

Dielectric Properties for Monitoring the Quality of Heated Oils

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Dielectric properties (dielectric constant ϵ' and dielectric loss ϵ'') were compared to conventional methods of analysis (viscosity, refractive index, iodine value, peroxide value and free fatty acids) for evaluating the frying quality of a blend of cottonseed and sunflower oils. The apparent relaxation time, τ , the activation energy H and the entropy change S for dielectric relaxation of the heated oil samples were calculated. Results indicate that dielectric constant and dielectric loss are useful tools for predicting deterioration occurring during heating of the oil.

KEY WORDS: Dielectric constant, dielectric loss, frying, oil deterioration.

A large portion of edible oil is consumed in frying of foods. It is known that during frying changes occur in the frying fat that may affect the flavor and nutritional value of foods (1). These changes include a variety of deteriorative reactions, including thermal oxidation, hydrolysis and polymerization (1-3). Various tests have been proposed to evaluate used frying oils to determine their suitability for further frying use. One reliable, efficient method in the evaluation of such oils is the measurement of dielectric properties (4). Fritch (5) reported that changes in dielectric constant can be used in a simple method for monitoring frying operations. Wu and Nawar (2) compared nine analytical methods, including changes in dielectric constant, for monitoring the quality of frying oils. They concluded that polymer content and changes in dielectric constant are useful for monitoring frying oil quality. Changes in dielectric constant also have been reported as useful (6) for determining the effects of treating spent frying shortenings for extending their utilization. Dielectric constant is the most convenient indicator for quality control in commercial deep-fat frying operations (1).

The present work evaluates the dielectric properties for monitoring the quality of a common frying oil during heating as simulation for food frying. In addition, these properties have been correlated with the conventional methods of analysis used for frying oil evaluation. This work is a continuation of an earlier study (7) on the application of dielectric properties in fats and oils technology.

MATERIALS AND METHODS

A vegetable oil blend (cottonseed and sunflower oils, fatty acid composition: 14:0, 0.2%; 16:0, 10.4%; 16:1, 0.1%, 18:0, 7.8%; 18:1, 42.2%; 18:2, 39.4%) was obtained from a local market. Six samples of oil (50 g each) were heated in 100-mL open beakers. The samples were stirred magnetically, and the temperature was thermostatically controlled during heating. Samples were heated at 180–190°C for 1, 3, 5, 9, 15 and 25 h. The samples were cooled to room temperature before analysis.

Dielectric measurements were taken on a Multidekometer type DK06 instrument (Wissenschaftlich-Technische Werkstätten GmbH, Weilheim Oberbayern, Germany)

with a frequency band ranging from 10^5 to 10^7 Hz (7,8). The dielectric constant ϵ' was measured directly, and the dielectric loss ϵ'' was calculated from the equation:

$$\epsilon'' = \frac{A}{f.R_x} - B \quad [1]$$

where A and B are the provided cell constant and correction factor, respectively, f is the measured frequency in MHz and R_x is the cathodic resistance in $M\Omega$. The measurements were based on the superheterodyne principle and the beat frequencies were displayed on a cathode ray tube. The apparatus was calibrated with liquids of known static dielectric constants. Viscosity of the samples at 25°C was measured according to ASTM standards (9). Acid value, iodine value, peroxide value and refractive index of the samples were determined by official AOCS methods (10).

