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Dielectric Spectroscopy Technique for the Detection of Black Seed Oil Adulterated with Sunflower and Palm Kernel Oil

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Abstract Black seed oil is famous for its medical efficacy against some life-threatening diseases. Owing to its high commercial value, sharp practices among traders have introduced cheaper oil samples as adulterants to raise their profits. This study explored the use of dielectric spectroscopy as a rapid, non-destructive and eco-friendly method for detecting adulteration in black seed oil (BSO) with palm kernel (PKO) and sunflower oil (SFO) as adulterants. Dielectric properties of pure black seed oil and its blends with palm kernel oil and sunflower oil were measured over a frequency range of 10Hz to 1MHz using impedance analyzer. The results showed significant differences in the dielectric spectra of pure black seed oil and adulterated samples. The procedure successfully detected adulteration levels as low as 5% palm kernel and sunflower oil in black seed oil. The capacitance value of BSO exceeds those of PKO and SFO. Therefore, the disparity in capacitance values was successfully used in discriminating levels of adulterant in the oil. As the temperature rises, the capacitance values of the BSO, SFO and PKO equally rise. But, all the samples maintain lower capacitance values than BSO. These results showed that the capacitance of the oil samples varied with temperature and the value for capacitance of the desired sample-BSO, is always higher at low and high temperatures. The distinguishing factor of capacitance can always be used to detect adulteration of the BSO by any oil. Dielectric spectroscopy offered a promising alternative to other expensive and highly technical methods for detecting adulteration in edible oils, with advantages in speed, simplicity, cost-effectiveness and eco-friendly.

Keywords: Dielectric spectroscopy, Adulteration, Black seed oil, Sun flower oil, Palm kernel oil.

I. Introduction

The integrity of oils within the food industry is paramount, as they serve as essential components in various culinary and nutritional applications. However, the widespread occurrence of oil adulteration poses significant challenges to ensuring product quality, authenticity, and consumer safety. Adulteration involves the deliberate dilution, substitution, or addition of inferior or cheaper oils to premium or higher-value oils, often for economic gain [1]. This deceptive practice not only compromises the nutritional value and flavor profile of the final products but also presents serious health risks to consumers. Among the diverse range of oils subject to adulteration, black seed oil and palm kernel oil are of particular interest due to their nutritional significance and economic value. Black seed oil, derived from the seeds of *Nigella sativa*, is renowned for its intended health benefits and medicinal properties [2]. Palm kernel oil, extracted from the kernels of oil palm fruits, is widely used in cooking, food processing, and various industrial applications [2].

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The demand for these oils continues to rise owing to the high cost of the black seed oil, making them susceptible to adulteration schemes aimed at maximizing profits at the expense of quality and safety. In response to the growing need for reliable methods to detect oil adulteration, advanced analytical techniques such as dielectric spectroscopy have emerged as valuable tools in the food industry [3]. Dielectric spectroscopy enables the rapid and non-destructive analysis of the dielectric properties of substances, offering insights into their composition, purity, and authenticity. By leveraging the unique dielectric natures of different oils, this technique holds promise for accurately identifying adulterated samples and safeguarding the integrity of oil products [4].

The integrity of oils within the food industry is fundamental to ensuring consumer safety, product quality, and regulatory compliance. Oils serve as essential ingredients in various culinary and nutritional applications, providing flavor, texture, and essential nutrients to a wide range of food products [5]. However, the pervasive issue of oil adulteration threatens to compromise these crucial aspects of food production and consumption [6].

