J Food Sci Technol (April 2015) 52(4):2238–2246
DOI 10.1007/s13197-014-1276-z

ORIGINAL ARTICLE

Effect of antioxidant tertiary butyl hydroquinone on the thermal and oxidative stability of sesame oil (*sesamum indicum*) by ultrasonic studies

N. Prasad · Basavarajaiah Siddaramaiah · Mujeeda Banu

Revised: 20 January 2014 / Accepted: 4 February 2014 / Published online: 1 March 2014

Abstract The aim of the current investigation is to evaluate the efficiency of tertiary butyl hydroquinone (TBHQ) as an antioxidant in sesame oil (*sesamum indicum*) by density, viscosity and ultrasonic velocity. The effects of varying amounts of TBHQ on the oxidation stability of sesame oil have been investigated. The antioxidant incorporated sesame oil system and control edible oil were subjected to heating at 180±5 °C continuously for a period of 4 h per day for consecutive 4 days. The parameters used to assess the thermal degradation and oxidation properties of the oils include ultrasonic velocity, viscosity, density and peroxide value. The fatty acid compositions of the oils were measured by gas chromatography. Adiabatic compressibility, intermolecular free length, relaxation time and acoustic impedance have been calculated from experimental data. Viscosity, density and ultrasonic velocity change in control oil is from 3.6553×10^{-2} to 11.1729×10^{-2} Nsm^{-2}, 912.59 to 940.31 kg/m^3 and 1,421 to 1,452 m/s respectively and in sesame oil with 200 ppm TBHQ is from 3.6793×10^{-2} to 6.4842×10^{-2} Nsm^{-2}, 913.78 to 922.45 kg/m^3 and 1,421 to 1,431 m/s respectively for 16 h of heat treated oil. The ultrasonic results obtained have shown reduction in thermal degradation and improvement in oxidation stability of antioxidant loaded oil in comparison to base oil. Hence, it can be recommended that sesame oil with 200 ppm TBHQ can be used for frying without adverse effect on physical properties. The ultrasonic velocity can be used for assessment of stability of frying oil.

N. Prasad · M. Banu (✉)
Department of Chemistry Vidya Vikas Institute of Engineering & Technology, Mysore, Karnataka 570 028, India
e-mail: mujeedabanu@gmail.com

B. Siddaramaiah
Department of Polymer Science & Technology, Sri Jayachamarajendra College of Engineering, Mysore, Karnataka 570 006, India

Keywords Acoustical parameters · Gas chromatography · Sesame oil · Peroxide value · TBHQ · Ultrasonic velocity

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 hydro peroxides being important oxidation products formed during deep-fat frying (Rossell 2001). These hydro peroxides decompose to give secondary products 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), butyl-1-4-hydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), and propylgallate (PG) of which, TBHQ has been found to be the most effective antioxidant (de Guzman et al. 2009; Pimpa et al. 2009).

Ultrasonic studies have been utilized for chemometrics for more than five decades as they are inherently well suited for 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; Rehab 2010; Okoye et al. 2009; 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) to understand the molecular interactions. The molecular interaction (Kesavasamy et al. 2008; Priya et al. 2010) and 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: (i) to investigate the TBHQ activity in sesame oil using ultrasonic velocity, density and viscosity; and (ii) to study the secondary parameters such as 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. Although literature search clearly indicates that there is lack of literature on ultrasonic studies on sesame oil-TBHQ formulations.

Materials and methods

Reagents and chemicals

Fresh sesame oil was obtained by the following procedure: dried seeds were milled (M/s. Sri Murugan Oil Mills, Mandya, India), the mixture obtained was cold pressed; the oil thus obtained was filtered. TBHQ was obtained from Sigma Aldrich and AR grade chemicals were used for the peroxide value determination.

Samples of sesame oil (control) and sesame 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 and for 4 days. As per ISO 9001:2008 norms (Indian Standard quality management systems-requirements) recommend TBHQ content is 150 ppm, allowed in vegetable oils. However, general standard for food additives allows the usage of antioxidant upto 200 ppm (Codex 1995). Hence, a maximum of 200 ppm TBHQ has been incorporated in this study. Oil samples were exposed for 0, 4, 8, 12 and 16 h at 180 °C. Then, the samples were cooled to room temperature and characterized. All measurements of heat treated oils were carried out in triplicate and average values are reported.

