromagnetic sensors can be approximated by using the following expression:

$$L = 1.39 \cdot 10^{-6}(OD + ID) \cdot N_L^{5/3} \cdot log\left(4 \cdot \frac{OD+ID}{OD-ID}\right) \quad (3)$$

where OD and ID represent the outer and inner diameter of the meander sensor in meter, while N_L is the number of meander loops. The presence of L enables the observation of the response variation of capacitance impedance at high frequency when the capacitance impedance began to change becoming an inductance impedance in the impedance spectra.

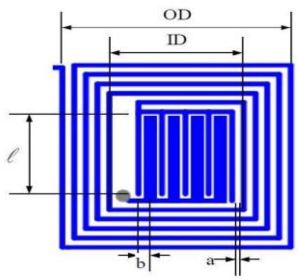


Figure 2 The structure of planar electrodes on the top surface of the planar sensor

The understanding about the interaction between the capacitance and the conductivity of the liquid solution are also needed. The cross-section of the planar electromagnetic sensor electrodes is illustrated in Figure 3. The liquid solution has their own capacitance and resistance namely C_E and R_E, respectively. Then, the coating layer protects the surface of the planar sensor and forms a constant capacitance known as a double layer capacitance, C_{dl}. The double layer capacitance relies on the surface area of the conductive copper lines [16].

Meanwhile, the resistance which is parallel connected to C_{dl} is known as a charge transfer resistance, R_{ct}. The resistance, R_{ct} depends on the rate of charge transfer of the electric and chemical potential that charge the interfaces [17]. Hence, it allows the reacting elements to be transported between the whole electrolyte and the interfacial reaction region.

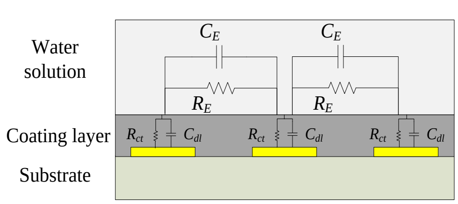


Figure 3 The physical representation of the planar electromagnetic sensor electrodes which consists of solution capacitance and resistance, C_E and R_E respetively, C_{dl} as a double layer capacitance and R_{ct} as a charge transfer resistance

3.2 The Development of Sensor Surface-Solution Interface

There are effects in ionic adsorption when the sensor is immersed into the liquid solution and give an impact on the liquid dielectric properties. When an external electric field is applied to the sensor, the electric dipoles in the liquid solution are attracted to the sensor interfacial area thus the dipoles re-alignment will occur. Hence, the effect of the external field is neutralized partially. However, this re-alignment is different depending on the tested materials. Therefore, the dielectric and magnetic responses in the frequency spectrum will be different and distinctive.

The charge from separated re-alignment dipoles influence the changes in capacitance of the liquid solution, C_E at the bulk liquid area. Thus, the charged surface formed between the coating layer and the liquid solution in the interfacial region will establish a double layer capacitance, C_{dl}. This layer were known as an electrical double layer (EDL) [11].

There are also an effect in the mobile ions with the influence of an external electric field. The existence of the liquid solution resistance, R_E is due to the movement of ion current in bulk liquid area by the influence of an external electric field. The charge transfer resistance, $R_{ct}$is from the kinetics of absorbed of desorbed in the interfacial region which vary as the properties in the bulk liquid area change [11]. As a result, a double layer capacitor was established as $R_{ct}$and C_{dl} are combined.

As for the external magnetic field from the meander sensor, a closed flow of electric current inside the medium will be induced. These electric current circulation can be referred as magnetic dipoles. The interaction between the generated magnetic field and external magnetic field depends on the type of mobile ions.