The adulteration of PKO with black seed oil is particularly troubling due to several reasons. Firstly, BSO is often more costly and more readily available than PKO, making it an attractive adulterant for unscrupulous producers seeking to maximize profits [7, 8]. Secondly, BSO may lack the same nutritional profile and stability as palm kernel oil, potentially leading to adulterated products with inferior quality and safety [9]. Thirdly, consumers may be unaware of the adulteration, assuming they are purchasing pure PKO and unknowingly consuming adulterated products with potential health risks. Current methods for detecting oil adulteration, including chromatographic techniques and spectroscopic methods may have limitations such as high cost, time-consuming procedures, or lack of sensitivity and specificity to accurately identify adulterated samples [1]. Therefore, there is a pressing need for alternative, reliable techniques that can efficiently and effectively detect adulterants in oils, particularly in the context of palm kernel oil adulteration with black seed oil [10].

Addressing this problem requires the development and validation of innovative detection methods that can reliably distinguish between pure oils and adulterated samples. One promising approach is the use of dielectric spectroscopy, which offers the advantages of rapid analysis, non-destructive measurement, and sensitivity to molecular composition changes. By investigating the feasibility of using dielectric spectroscopy for detecting palm kernel oil adulteration with black seed oil, this study aims to contribute to improved quality assurance practices, consumer protection, and industry integrity within the food sector [4].

The aim of this study is to apply dielectric spectroscopy in determining the adulteration of black seed oil by PKO and Sunflower oil.

II. Materials and Methods

Samples of palm kernel oil (PKO) and sunflower oil (SFO) were purchased from Justrite Mall, Osogbo, Osun state. The black seed oil (BSO) was purchased from local producer at Osogbo, Osun State. They were properly labelled and stored in appropriate containers to prevent contamination.

A. Experimental Procedure

i. pH, Total Dissolved Solids (TDS) and Electrical Conductivity

Hand-held pH meter was used to test for the pH, total dissolved solid and the electrical conductivity of all samples which also helps in measuring the concentration of ionic activity in the samples.

ii. Dielectric Spectroscopy

Dielectric Spectroscopy analysis was performed using impedance analyzer- LCR instrument (EAST-TESTER, Guangzhou, China). Sample cell was made of square acrylic plastic with parallel copper plates as electrodes. Parameters like capacitance (C), impedance (Z) and dissipation factor (D), Admittance (Y), Susceptance (B, Conductance (G) and phase angle () were measured. Pure and blend phases of the samples were prepared for analysis. The dielectric measurement cell was constructed with square acrylic plastic as a parallel-plate system. The terminals were made of copper plates.

To prepare pure phase, sample of oil was put into the dielectric cell and connected to the terminals of the LCR instrument. The machine was allowed to warm up and equilibrate for more than 30 minutes before start of the measurement. The frequency was set and the measurements parameters were selected. Pair of parameters were saved at every frequency. The frequencies of operations are 10, 100, 500, 1000, 10000, 50000, 100000 and 1MHz. To evaluate the detection of PKO and SFO in blend phases with Black Seed Oil, samples with known adulteration levels were prepared. Adulterated samples were created by adding PKO or SFO to the BSO at preset concentrations of 5%, 10%, 15%, 20%, 25% and 30% by volume. Measured volumes of PKO were added to Black Seed oil in labeled beakers. Each mixture was thoroughly stirred for 10 minutes using a magnetic stirrer to ensure homogeneity and then check for the parameters listed above at each frequency of measurement.

Effects of temperature was examined by raising the temperature of the samples from 40°C to 70°C. The temperature range for this study was selected based on typical processing and storage conditions of edible oils, encompassing common thermal environments that oils might be exposed to during industrial processes and storage. A laboratory grade heating mantle with a precise temperature control system was used to heat the samples. The setup ensured uniform temperature distribution and accurate temperature maintenance within the specified range.

B. Dielectric Calculations

The following relationships were employed to extract parameters of interest. The complex permittivity (ε) comprises two parts: real (ε') and imaginary (ε'') parts as expressed in eqs. (1)-(3) [11],

$$\varepsilon = \varepsilon' - j\varepsilon'' \tag{1}$$

$$\varepsilon'(\omega) = \frac{C(\omega)d}{\varepsilon_o A} \tag{2}$$

$$\varepsilon''(\omega) = \frac{R^{-1}(\omega)d}{\omega\varepsilon_o A} \tag{3}$$

ε' is the real part of the complex permittivity (ε) called dielectric permittivity. The imaginary part, ε'', is the dielectric loss factor. "A" is the area of the plate which serves as the electrodes, 'd' is the distance between the two parallel plates, $\omega = 2\pi f$, where f is the frequency. ε_o is the permittivity of the vacuum. The capacitance at set frequency is C(ω).