Techniques

The density (ρ) of the pure oils and mixtures has been measured using a 10 mL specific gravity bottle and distilled water was used as the reference. The viscosity (η) of the oil and oil-antioxidant mixtures were measured using an Ostwald's viscometer (Advance Technocracy Inc.; Ambala; India) and it was calibrated with doubly distilled water. The Ostwald's viscometer (Saeed et al. 2012; Kimilu et al. 2011) was immersed in a temperature controlled water bath. The time of flow was measured using a Racer stopwatch with an accuracy of 0.1 s. Viscosity was determined using the relationship,

$$\eta_2 = \eta_1 \frac{t_2 \ \rho_2}{t_1 \ \rho_1} \tag{1}$$

where, η_1 is the viscosity of water, t_1 is the time of flow of water, ρ_1 is the density of water, η_2 is the viscosity of the experimental liquid, t_2 is the time of flow of the experimental liquid and ρ_2 is the density of the experimental liquid.

The velocity (U) 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±0.005 %. 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. 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 recorded. The wavelength and velocity of the ultrasonic waves in the liquid is given by, $\lambda=2d/n$ and $U=f\lambda$ respectively, where, f is the frequency of the ultrasonic wave.

Secondary parameters

Adiabatic compressibility

The adiabatic compressibility (β) 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 using the thermodynamic relation as in

$$\beta = \frac{1}{v}\left[\frac{\delta_v}{\delta_p}\right] \tag{2}$$

where, V is the volume, δ_v is the relative change in volume and δ_p is the relative pressure change. It can also be calculated from the ultrasonic velocity (U) and the density of the medium

(ρ) using the equation of Newton Laplace (Priya et al. 2010) as follows,

$$\beta = \frac{1}{U^2{}_{\rho}} \tag{3}$$

Inter molecular free length

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

$$L_f = K_T \beta_{ad}^{\frac{1}{2}} \tag{4}$$

where, K_T is the temperature-dependent constant 201.1209×10^{-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 temperature and 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 (τ) can be calculated from Eq. (5) (Priya et al. 2010).

$$\tau = \frac{4}{3}\beta\eta \tag{5}$$

Acoustic impedance

The specific acoustic impedance (Z) is given by Eq. (6) (Ernest and Kavitha 2011)

$$Z = U\rho \tag{6}$$

where, U and ρ are the velocity and density of the oil respectively.

The changes in ultrasonic velocity, density, viscosity, adiabatic compressibility, intermolecular free length, relaxation time and acoustic impedance of sesame oil with and without TBHQ were calculated.

Chemical analysis

Fatty acid composition by gas chromatography

Fatty acid methyl esters (FAME) of the oil samples were prepared by trans esterification, according to AOCS method No: Ce 1-62, 1998 (Firestone 1998). FAMEs were analyzed by gas chromatography (GC) (Fisons 8000, Co., Italy), equipped with a hydrogen flame ionization detector (FID) and a fused silica capillary column (100 m×0.25 mm i.d.), coated with 0.20 μm SP2560 (Supelco Inc., Bellefonte, PA) as the stationary phase. The oven temperature was programmed from 140 °C to 240 °C at 4 °C/ min with an initial hold at 140 °C for 5 min. The injector and FID (Flame ionization detector) were at 260 °C. A reference standard FAME mix (Supelco Inc.) was analyzed under the same operating conditions to determine the peak identity. A comparison between the retention times of the samples with those of authentic standard mixture, run on the same column under the same conditions, was made to facilitate identification. The FAMEs result were expressed as relative area percentage.

Peroxide value determination

A typical procedure to evaluate the peroxide values is (Kishk and Al-Sayed 2007); 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. Then, 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) was calculated using the formula given in Eq. (7)

$$PV = \frac{V_{Na_2S_2O_3} \times N_{Na_2S_2O_3} \times 1,000}{\text{Weight of sample}} \tag{7}$$

where, V is the volume and N is the normality sodium thoisulphate solution.

Free fatty acids

The free fatty acid (FFA) content as the percentage of oleic acid was determined using AFNOR NF T 60- 204 standard method. Acid value was defined as the amount (mg) of KOH required to neutralize FFA in 1 g of oil sample dissolved in a mixture of diethyl ether and ethanol.

Polar compounds

The contents of total polar compounds were determined using the method proposed by IUPAC, 1992 (Izbaim et al. 2010).

