Stability of Peanut (Arachis hypogaea) Oil with TBHQ (Antioxidant Tertiary Butyl Hydroquinone) by Ultrasonic Studies

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ABSTRACT

The efficiency of TBHQ (tertiary butyl hydroquinone) as an antioxidant in peanut (Arachis hypogaea) oil was evaluated by ultrasonic studies. The effect of TBHQ on the oxidation stability of peanut oil was examined. The antioxidant-peanut oil system, in parallel with a control experiment, was subjected to heating at 180 ± 5 °C continuously for a daily period of 4 h for four consecutive days. The parameters used to assess the thermal degradation and oxidation properties of the antioxidant in oils were: ultrasonic velocity, viscosity, density and peroxide value. The adiabatic compressibility, intermolecular free length, relaxation time and acoustic impedance were calculated from the experimental data. Changes in the viscosity, density and ultrasonic velocity in the control were from 0.26553 × 10^{-1} to 1.28729 × 10^{-1} kg.m^{-1}.s^{-1}, 912.59 to 938.31 kg.m^{-3} and 1422 to 1480 m.s^{-1}, respectively, and in peanut oil with 200 ppm TBHQ were from 0.29129 × 10^{-1} to 0.573459 × 10^{-1} kg.m^{-1}.s^{-1}, 913.58 to 922.45 kg.m^{-3} and 1426 to 1446 m.s^{-1}, respectively, with the 16 h of heating. The results obtained showed an improvement in the thermal degradation and oxidation stability of the formulation compared with the base oil, while ultrasonic studies helped to determine the stability of the edible oil. Hence, it is recommended that peanut oil with TBHQ can be used for frying without any adverse effect and ultrasonic properties can be used for the assessment of the stability of frying oil.

Keywords: ultrasonic velocity, acoustic parameters, peanut oil, TBHQ (tertiary butyl hydroquinone), peroxide value.

INTRODUCTION

Deep-fat frying is one of the oldest methods of food preparation. A series of complex reactions occur during the frying process due to the high temperature which include the hydrolysis, oxidation and polymerization of oils with hydroperoxides being important oxidation products formed during deep-fat frying (Rossell, 2001). These hydroperoxides decompose to give secondary product such as esters, aldehydes, alcohols, ketones, lactones and hydrocarbons. The change in quality of food and the loss of nutritional value is due to the secondary products formed, which also affect taste, flavor and aroma of the food. It has been also found that certain secondary products formed during the oxidation are toxic (Nawar, 1996; Min and Boff, 2001). Acceptable synthetic antioxidants are used to avoid these reactions. The important antioxidants used in the food industry are butylated hydroxyanisol (BHA), butyl1-4-hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), propylgallate (PG) of which, TBHQ has been found to be the most
effective antioxidant (Guzman et al., 2009; Pimpa et al., 2009).

Ultrasonic studies have been utilized for chemo metrics for more than five decades as they are inherently well suited to the characterization of composition, reacting system conditions, mixing and multiphase properties and provide real time images and help in characterization process. For example, the measurement of ultrasonic speed (Izbaim et al., 2009) enables the accurate determination of some useful acoustic and thermodynamic parameters and the variation in the acoustic parameters is due to the molecular interactions in liquid mixtures (Ali et al., 2004; Aralaguppi and Barragi 2006).

A few studies (Sarmento et al., 2006; Okoye et al., 2009; Ali, 2010; Valantina et al., 2010) have revealed that the measurement of viscosity and density can be used to determine the oxidative stability and ultrasonic velocity (Izbaim et al., 2009). The molecular interaction, (Kesavasamy et al., 2008; Priya et al., 2010) and that ultrasonic velocity (Izbaim et al., 2010) can be used to determine the stability of oil. However, the effect of a synthetic antioxidant on the ultrasonic velocity has not been fully elucidated.

The objectives of this paper were: (a) to investigate the antioxidant activity of TBHQ in peanut oil using ultrasonic velocity, density and viscosity; and (b) to study the secondary parameters of adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance and peroxide value which can be used to correlate the degree of unsaturation and antioxidant activity.

In the current paper, the antioxidant stability in peanut oil at different times of heating was investigated using the parameters of viscosity (Sarmento et al., 2006; Valantina et al., 2010) and the density and ultrasonic velocity (Kesavaswamy et al., 2008; Priya et al., 2010). These parameters were measured at different times of heating as it was reported that the antioxidant stability of TBHQ with peanut oil is even better at high temperature and after prolonged heating (Okoye et al., 2009; Ali, 2010).

MATERIALS AND METHODS

Materials

Fresh peanut oil was obtained by grinding peanut oil seed in the Sri Murugan Oil Mills Mandya, India. TBHQ was purchased from Sigma Aldrich and Analar grade chemicals were used for the peroxide value determination.