C. Data Analysis

Analysis of the dielectric spectra obtained from both pure and blend phases were performed by checking for characteristic peaks or patterns in the spectra that may indicate the presence of adulterants. The analysis further compared the dielectric properties of the samples to identify any deviations or anomalies that could suggest adulteration. Excel spreadsheet was mainly used to process the data. Plots were generated and appropriately labelled to indicate different samples and conditions examined in this study.

III. Results and Discussion

A. pH, Total Dissolved Solid (TDS) and Electronic conductivity for pure phase

As shown in Table 1, all of the samples showed same conductivity and TDS values. Both palm kernel oil and Black Seed Oil show similar pH which is acidic. But the SFO is only slightly acidic. The acidic nature of the samples was due to the natural fatty acid composition of the oils [11]. The Not detectable (ND) conductivity means that there are no conductive ions in the oil. Also, not detectable (ND) TDS readings suggested that there are no dissolved solids inside the oil samples. These results can be used as a baseline for quality control and to detect any potential adulteration or contamination in the oils. Both oils have Not detectable conductivity (ND), indicating they are free from ionic contaminants. Both oils have not detectable TDS (ND ppm), indicating they are free from dissolved solids and impurities. Palm kernel oil has a slightly lower pH (5.11) compared to Black Seed oil (5.54), which may be due to differences in their fatty acid compositions. This shows that SFO has lower fatty acid content [12].

TABLE 1: pH, TDS and Electrical Conductivity of Pure Phases

Pure phase	pH	Electrical Conductivity (μS/cm)	TDS (ppm)
Palm kernel oil	5.12	ND	ND
Black Seed oil	5.54	ND	ND
Sunflower	6.42	ND	ND

ND: Not detectable

In the blend phases for PKO in BSO, the pH values fluctuate slightly between 5.50 and 5.21, indicating a minimal change in the oils acidity as the adulteration increased from 5%-30%. This is shown in Table 2. This suggested that the adulterant might not be significantly altering the oils chemical composition. The conductivity remains at ND for all levels of adulteration, indicating that the adulterant did not introduce ionic contaminants into the oil. The TDS remains at ND ppm for all levels of adulteration indicating that the adulterants did not introduce ionic contaminants into the oil.

For the SFO in BSO, Table 2 also shows the pH values fluctuate slightly between 5.74 and 6.26, indicating slight rise in the pH of the BSO as the concentration of the SFO increases. Again, the conductivity remains at ND for all levels of adulteration, indicating that the adulterant did not introduce ionic contaminants into the oil. The TDS remains at ND ppm for all levels of adulteration indicating that the adulterants did not introduce ionic contaminants into the oil.

TABLE 2: pH, TDS and Electrical Conductivity of Blended Phases

Adulteration	pH	Conductivity	TDS
5% PKO	5.50	ND	ND
10% PKO	5.47	ND	ND
15% PKO	5.41	ND	ND
20% PKO	5.36	ND	ND
25% PKO	5.24	ND	ND
30% PKO	5.21	ND	ND
5% SFO	5.74	ND	ND
10% SFO	5.81	ND	ND
15% SFO	5.95	ND	ND
20% SFO	6.10	ND	ND
25%SFO	6.19	ND	ND
30% SFO	6.26	ND	ND

ND: Not detectable

B. Dielectric Spectroscopy Study of Black Seed Oil Adulterated with PKO and SFO

i. PKO as adulterant and apacitance of pure phases

The capacitance values for pure phases of PKO, BSO and SFO are shown in Figure 1. In the figure, it can be seen that generally, the capacitance decreases with increasing frequency. The capacitance value of BSO is the highest and far exceeds that of the PKO and SFO. That of pure PKO is found to exceed that of SFO. From the figure, the slopes of the capacitance profiles are steeper at lower frequency up to 100000Hz. Afterwards, the profiles become flat for all samples. Capacitance measures the amount of charges stored in a medium. Therefore, based on figure readings, more charges are stored in the BSO than others.