Results and discussion

In this study, the stability of sesame oil at different times of heating and at different amounts of TBHQ has been investigated using the parameters of viscosity (Sarmento et al. 2006; Valantina et al. 2010), density and ultrasonic velocity (Kesavasamy et al. 2008; Priya et al. 2010). These parameters were evaluated after different times of heating. It was found

that the antioxidant stability of TBHQ with sesame oil was better even at high temperature and after prolonged heating (Okoye et al. 2009; Rehab 2010).

The study of thermal degradation and antioxidant stability of the sesame oil was carried out by heating the oil at 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 at different concentrations were measured at 30 °C.

Density

The variations in the density of oils are studied with different heating time. The Fig. 1 shows the variation of density (ρ) with heating time. The density of heated sesame oil gradually and substantially increased with the increased period of heating. Incorporation of 200 ppm of TBHQ in to oil causes little increase in the density values as compared to the control oil. The density of the oil containing 200 ppm of TBHQ hardly changed as there are no molecular changes due to the antioxidant activity of the oil. The variation in density is due to severe damage in chemical composition as there is an increase in the saturation composition of the oil (Valantina et al. 2010).

Viscosity

The changes in the viscosity values as a function of heating time is shown in Fig. 2. Generally, the viscosity (η) 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. The Fig. 2 shows that the control had the highest values of viscosity whereas oil with 200 ppm of TBHQ had the lowest viscosity values. These results suggested that oil with 200 ppm of TBHQ will change the viscosity to a small extent during the frying process. The highest level of TBHQ mixed oil exhibits the lowest change in oil viscosity. The obtained results were in good agreement with the results

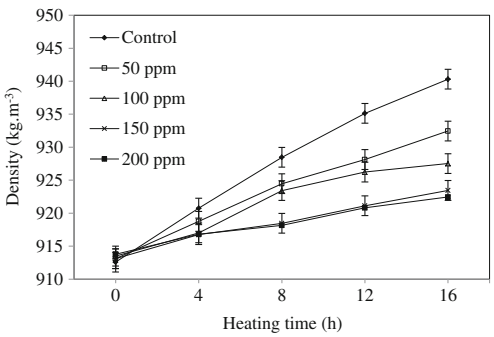

Fig. 1 Variation of density as a function of heating time for sesame oil and sesame oil with different concentrations of tertiary butyl hydroquinone

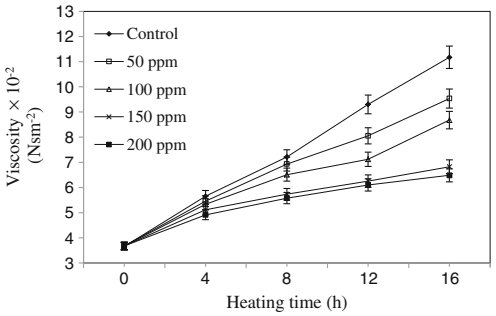

Fig. 2 The viscosity as a function of heating time for the control and sesame oil with different concentrations of tertiary butyl hydroquinone

published elsewhere (Rehab 2010; Farag et al. 2003; Shaker 2006; Anany 2007). They reported that the fried oil with various dosages of phenolic compounds didn't alter the viscosity during the frying process.

The viscosity of oil increases with duration of frying 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).

Ultrasonic velocity and acoustical parameters

The ultrasonic velocity and attenuation depends on the physico-chemical properties of the oil (McClements 1997). Majority of the studies which used ultrasonic evaluation of food properties use ultrasonic velocity, as it is more reliable than attenuation and related to the physical and chemical properties of the medium (Benedito et al. 2007). After each frying period the ultrasonic velocity increases and thus it is possible to distinguish the two oils (Izbaim et al. 2010).