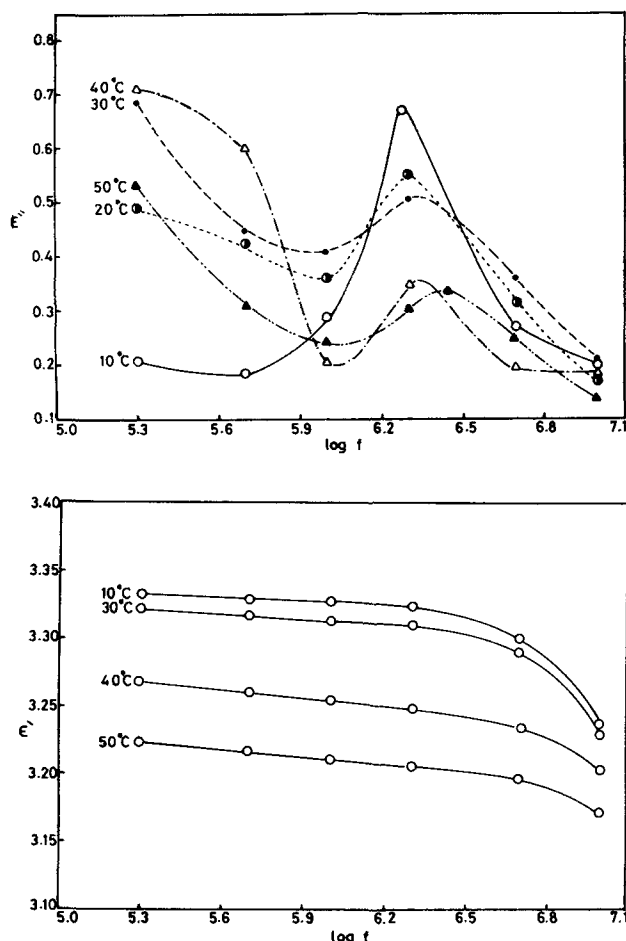


FIG. 1. Variation of the dielectric constant ϵ' and the dielectric loss ϵ'' , with frequency for unheated oil at different temperatures.

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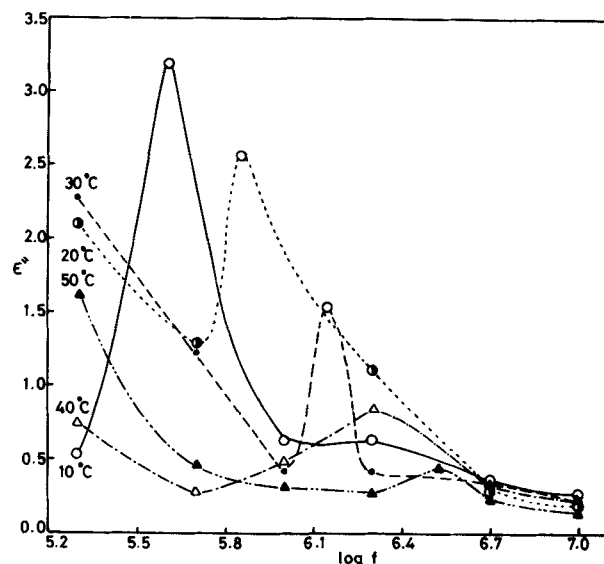
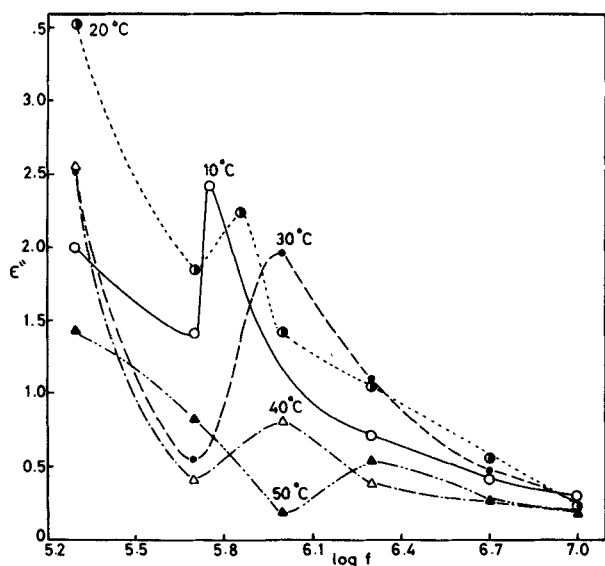
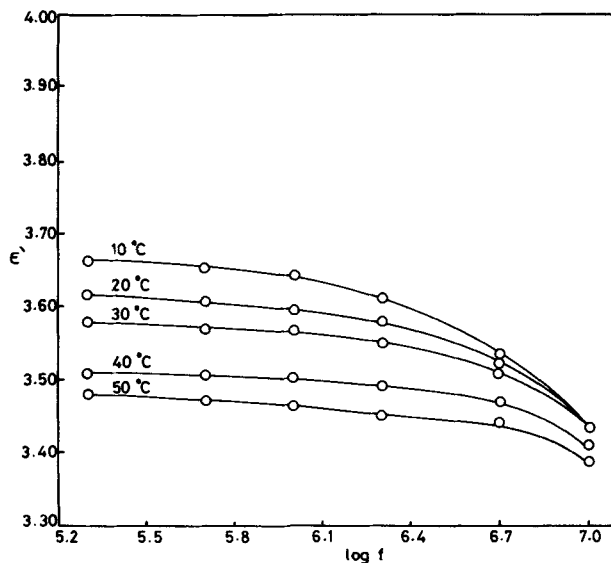
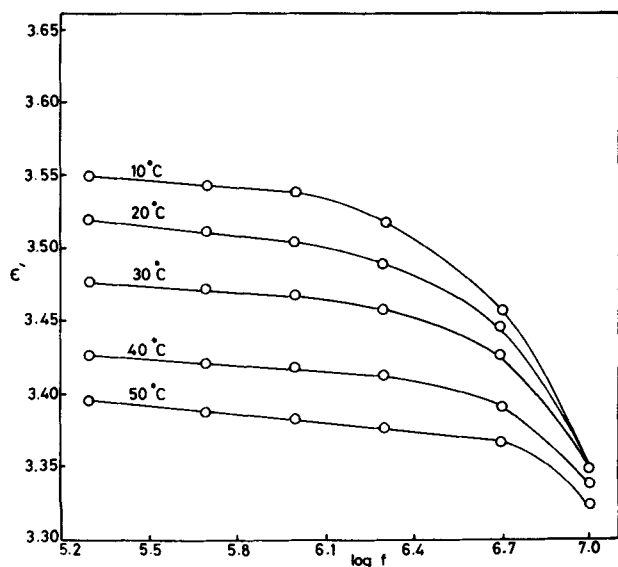