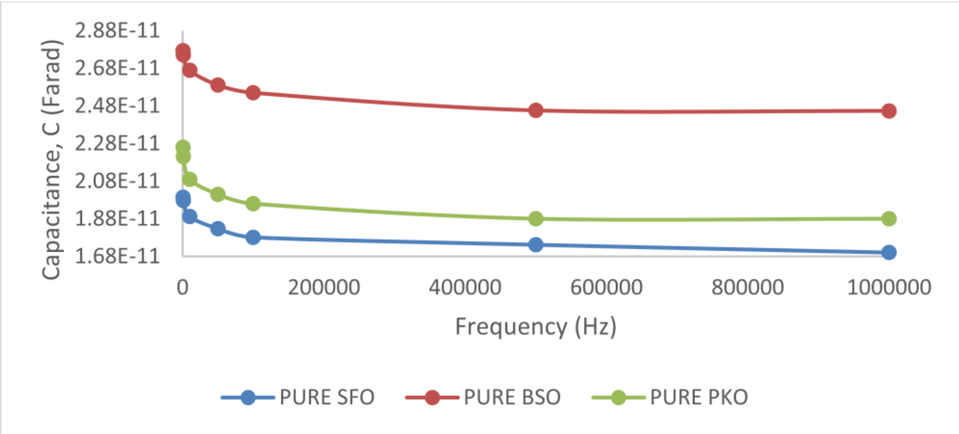

Figure 1: Capacitance of Pure Phases (BSO, SFO and PKO)

The results can be used to distinguish the BSO from other oil samples. Thus, it is expected that the presence of adulterants (PKO and SFO) in BSO will lead to gradual decline in the value of its capacitance or ability to store electric charges.

Figure 2 shows the capacitance of the blended oil phases for SFO in BSO. That capacitance of pure phase BSO is the highest. As the SFO is added to the BSO, the capacitance of the blended sample decreases with more SFO. This shows that the ability of the blended sample to store electrical charges decreases as the amount of SFO increases. Capacitance is the ability of a material to store electric charges. Based on the capacitance values, the dielectric permittivity of a material can be obtained to develop relationship for estimating the material's components which can then be used to monitor changes in the material's contents. The adulteration of Black Seed oil with SFO oil decreases the blend's ability to store charges. The capacitance value of SFO is lower than that of pure BSO. This trend can serve as means to detect the presence of adulterant in the BSO. It is expected that the PKO will behave similarly, since they both have lower capacitance values than BSO.

Figure 3 shows the effect of adulteration of BSO with PKO. Similar to what was observed in Figure 2, the capacitance values decrease as the concentration of the PKO rises in the BSO. Thus, it can be inferred that the presence of adulterant lowers the energy storage potential of the BSO.

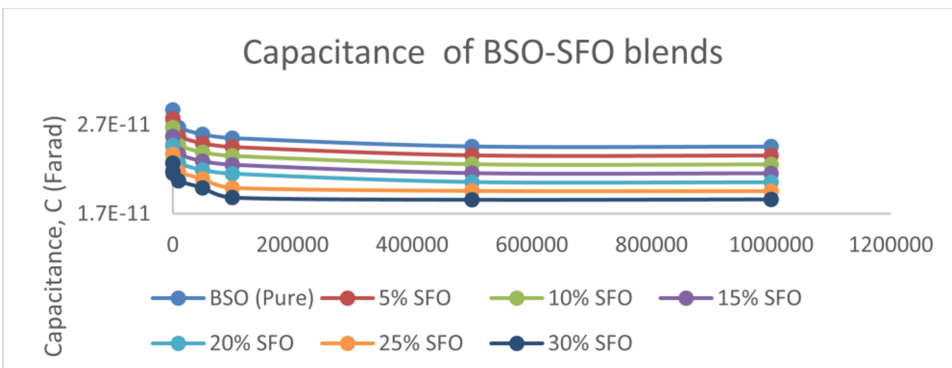

Figure 2: Capacitance of Adulterated Oil (SFO in BSO)