The variation in the velocity of ultrasonic sound with heating time is indicated in Fig. 3. It was observed that the ultrasonic velocity increased linearly as the density and the viscosity was increased with the heating time. The ultrasonic velocity increased significantly in the control oil. The insignificant change in the ultrasonic velocity was noticed for

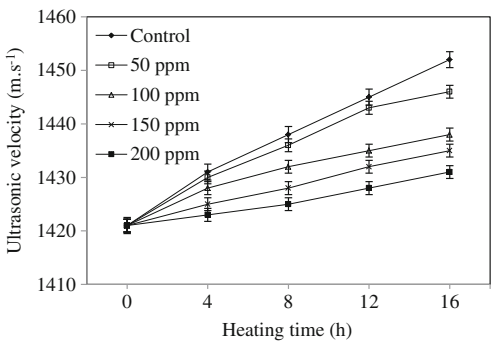

Fig. 3 Effect of heating time on ultrasonic velocity of the control and sesame oil with different concentrations of tertiary butyl hydroquinone

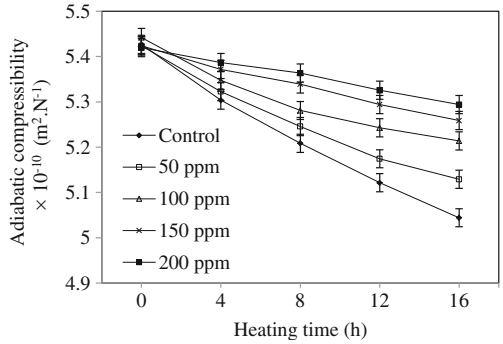

Fig. 4 Variation of adiabatic compressibility of the control and sesame oil with different concentrations of tertiary butyl hydroquinone with heating time

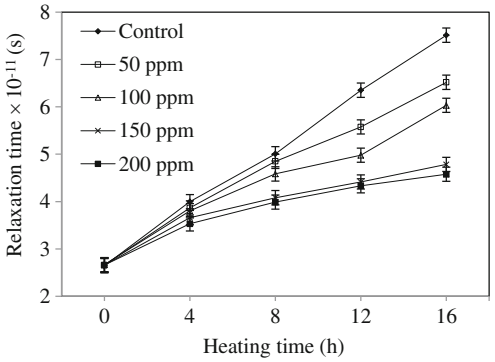

Fig. 6 Variation of relaxation time of the control and sesame oil with different concentrations of tertiary butyl hydroquinone as a function of heating time

sesame oil with 200 ppm of TBHQ. Figures 4, 5, 6 and 7 illustrate the interaction between the ultrasonic waves and the composition of oil molecules. The increase in the ultrasonic velocity was due to 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 for oil with 200 ppm of TBHQ as compared to the changes in the adiabatic compressibility and free length in the base oil. The adiabatic compressibility and free length are deciding factors of the ultrasonic velocity in liquid systems (Priya et al. 2010). The decrease in the values 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 due to the effect of TBHQ (Guzman et al. 2009). Hence, the values of free length which indicates the intermolecular distance didn't reduce as a result of using TBHQ.

The changes in the relaxation time of oil as a funtion of heating time are shwon in Fig. 6. It was found that relaxation time is increased with the heating period generally. The base oil showed greater enhancement and least increment were found in oil with 200 ppm of TBHQ. The dispersion of ultrasonic velocity in the system should contain information about the characteristic time, τ of the relaxation process that causes dispersion, where, τ is in the order of 1×10^{-11} s due to the structural relaxation process (Kinsler and Rray 1989) and in such a situation, the molecules get rearranged due to a co-operative process (Ali et al. 2000).

The acoustic impedance is calculated using ultrasonic velocity and density and it was plotted as a function of heating time as shown in Fig. 7. It was found that the acoustic impedance was low in the oil with TBHQ and without heating. With increased heating time, the acoustic impedance increased in the base oil, but to a slight variation in the oil with 200 ppm of TBHQ. 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 measured acoustical parameters such as β, τ, L_f and Z were correspondingly 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 occurred to a lesser extent and hence very small structural changes occurred

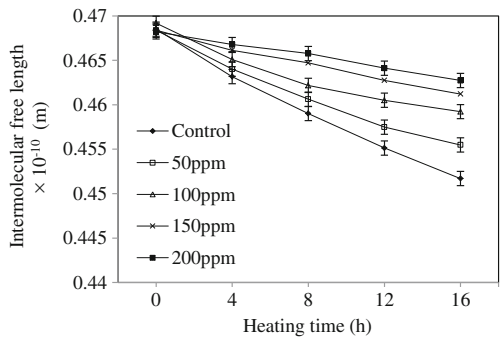

Fig. 5 Effect of heating time on intermolecular free length of the control and sesame oil with different concentrations of tertiary butyl hydroquinone