FIG. 2. Variation of the dielectric constant ϵ' and the dielectric loss ϵ'' , with frequency for heated sample (5 h) at different temperatures.

FIG. 3. Variation of the dielectric constant ϵ' and the dielectric loss ϵ'' , with frequency for heated sample (9 h) at different temperatures.

RESULTS AND DISCUSSION

The dielectric constant, ϵ' , and the dielectric loss, ϵ'' , were measured for the oil samples heated for 1, 3, 5, 9, 15 and 25 h in comparison with a control sample of unheated oil. The results are shown graphically in Figures 1–4, in which the dispersion absorption bands appear at all temperatures. These Figures show that the dielectric constant decreased when the temperature of the measurements was increased. This is due to the decrease of oil density and also to the increase in the mobility of the molecules, which facilitate the effect of the strong internal electric field (11). Also, ϵ' decreases with increasing frequency, which is due to the dielectric dispersion of the applied electric field (12). The apparent relaxation times τ , the activation energy H and the entropy change S for dielectric relaxation were calculated (7,8), and the results are reported in Table 1. The relaxation times τ increased by increasing the heating

time up to 9 h, then decreased after 15 h. Activation enthalpies H and entropy changes S show marked variations at different heating periods of the oil. They increased up to 9 h, then decreased. These variations can be explained by the coagulation and condensation of oil molecules within the time period of 0–9 h (13), followed by degradation and decomposition of the molecules (or aggregates) occurring at heating periods beyond 9 h.

Figures 5 and 6 show that acid value, refractive index, viscosity and dielectric constant increased proportionally with heating time when the oil was heated at 180–190°C. After 15 h of heating, an inflection to a sudden viscosity increase is obtained, after which it unexpectedly increases to a high value. The refractive index increases with the progress in lipid deterioration during the early stages of heating, then it reaches a plateau after 15 h of heating. The peroxide value curve represents the three

TABLE 1

Relaxation Times, Activation Enthalpies and Entropy Change of Edible Oil Heated for Different Periods