3.3 Planar Electromagnetic Sensor Equivalent Circuit

Figure 4 shows the equivalent circuit model corresponding to the planar electromagnetic sensor. The impedance circuit for the planar electromagnetic sensor in Figure 4 consists of the inductance of the planar coil, L, the capacitance of the liquid sample C_E and the resistance R_E of the liquid sample. C_{dl} and R_{ct} are the double layer capacitance and the charge transfer resistance, respectively. Lastly, C_c indicates a constant parasitic capacitances. Therefore, the circuit can be described as follows:

$$Z = j\omega L + \frac{\frac{1}{j\omega C_c}\left(\frac{R_E}{1+R_E j\omega C_E} + \frac{R_{ct}}{1+R_{ct} j\omega C_{dl}}\right)}{\frac{1}{j\omega C_c} + \left(\frac{R_E}{1+R_E j\omega C_E} + \frac{R_{ct}}{1+R_{ct} j\omega C_{dl}}\right)} \quad (4)$$

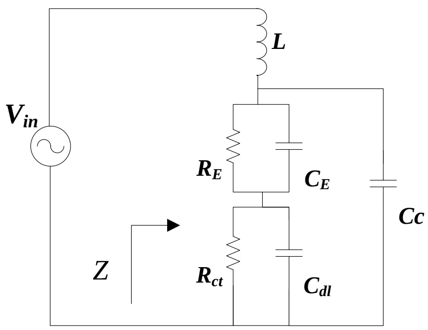


Figure 4 The equivalent circuit model for the planar electromagnetic sensor

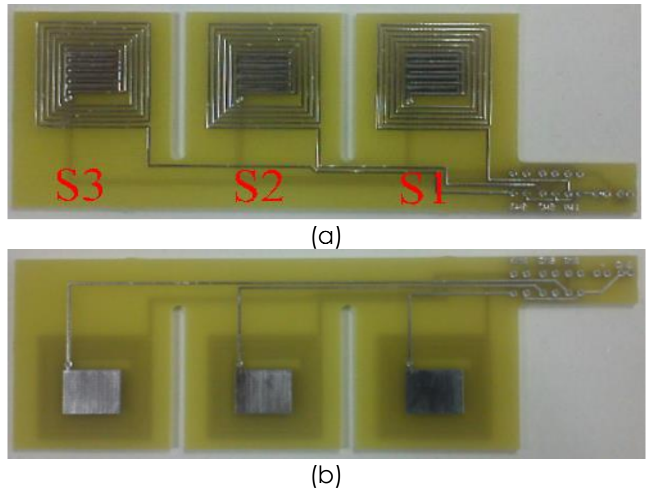


Figure 5 (a) Top surface of the planar sensor array (b) bottom surface of the planar sensor array

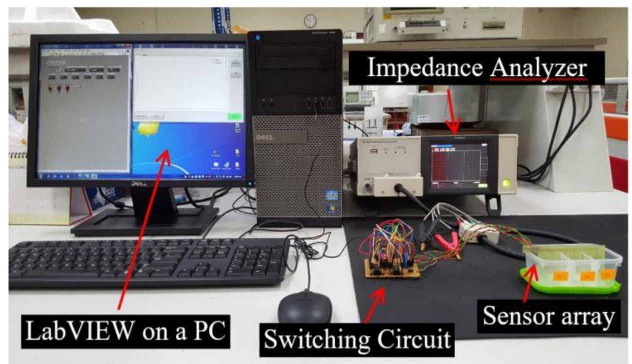


Figure 6 Experimental setup for palm cooking oil impedance measurements

4.0 EXPERIMENT

This section covers the cooking oil samples preparations, setups and procedure for impedance measurement in palm cooking oil discrimination.

4.1 Samples Preparation

Three types of market palm cooking oil samples were used such as double refine palm cooking oil, refined and deodorized palm cooking oil with peanut and sesame oil, plus a packed of filtered palm cooking oil. One liter of volume were prepared for each of the cooking oil samples. The cooking oil samples was filled into a custom-made container that consists of three separated oil columns. Each of the column contained one particular type of cooking oil sample as configured in Figure 7.