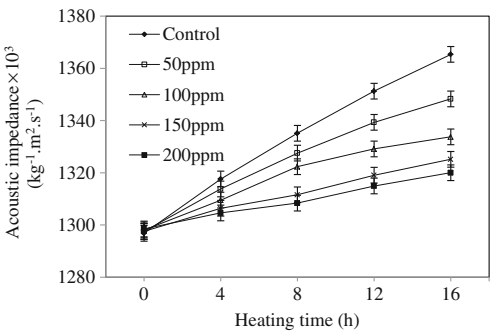

Fig. 7 Variation of acoustic impedance of the control and sesame oil with different concentrations of tertiary butyl hydroquinone as a function of heating time

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, larger changes have been occurred during heating in the adiabatic compressibility, intermolecular free length, relaxation time and acoustical impedance.

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 same acoustical parameter values as shown for 200 ppm of TBHQ loaded oil. In India, 150 ppm of TBHQ is allowed in vegetable oils whereas the general standard for food additives (Codex 1995) allows the usage of antioxidant upto 200 ppm. Hence, the maximum stability of oil can be maintained with 200 ppm of TBHQ.

Fatty acid composition

Gas chromatography (GC) is a useful analytical technique for studying the effect of different conditions on the fatty acid composition of fats (Kowalski 2007). The incorporation of TBHQ enhanced the oxidative stability of the heated oil samples. The estimated concentration of the unsaturated fatty acids by relative GC peak areas showed that sesame oil samples treated with 200 ppm TBHQ had significantly lower values in comparison with base oil.

The fatty acid (FA) profile of sesame oil with 200 ppm of TBHQ showed slight changes in the FA composition in heated oils, which reflected that antioxidant addition in the unsaturated oils controls the thermal degradation of oils. The reduction in the amount of linoleic acid noticed with the increase in concentration of oleic acid (Akhtar et al. 2012).

Tables 1 and 2 indicate the results for the fatty acid profiles of the sesame oil and formulated oil samples after each heating period. The FA composition of oil has marked effects on its frying performance as well as on its physical and chemical behaviors. The FA profile of the frying oils changed as a result of cyclization, polymerization and hydrolytic, oxidative and other chemical reactions promoted by frying conditions (Nawar 1996). The linoleic acid level in deep-frying oils appears to be an obviously negative factor in oil stability. In this study, changes in the fatty acid profile of oils during frying are basically among the unsaturated fatty acids, whereas the saturated fatty acids are slightly increased. Sesame oil had higher linoleic acid content (44.2 %). The frying stability of highly unsaturated vegetable oils such as sesame oil can be improved by incorporation of TBHQ to reduce the change of linoleic acid, and consequently to improve their oxidative and heat stabilities.

Pure sesame oil contained, palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid and α-linolenic acid in the proportions of 11.2 %, 0.45 %, 0.45 %, 36.9 %, 44.2 % and 0.35 % respectively. The compositions of palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, and α-linolenic acid have been changed to 19.8 %, 0 %, 12.86 %, 36.85 %, 29.23 % and 0 % respectively and in formulated oil it has changed to 15.28 %, 0 %, 8.16 %, 36.75 %, 37.23 % and 0 % respectively after the frying period of 16 h. These data indicates that the amount of unsaturated fatty acid decreased gradually during repeated deep fat frying cycles. This may be due to oxidative and thermal degradation reactions during repeated deep fat frying cycles in the unsaturated fatty acid constituents of triacylglycerols (Harish et al. 2006). Comparable changes were observed in the formulated oils during repeated frying as compared to the pure oil.

Peroxide value

Hydro peroxides are the primary products of the oxidation of lipids; therefore, determination of peroxides can be used as an oxidation index (OI) for the early stages of lipid oxidation (Barthel and Grosch 1974). Changes in the peroxide values of the sesame oil samples under investigation during the heating process are shown in Fig. 8. At the end of the frying period, the peroxide value (PV) of sesame oil without antioxidant was about 26.88 meq. of oxygen/kg of fat and the sesame oil mixed with 50, 100, 150 and 200 ppm of TBHQ was about 18.56, 14.67, 10.80 and 8.48 meq. of oxygen/kg of fat.