Temperature	Relaxation times ($\tau \times 10^{-8}$)				
	Samples heated at different periods (h)				
	Zero control	3	5	9	15
10	8.5514	14.1920	28.3160	39.9980	50.3550
20	7.9807	12.6480	22.4920	24.1010	35.6480
30	7.4480	10.5200	17.8660	12.0790	21.4800
40	7.1128	8.9545	15.9230	8.3568	17.0620
50	5.6499	6.3393	6.7926	7.1128	15.9230
ΔH K.Joule/mole	1.3265	3.6480	5.9280	8.0559	5.1300
ΔS Joule/degree/mole	-21.1644	-14.41	-7.93	-0.11	-11.31

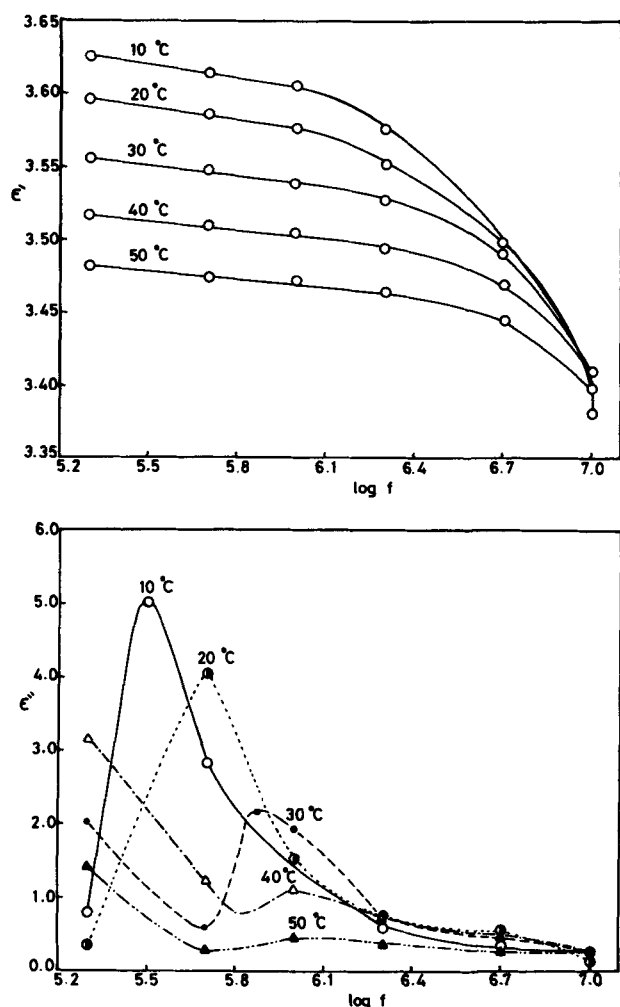


FIG. 4. Variation of the dielectric constant ϵ' and the dielectric loss ϵ'' , with frequency for heated sample (15 h) at different temperatures.

known stages of autoxidation of fats and oils, namely induction period, peroxide formation and peroxide decomposition (14). Thus, the peroxide value stays low during the primary induction period of 0–5 h, then it increases rapidly until it reaches its maximum value (after 15 h).