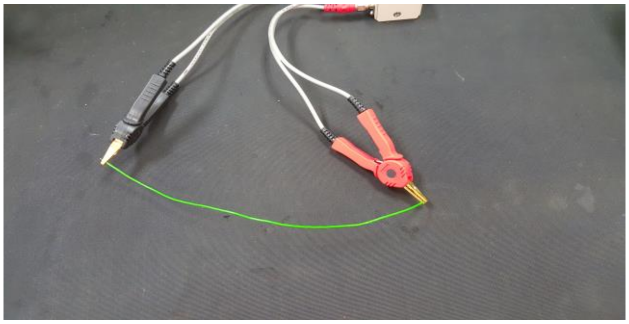
4.2 Experimental Setup

The experimental setup for cooking oil impedance measurement is shown in Figure 6. A fabricated planar sensor array of the top and bottom layer is shown in Figures 5(a) and (b) which consists of three identical planar electromagnetic sensor namely S1, S2 and S3 parallel connected to each other. For measuring the output impedance of the sensor array, the Hioki IM3570 impedance analyzer was used and interfaced with the LabVIEW software for data collection.

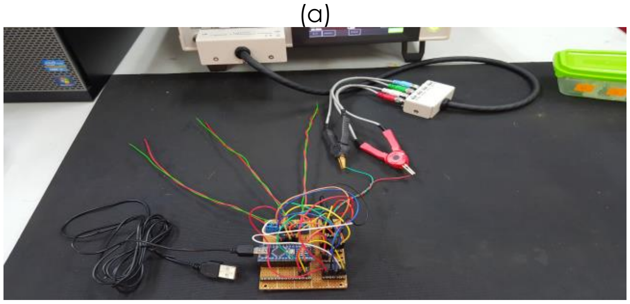
An Arduino Nano microcontrollers controls the switching process of the switching circuit to ensure that the planar electromagnetic sensor array measures only one specific oil column during the impedance measurement as the impedance analyzer has only one input channel.

4.2 Impedance Measurements

Before conducting the impedance measurements, calibration was carried out to take into account the impedance of the switching circuit and the resistance of the sensor cables to ensure that the measurement is accurate. Figure 7(a) shows one of the sensor cables with a length of 230 mm was measured by an impedance analyzer to determine the resistance of the cable. All of the sensor cables were cut with the same length. Moreover, the impedance of the switching circuit with the connected sensor cables were also measured at two condition which are operational and non-operational state. This calibrations was to observe the noises of the switching IC when the switching board is operated. The calibration for the switching board is illustrated in Figure 7(b).



(a)



(b)

Figure 7 (a) Calibration for the sensor cable (b) the switching circuit calibration with the connected sensor cables

For the impedance measurement procedures, the planar electromagnetic sensors array were immersed in the filled separated oil columns as shown in Figure 8. S1, S2 and S3 were assigned to double refined palm oil, refined palm oil with peanut and sesame oil, and filtered palm oil, respectively. Then, an impedance analyzer was set at a constant 5 Vpp sinusoidal signal with a frequency sweep of 10 kHz to 1 MHz with 267 data points per decade on log scale. To ensure the repeatability and reliability of the results, 20 sets of impedance measurements were taken per each oil column. Then, an average of the datasets for each oil columns was graphically presented.

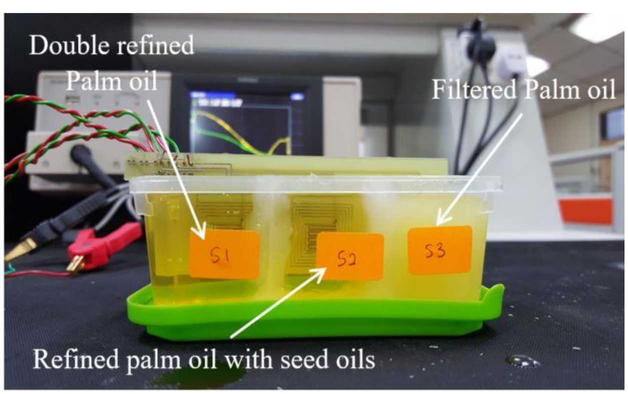


Figure 8 Palm cooking oil samples preparation with the planar sensor array immersed in the seperated columns

5.0 RESULTS

The results for the 20 datasets of the double refined palm oil measured using S1 are graphically shown in Figure 9. The impedance begin to drop dramatically when the frequency increases from 20 kHz and saturated when above 420 kHz. On the other hand, the phase response in Figure 9(b) shows a strong capacitive characteristic between 20 kHz and 450 kHz. However, the capacitive characteristic drops and begin to be more inductive when the frequency is above 450 kHz.