Methods

Samples of peanut oil (control) and peanut oil with 50, 100, 150 and 200 ppm of TBHQ were heated in an oil bath to a temperature of 180 °C continuously for 4 h per day for 4 days. Oil samples were taken at 0, 4, 8, 12 and 16 h of the heating period. Then, the samples were cooled to 30 °C for subsequent determination. All measurements were carried out in triplicate.

Density measurement

The density of the pure liquids and mixtures was measured using a 10 mL specific gravity bottle. Distilled water was used as the reference. The density was measured using the formula in Equation 1:

$$\rho_2 = \frac{W_2}{W_1} \rho_1$$

where, $W_1$ is the weight of distilled water, $W_2$ is the weight of the experimental liquid, $\rho_1$ is the density of water and $\rho_2$ is the density of the experimental liquid.

Viscosity measurement

The viscosity of the oil and oil-antioxidant mixtures were measured using an Ostwald’s viscometer (Advance Technocracy Inc.; Ambala; India) calibrated with doubly distilled water. The Ostwald’s viscometer was immersed in a temperature controlled water bath. The time of flow was measured using a Racer stopwatch (Swastik Scientific Company; Mumbai, India) with an
accuracy of 0.1 s. Viscosity was determined using the relationship shown in Equation 2:

$$\eta_2 = \eta_1 \frac{t_2 \rho_2}{t_1 \rho_1}$$  \hspace{1cm} (2)

where, \(\eta_1\) is the viscosity of water, \(t_1\) is the time of flow of water, \(\rho_1\) is the density of water, \(\eta_2\) is the viscosity of the experimental liquid, \(t_2\) is the time of flow of the experimental liquid and \(\rho_2\) is the density of the experimental liquid.

**Ultrasonic velocity measurement**

The velocities of ultrasonic waves in the mixtures were measured using an ultrasonic interferometer (Mittal Enterprises; New Delhi, India) working at a fixed frequency of 2 MHz with a tolerance of \(\pm 0.005\%\). The general equipment layout is shown in Figure 1. The measuring cell was a specially designed, double-walled vessel to provide a constant temperature. The high frequency generator excited a quartz crystal fixed at the bottom of the measuring cell, at its resonant frequency. The capacity of the cell was 12 cm\(^3\). A fine micrometer screw, with a least count of 0.01 mm at the top of the cell, was used to raise or lower the reflector plate in the liquid through a known distance. The measuring cell was connected to the output terminals of the high frequency generator through a shielded cable. Ultrasonic waves in the quartz crystal were reflected from the reflector plate, with stationary waves being formed in the region between the reflector plate and the quartz crystal. The micrometer was slowly moved till a number of maximum readings (n) of the anode current had passed. The total distance (d) moved by the micrometer was noted.

The wavelength of the ultrasonic waves in the liquid is given by \(\lambda = 2d/n\). The velocity of the ultrasonic waves in the liquid is given by \(V = \lambda f\), where \(f\) is the frequency of the ultrasonic wave.

**Peroxide value determination**

Peroxide values of the oil samples were determined (American Oil Chemist Society, 1993). A sample of 0.5–1 g of the oil was taken in a clean 250 mL iodine flask and dissolved in 30 mL glacial acetic acid and 20 mL chloroform. Then, 0.5 mL of saturated potassium iodide was added to the flask and kept in the dark for 15 min. Next, 50 mL distilled water was added and titrated against 0.02 N sodium thiosulphate solution using starch as an indicator. From the titer value, the peroxide value (PV) expressed as the milli-equivalent of peroxide oxygen per kilogram of fat of the sample was calculated using the formula in Equation 3:

$$PV = \frac{V_{Na_2S_2O_3} \times N_{Na_2S_2O_3} \times 1,000}{\text{Weight of sample}}$$  \hspace{1cm} (3)

where \(V\) is the volume and \(N\) is the normality.

**Adiabatic compressibility**

The adiabatic compressibility (\(\beta\)) is defined as the decrease of volume per increase of pressure when no heat flows in or out. Such a change is related to the compressibility of the medium by the thermodynamic relation.

![Figure 1](image)

*Figure 1*  Ultrasonic interferometer and other equipment used in the study.
represented by Equation 4:

$$\beta = \frac{1}{V} \left[ \frac{\delta_v}{\delta_p} \right]$$  \hspace{1cm} (4)

where \(V\) is the volume, \(\delta_v\) is the relative change in volume and \(\delta_p\) is the relative pressure change. It can also be calculated from the ultrasonic velocity (U) and the density of the medium (\(\rho\)) using the equation of Newton Laplace (Priya et al., 2010) shown in Equation 5:

$$\beta = \frac{1}{U^2 \rho}$$  \hspace{1cm} (5)

**Inter molecular free length**

The adiabatic compressibility of liquid can be expressed in terms of the intermolecular free length (\(L_f\)) which is the distance between the surfaces of the neighboring molecules and is given by Equation 6 (Priya et al., 2010):

$$L_f = K_T \beta_{\text{ad}}^{\frac{1}{2}}$$  \hspace{1cm} (6)

where, \(K_T\) is the temperature-dependent constant 201.1209 \(\times 10^{-8}\) at 303 K.