Table 1 Changes in the fatty acid composition (%) of sesame oil during heating process

% Fatty acid composition	Duration of heating (h)				
	0	4	8	12	16
C16:0	11.2±0.9	14.34±0.35	15.67±0.42	18.3±0.45	19.8±0.51
C16:1	0.45±0.02	0.31±0.02	–	–	–
C18:0	4.21±0.07	5.77±0.23	7.34±0.17	10.29±0.31	12.86±0.34
C18:1	36.9 ±1.5	38.23±1.17	41.26±1.25	38.97±1.16	36.85±1.15
C18:2	44.2 ±1.4	39.85±1.23	34.38±1.18	31.42±1.15	29.23±1.14
C18:3	0.35 ±0.01	0.32±0.01	0.11±0.01	–	–

C16:0, palmitic acid; C16:1, palmitoleic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid; α-C18:3, α-linolenic acid

Table 2 Changes in the fatty acid composition (%) of sesame oil with 200 ppm TBHQ during heating process

%Fatty acid composition	Duration of heating (h)				
	0	4	8	12	16
C16:0	11.2±0.8	12.34±0.34	13.97±0.38	14.33±0.33	15.28±0.35
C16:1	0.46±0.02	0.41±0.02	0.25±0.018	0.0	0.0
C18:0	4.22±0.07	4.84±0.24	5.44±0.095	6.79±0.88	8.16±0.85
C18:1	36.8±1.5	37.13±1.18	38.26±1.18	37.71±1.12	36.75±1.13
C18:2	44.9±1.4	42.85±1.25	40.13±1.22	39.22±1.12	37.23±1.16
C18:3	0.35 ±0.01	0.34±0.01	0.18±0.012	0.0	0.0

C16:0, palmitic acid; C16:1, palmitoleic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid; α-C18:3, α-linolenic acid

In general, the peroxide values of sesame oil increased substantially during heating and were strongly correlated with a prolonged heating period. The lowest PV value at the end of heating period was noticed for sesame oil treated with 200 ppm of TBHQ. The results indicated that the antioxidative effect of TBHQ was strongly depends upon its concentration. These results were consistent with the data published elsewhere (Azuma et al. 1999; Rehab 2010; Farag et al. 2003; Shaker 2006; Anany 2007).

Several studies indicated the effect of the frying process on the physico-chemical and sensory properties of fried oil. Many scientist (Clark and Serbia (1991), White (1991), Tyagi and Vasistha (1996) and Pimpa et al. (2009) have 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. These parameters clearly indicate that the state of oil deterioration and sesame oil with 200 ppm of TBHQ was more stable chemically than the base oil.

Free fatty acid value

Formation of free fatty acids (FFA) during frying process is considered to be a measure of rancidity of oils. The percentage of FFA formed during the heating process has been indicated in the Table 3. Initially, the base oil and the TBHQ loaded oils had a similar FFA content, as the heating period is continued the sesame oil showed a higher FFA values than the TBHQ loaded oils. FFA is formed due to hydrolysis of triglycerides and may get promoted by the reaction of oil with moisture (Frega et al. 1999). Addition of antioxidant caused significant reduction in FFA values of sesame oil. FFA content is the frequently used data to probe the life of frying oil, but it is not recommended to be the only indicator. As a result of the cleavage of triglycerides during oxidation and hydrolysis, FFAs are formed. Previous studies of frying oils have shown that the content of FFA increases during deep-frying and other volatile substances affect the smoke point (Kalapathy and Proctor 2000). Oils with high FFA are known to have a lower smoke point (Augustin et al. 1987) and the surfactant effect of FFA contributes to foaming which leads to further oxidation of the oil. As expected, FFA contents of the sesame and sesame oil with TBHQ increased during frying process.

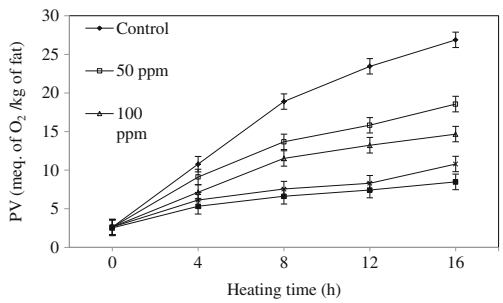

Fig. 8 Variation of peroxide value (PV) of the control and sesame oil with different concentrations of tertiary butyl hydroquinone with heating time