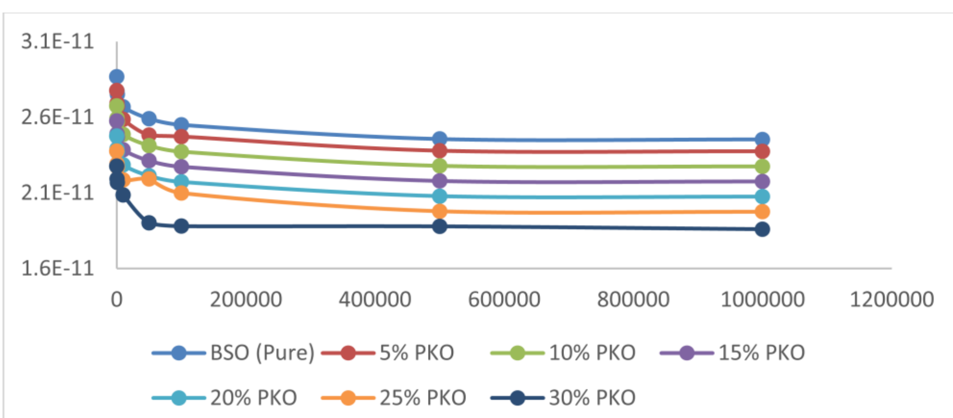

Figure 3: Capacitance of Adulterated Oil (PKO in BSO)

ii. Effect of temperature on pure PKO and black seed oil

Figure 4 shows that the higher the temperature, the higher the capacitance of the pure BSO. The temperature increases the capacitance and the ability of the materials to store charges. The slope of capacitance change is higher at lower. frequency.

The behaviour of the oil at higher temperature could be traced to the expansion of the dipole at higher temperature. The higher energy at higher temperature increases the energy of the electronics and nuclear elements. This stretches them and make them more aligning to the passing radiation. Thus, higher capacitance is recorded at higher temperature

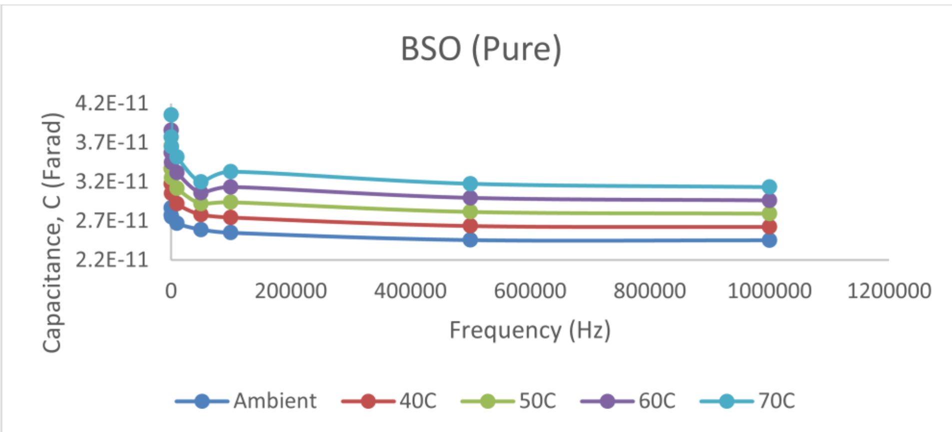

Figure 4: Effect of Temperature on Capacitance of pure BSO

Similarly, Figure 5 shows that the effect of temperature remains consistent with PKO. As the temperature rises, so the capacitance of the PKO. These results show that the capacitance of the oil samples will vary with temperature. However, the good news is that since the value for capacitance of the desired sample-BSO, is always higher at low and high temperatures, it is a good observation that the value of the capacitance for the BSO will consistently be distinguished under every circumstance.