The overall response for discriminating three types of palm cooking oil are plotted in Figure 10 which shows the impedance and phase responses. However, in order to simplify the comparison, the equivalent circuit in equation (4) was referred. The reduction in the interfacial impedance can be observed between 20 kHz and 220 kHz even though the impedance on the interfacial region ($R_{ct}$and C_{dl}) is relatively less than the impedance on the bulk solution area ($R_E$and C_E).

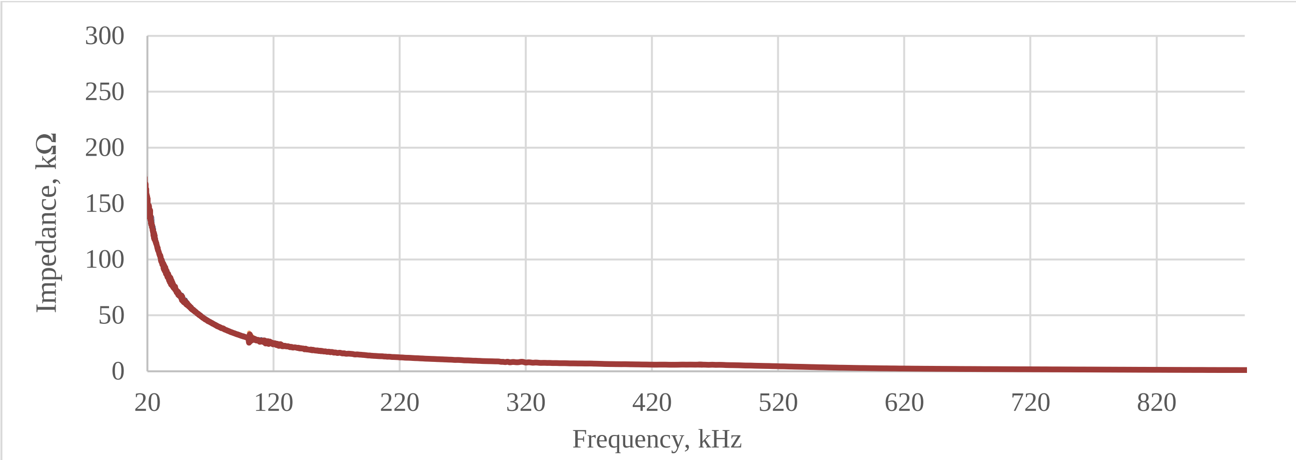
Thus, to correlate the palm cooking oil samples with the conductivity and permittivity, equations (1) and (2) are used in which the samples with a lowest impedance response has the highest conductivity, σ. Therefore, the double refined palm cooking oil shows the lowest impedance response between the frequencies of 50 kHz and 220 kHz as shown in Figure 10. Furthermore, the difference in relative permittivity, ε_r response of the samples also can be observed on the phase graph in Figure 11 between the frequencies of 120 kHz and 520 kHz. Hence, it shows that the planar electromagnetic sensors were able to differentiate the samples specifically in the impedance and phase responses.