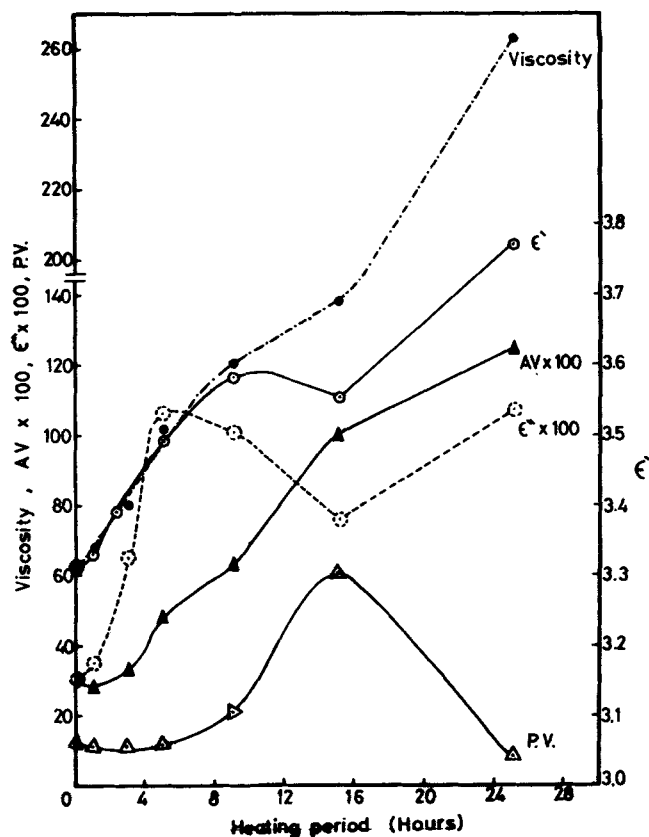


FIG. 5. Monitoring edible oil heated at 180–190°C by different methods.

In the final stage, the peroxides decompose and reach a minimum value of 8.1 after 25 h. During heating, the dielectric loss ϵ'' generally reaches a maximum value at 5 h, but the peroxide value reaches its maximum only after 15 h. Thus, ϵ' shows a marked decrease when peroxide reaches its maximum value. This may be attributed to the possibility that ϵ'' is more sensitive to hydroperoxides formation than to their decomposition products. Therefore, when peroxide reaches its maximum value, there are decomposition reactions that take place simultaneously, and ϵ' can be taken as a true measure for the hydroperox-

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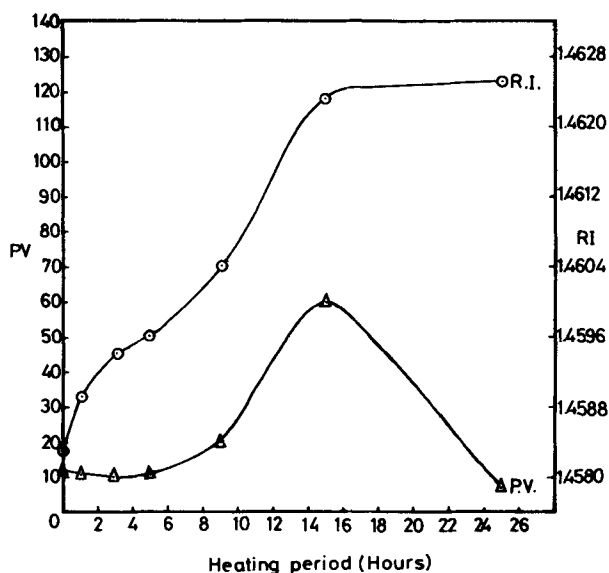


FIG. 6. Monitoring edible oil heated at 180–190°C by peroxide value and refractive index.

ides, but not for their decomposition products. In addition to those observations, it should be noted that as ϵ'' decreases, acid value, refractive index and viscosity increase markedly. The behavior of ϵ'' can be explained by the formation of highly polar molecules (or aggregates) through condensation of the molecules, while degradation results in the formation of smaller segments of lower polarity. It is well known that as the polarity increases, the dielectric loss also increases (15).

Wu and Nawar (2) reported the ϵ' increases because of a marked increase in the polarity of some compounds. In light of that finding, it is of interest to determine ϵ' in heated oil samples as an arbitrary measure of polar compounds. We observed that all samples, separately heated for different periods, generally show only slight increases in ϵ' value (Fig. 5). The calculated values for relaxation time τ , activation energy H and entropy change S are in harmony with ϵ' and ϵ'' for all samples because of the for-

mation of polar compounds, such as aldehydes, ketones, esters and acids (8, 11, 15). Viscosity, ϵ' and ϵ'' change, in a similar manner by heating the oil for different periods. After 15 h heating, there are sudden rises in all their values. These changes also correspond to markedly higher peroxide values and lower iodine values.

These results lead to the conclusion that one can monitor the beginning of deterioration of oil during heating or frying, particularly from the ϵ'' values, but also from ϵ' data. We found that after 25 h heating, obvious deterioration can be observed from the markedly high viscosity, as well as from ϵ' and ϵ'' values. These changes took place despite the fact that peroxide values were rather low, which suggests that the peroxides are nearly converted to polymeric compounds after 25 h of heating. Thus, dielectric properties can be used advantageously to determine the degree of deterioration that occurs in oils during heating or frying.

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