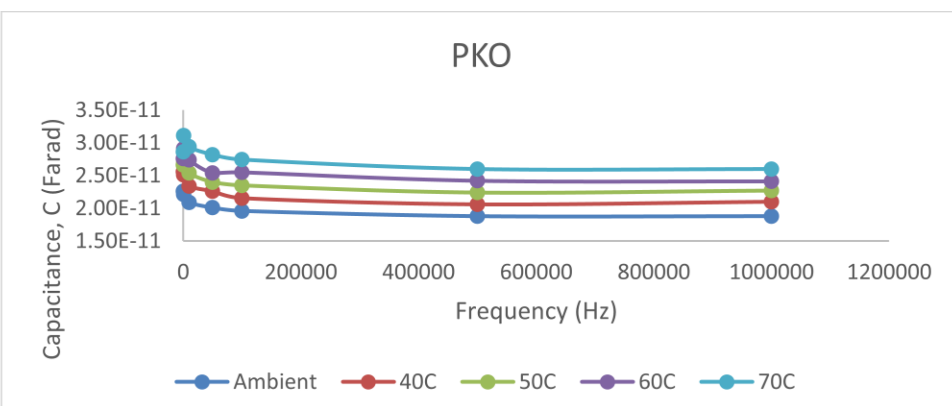

Figure 5: Effect of Temperature on Capacitance of Pure PKO

Figure 6 shows the comparison of capacitance for BSO and PKO at 70 ℃ as expected that of BSO remains consistently higher at all frequencies. So, the distinguishing factor of capacitance can always be used to detect adulteration of the BSO by any oil.

To use concise value of discriminant for detecting the adulteration level, Figure 7 presents relative permittivity profiles for SFO in BSO. Relative permittivity is the ratio of capacitance of material in the measuring cell to that of the empty cell

$$\text{Relative permittivity, } \varepsilon_r = \frac{C_{oil}}{C_{air}} \quad (4)$$

Where C_{oil} is the capacitance of the oil, when the measuring cell was completely filled the oil sample. C_{air} is the capacitance of the empty (air-filled) cell. Figure 7 shows that the relative permittivity of BSO remains higher and that the value decreases as the concentration of the adulterant becomes higher.