6.0 CONCLUSION

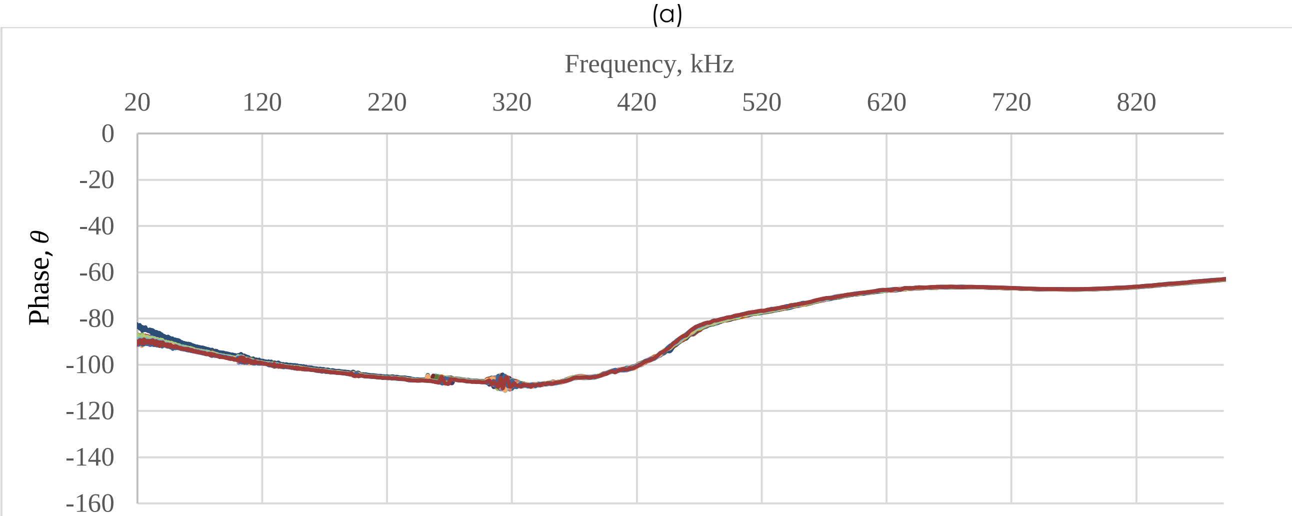
This paper has proved that there are possibilities in discriminating several types of palm cooking oil samples using the EIS technique and planar electromagnetic sensor based on impedance and phase representation between the frequency ranges of 20 kHz and 420 kHz. Moreover, this paper also shows that the EIS technique succeeded in reducing the experimental cost with less complexity using low-cost sensor fabrications.

Acknowledgement

The authors would like to acknowledge the financial assistance from the Fundamental Research Scheme Grant (FRGS) from the Ministry of Higher Education Research (MOHE) Malaysia (Vote No. 4F594) and in part in by the Science Fund through the Ministry of Science, Technology and Innovation Malaysia (Vote No. 03-01-06-SF1216).



(a)



(b)

Figure 9 (a) Impedance vs frequency (b) phase vs frequency for 20 datasets of double refined palm oil sample using S1 sensor