**Relaxation time**

The relaxation time is the time taken for the excitation energy to appear as transitional energy and it depends on the temperature and on impurities. The dispersion of the ultrasonic velocity in a mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (\(\tau\)) can be calculated from Equation 7 (Priya et al., 2010):

$$\tau = \frac{4}{3} \beta \eta$$  \hspace{1cm} (7)

**Acoustic Impedance**

The specific acoustic impedance (\(Z\)) is given by Equation 8 (Ernest, 2011):

$$Z = U \rho$$  \hspace{1cm} (8)

where, \(U\) and \(\rho\) are the velocity and density of the liquid, respectively.

The changes in the ultrasonic velocity, density, viscosity, adiabatic compressibility, intermolecular free length, relaxation time and acoustic impedance of TBHQ in peanut oil were calculated.

**RESULTS AND DISCUSSION**

In this study, the antioxidant stability in peanut oil at different times of heating was investigated using the parameters of viscosity (Sarmento et al., 2006; Valantina et al., 2010), and density and ultrasonic velocity (Kesavasamy et al., 2008; Priya et al., 2010). These parameters were measured after different times of heating. It was found that the antioxidant stability (Okoye et al., 2009; Ali, 2010) of TBHQ with peanut oil was better even at high temperature and after prolonged heating.

The study of thermal degradation and antioxidant stability in the peanut oil was carried out by heating the peanut oil to a frying temperature of 180 °C. After heating for the desired time, the viscosity, density and ultrasonic velocity of the control and the oil with TBHQ added at different concentrations was measured at 30 °C. The values depicted in Figures 2, 3 and 4 show the substantial increases in viscosity, density and ultrasonic velocity, respectively, for the control compared with the oil with TBHQ added.

**Viscosity**

Generally, the viscosity values gradually and substantially increased with an increase in the heating period. Adding 50, 100, 150 and 200 ppm of TBHQ led to different increments in the viscosity values during the heating period. Figure 2 shows that the control had by far the highest value of viscosity whereas oil with 200 ppm of TBHQ had the lowest viscosity values. These results suggested that mixing oil with 200 ppm of TBHQ will only change the viscosity to a small extent during the frying process.

The highest level of TBHQ mixed with oil induced the lowest change in oil viscosity. The
obtained results were in good agreement with the findings of Farag et al. (2003), Shaker (2006), Anany (2007) and Ali (2010) who found that mixing fried oil with various levels of phenolic compounds did not vary the viscosity during the frying process.

The viscosity increases with frying time due to oxidation, isomerization and polymerization reactions. An oxidation reaction leads to the formation of carbonyl or hydroxyl groups bonded to a carbon chain resulting in flux among the molecules that in turn increases the viscosity. (Valantina et al., 2010).

**Density**

Figure 3 shows the variation of density with heating time. The density of heated peanut oil gradually and substantially increased with the increased period of heating. Mixing oil with 200 ppm of TBHQ caused little increase in the density values compared to the control. The density of oil containing 200 ppm of TBHQ hardly changed as there are no molecular changes due to the antioxidant activity of the oil. The increase in density is due to increased structural changes as there is an increase in the saturation composition of the oil (Valantina et al., 2010).

![Figure 2](image1.png)

**Figure 2** Variation of viscosity of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.

![Figure 3](image2.png)

**Figure 3** Variation of density of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.
Ultrasonic velocity and acoustical parameters

Figures 4, 6, 7, 8 and 9 illustrate the interaction between the ultrasonic waves and the composition of molecules.

The increase in the ultrasonic velocity was due to the decrease in the free length and adiabatic compressibility. It was observed that for a given concentration of TBHQ and heating time, as the number of double bonds broke, the sound velocity increased. The adiabatic compressibility and free length were found to differ very little in oil with 200 ppm of TBHQ compared to the changes in the adiabatic compressibility and free length in the base oil alone. The adiabatic compressibility and free length are deciding factors of the ultrasonic velocity in liquid systems (Priya et al., 2010). The decrease in the value of the free length indicates that the triglyceride molecule with unsaturated bonds is likely to collapse as a result of the oxidation process (Okoye et al., 2009). The structures of triglycerides are kept intact by the effect of the TBHQ oxidant (de Guzman et al., 2009). Hence the value of the free length which indicates the intermolecular distance did not decrease as a result of using TBHQ.