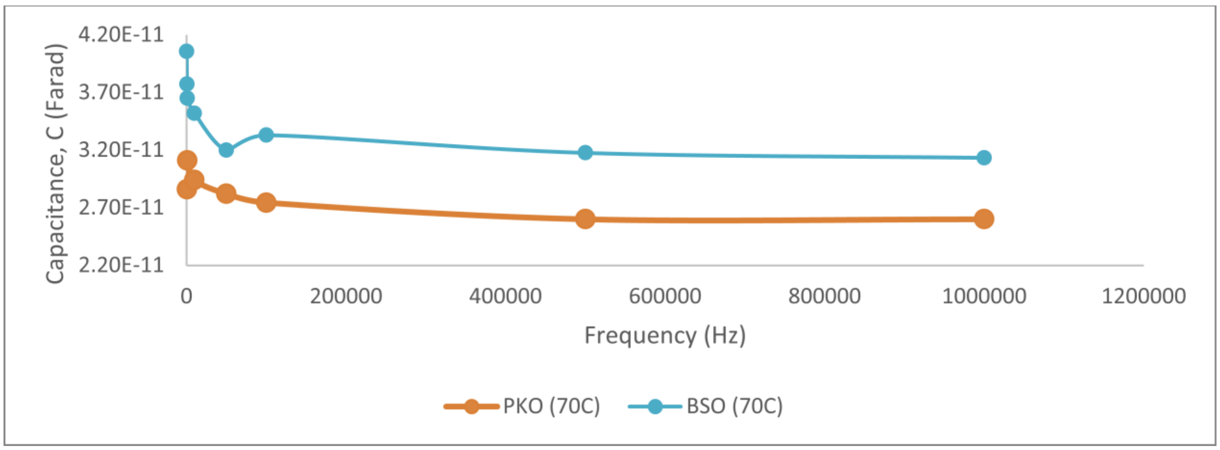

Figure 6: Comparison of Capacitance values of Pure PKO and BSO at 70C

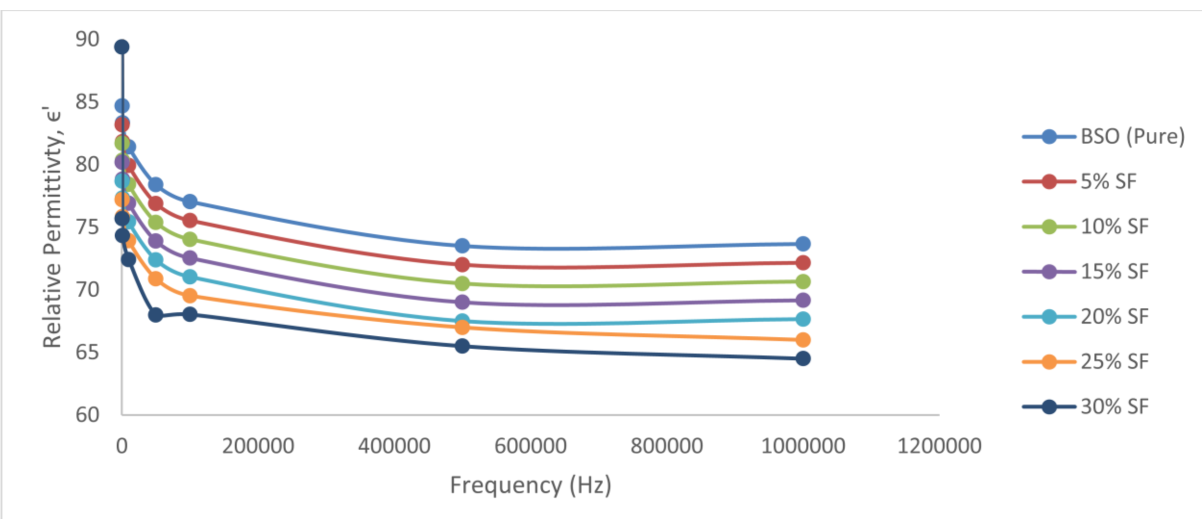

Figure 7: Relative Permittivity of Capacitance of BSO-SFO (SF) Blend

IV. Conclusion

This study employed dielectric spectroscopy, as a rapid, non-destructive analysis, and cost-effective method for detecting adulteration in Black Seed oil. The results showed significant differences in the dielectric spectra of pure black seed oil and adulterated samples. The model successfully detected adulteration levels as low as 5% palm kernel and sunflower oil in black seed oil. The capacitance value of BSO exceeds those of PKO and SFO. Therefore, this disparity in capacitance values was successfully used in discriminating levels of adulterant in the oil. As the temperature rises, the capacitance values of the BSO, SFO and PKO equally rise. But, all the samples maintain lower capacitance values than BSO. These results showed that the capacitance of the oil samples varied with temperature and the value for capacitance of the desired sample-BSO, is always higher at low and high temperatures. The distinguishing factor of capacitance could always be used to detect adulteration of the BSO by any oil. Dielectric spectroscopy offered a promising alternative to other expensive and highly technical methods for detecting adulteration in edible oils, with advantages in speed, simplicity, and cost-effectiveness. Black Seed oil and other samples have distinct dielectric profiles which can be a valuable tool for quality control and authentication of black seed oil, ensuring its purity and safety for consumption.

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