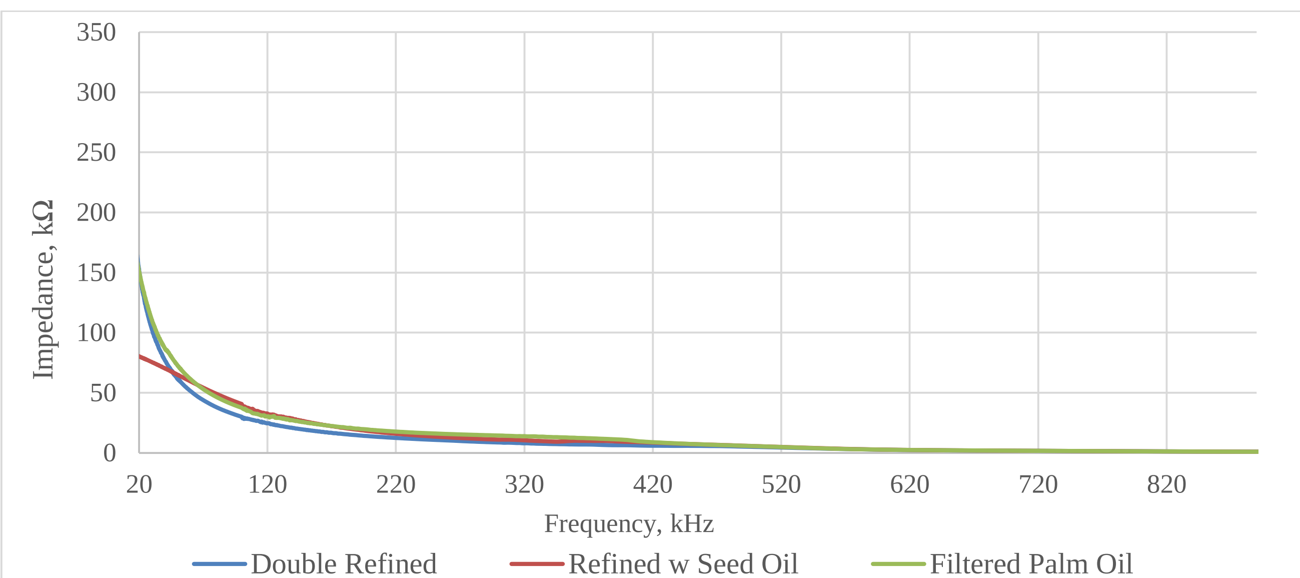


Figure 10 Impedance vs frequency for three types of palm cooking oil samples

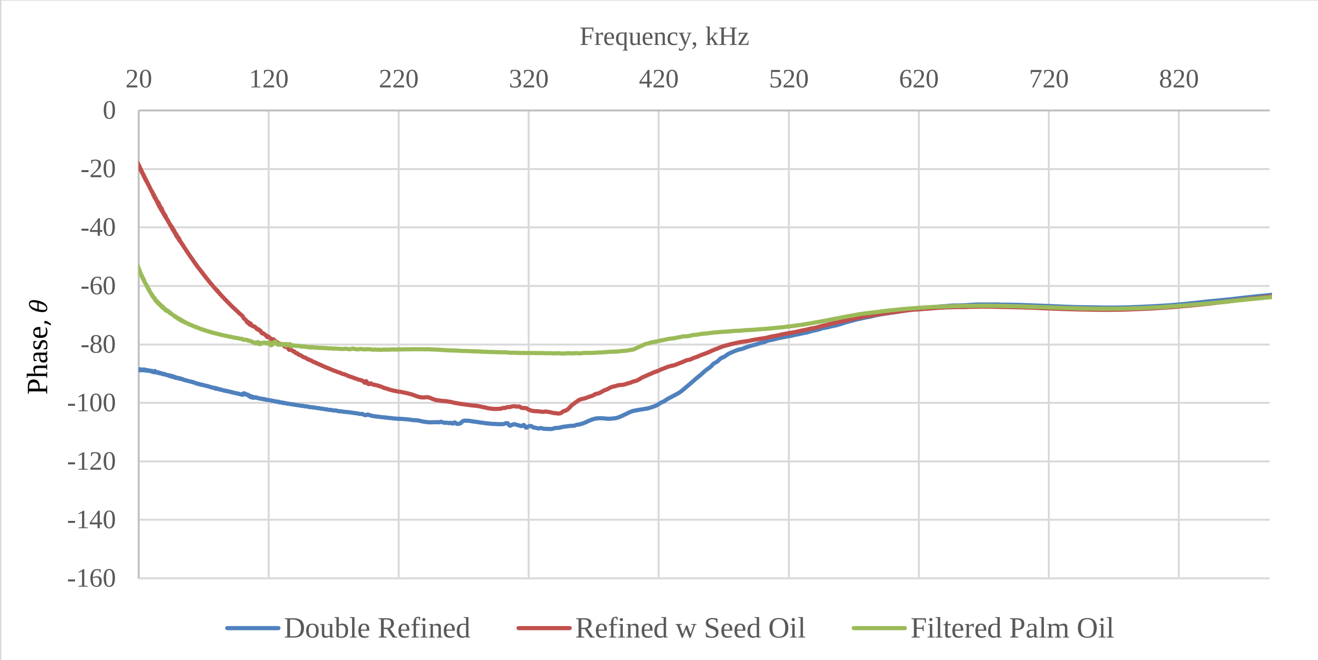


Figure 11 Phase vs frequency for three types of palm cooking oil samples

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