The acoustic impedance was low in the oil with TBHQ added and without heating. With increased heating time, the acoustic impedance increased in the base oil, but to very little extent in the oil with 200ppm of TBHQ added. The excess parameters play a major role in understanding the nature of intermolecular interactions in liquid mixtures (Ernest and Kavitha, 2011). The intermolecular free length and acoustical impedance depend upon the intermolecular attractive and repulsive forces. Excess acoustical impedance may be due to the geometrical effect allowing the fitting of molecules of different sizes after collapsing the triglyceride structure.

The relaxation time increased with the heating period. The dispersion of ultrasonic velocity in the system should contain information about the characteristic time $\tau$ of the relaxation process that causes dispersion, where $\tau$ is in the order of $1 \times 10^{-11}$ s due to the structural relaxation process (Kinsler and Ray, 1989) and in such a situation, the molecules get rearranged due to a co-operative process (Ali et al., 2000).

Correspondingly, the other acoustical parameters ($\beta$, $\tau$, $L_f$ and $Z$) were also found to change to a large extent in the control. The addition of the antioxidant TBHQ did not allow any breaking up of the molecular clustering in the oil. The interaction between the molecules of oil

**Figure 4** Variation of ultrasonic velocity of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.
Figure 5  Variation of peroxide value (PV) of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.

Figure 6  Variation of adiabatic compressibility of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.

Figure 7  Variation of intermolecular free length of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.
occurred to a lesser extent and hence very small structural changes occurred during heating in the presence of an antioxidant. In the control, as the antioxidant activity is much less, there is a break up in the molecular clustering, releasing several dipoles for the interaction. In view of the greater interactions, increased amounts of change occurred during heating in the adiabatic compressibility, intermolecular free length, relaxation time and acoustical impedance.

It was observed that the ultrasonic velocity increased along with the density and viscosity as the heating time was increased. The ultrasonic velocity increased to a large extent in the control. The smallest increase in the ultrasonic velocity was recorded for peanut oil with 200 ppm of TBHQ. With the addition of 50 ppm, 100 ppm and 150 ppm of TBHQ, there was retardation in the variation of the ultrasonic velocity, density and viscosity but not to the extent shown with the addition of 200 ppm of TBHQ. Furthermore, as the concentration of TBHQ increased, there was a linear improvement in the stability of the oil. However, 150 ppm of TBHQ produced nearly the

![Figure 8](image1)

**Figure 8** Variation of relaxation time of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.

![Figure 9](image2)

**Figure 9** Variation of acoustic impedance of the control and peanut oil with different concentrations of tertiary butyl hydroquinone with heating time.
same acoustical parameter values as did 200 ppm of TBHQ. In India, 150 ppm of TBHQ is allowed in vegetable oils whereas the general standard for food additives (Codex, 1995) allows the usage of 200 ppm. Hence, the maximum stability of oil can be maintained with 200 ppm of TBHQ added.

**Peroxide value**

Hydro peroxides are the primary products of the oxidation of lipids; therefore, determination of peroxides can be used as an oxidation index for the early stages of lipid oxidation (Barthel and Grosch, 1974). Changes in the peroxide values of the peanut oil samples under investigation during the heating period are shown in Figure 5.

In general, the peroxide values of peanut oil increased substantially during heating and were strongly correlated with a prolonged heating period. At the end of the frying period, the peroxide value of peanut oil without antioxidant was about 26.78 milli-equivalents of peroxide oxygen per kilogram of fat and the peanut oil mixed with 50, 100, 150 and 200 ppm of TBHQ was about 18.12, 14.37, 10.4 and 8.18 milli-equivalents of peroxide oxygen per kilogram of fat. The lowest PV value at the end of heating period was for peanut oil treated with 200 ppm of TBHQ. The results indicated that the antioxidative effect of TBHQ was dependent upon its concentration. These results were consistent with the findings of Azuma et al. (1999), Farag et al. (2003), Shaker (2007) and Ali (2010).

Several studies indicated the effect of the frying process on the physico-chemical and sensory properties of fried oil. Clark and Serbia (1991), White (1991) Tyagi and Vasistha (1996) and Pimpa et al. (2009) reported that frying oils used continuously or repeatedly at high temperature in the presence of oxygen and water from the food being fried, were subject to thermal oxidation, polymerization and hydrolysis. Hence the resulting decomposition products adversely affected the flavor and color.

**CONCLUSION**

The variation in the parameters $\eta, \rho, U, \beta$, $L_f$ and $Z$ of peanut oil with 200 ppm of TBHQ compared with the control showed that the composition of the oil did not become saturated due to the presence of the antioxidant TBHQ on heating. Peanut oil with TBHQ added can be used at frying temperatures. Peanut oil with TBHQ added has better thermal stability than peanut oil alone. Ultrasonic velocity and acoustical parameters can be used to assess the stability of peanut oil.

**LITERATURE CITED**