Changes of polar compounds in oil

Generally, degradation of oil during frying is accompanied by increasing the polar compounds of oil (Innawong et al. 2004). Many researchers reported that the total polar components (TPC) to be the most reliable indicator of oil degradation (Fritch 1981; Gere 1982). Polar compounds include all oxidized triglycerides, dimerized triglycerides, FFAs, monoglycerides, diglycerides, sterols, carotenoids, antioxidants, antifoamers, hydrogenation catalyst residues and soaps (Blumenthal 1996). Table 4 shows the percentage of TPC formed during heating in sesame oil and sesame oil with 200 ppm of TBHQ. Initially, the TPC contents of base oil and formulated oil were similar. The increase in the rate of TPC formation in the base oil was different from formulated oil. After 16 h of frying, the final TPC values were 18.5 % in

Table 3 Variation of % free fatty acids (as oleic acid) with different heating periods of sesame oil with and without TBHQ

Sample	0 h	4 h	8 h	12 h	16 h
Sesame oil	0.11	0.14	0.18	0.23	0.31
Sesame+200 ppm TBHQ	0.10	0.12	0.15	0.17	0.18

Table 4 Variation of % polar compounds with different frying periods of sesame oil with and without TBHQ

Sample	0 h	4 h	8 h	12 h	16 h
Sesame oil	4.1	7.6	11.5	15.8	18.5
Sesame+200 ppm TBHQ	4.15	6.2	7.9	9.1	10.5

base oil and 10.5 % in formulated oil. These parameters are indicators of the state of oil degradation and the results indicated that sesame oil with 200 ppm of TBHQ was more stable chemically than sesame oil without TBHQ. Polar compounds are sum of non triglycerides of oil including fatty acids, alkaline pollutions, sterols, tocoferols, mono and di triglycerides, alcohols, aldehydyes, ketones and other soluble compounds in oil that are more polar than triglycerides (Melton et al. 1994). According to few researchers (Billek et al. 1978; Paradis and Nawar 1981) the degradation of oils can be measured by polar compounds which indicate the breakdown of triglycerides. Polar compounds accumulate on the surface of frying pan and foods during of frying. It can be imagined that the most poisonous material are exist in the polar compound of oil (Frankel and Huang 1994). If the total polar compounds exceeds more than 25 %, the oil should be disposed (Romero et al. 2000) according to FDA regulations. Hence, on further heating for 10 h it would be expected that sesame oil may not be fit for usage.

Conclusion

In the current study a method has been developed which makes use of simple methods such as density, viscosity and ultrasonic velocity to determine the stability of sesame oil. Mixing different concentration of TBHQ (50, 100, 150 and 200 ppm) with sesame oil provides improvement in antioxidative potency of these edible oils. Subsequently, the oil would have longer shelf-life, stability and more nutritional value. The addition of the 200 ppm TBHQ resulted in the retardation of oxidative deterioration. TBHQ was found to be the most effective at the concentration of 200 ppm, however at 150 ppm of TBHQ concentration the density and viscosity showed the nearly same variation as that of 200 ppm of TBHQ. Also in the present study the variation in the secondary parameters such as β, τ, L_f and Z of sesame oil with TBHQ as compared with the control oil. It is found that the composition of the oil did not become saturated due to the presence of the antioxidant (TBHQ) on heating process and at 200 ppm TBHQ. The stability is effectively retained which is also as per the general standard for food additives. However, the secondary parameters at 150 ppm of TBHQ were nearly same as that of 200 ppm TBHQ. Hence, addition of 150 ppm of TBHQ may be preferred. Sesame oil with TBHQ has better thermal stability than sesame oil without antioxidant. Ultrasonic velocity and acoustical parameters can be used to assess the stability of sesame oil. This methodology could be useful to evaluate the oxidative state of edible oils in a simple and fast way.

References

Akhtar H, Tariq I, Mahmood S, Hamid S, Khanum R (2012) Effect of antioxidants on stability, nutritional values of refined sunflower oil during accelerated storage and thermal oxidation in frying. Bangladesh J Sci Ind 47(2):223–230

Ali A, Kumar A, Abida J (2004) Ultrasonic and volumetric studies of molecular interaction in acetonitrile + 1-alkanols C_6, C_8, C_{10} binary mixtures at different temperaturas. J Chi Chem Soc 51:477–485

Ali A, Hyder S, Nain AK (2000) Intermolecular interactions in ternary liquidmixtures by ultrasonic velocity measurements. J Phys Ind 74B:63–67

Anany AM (2007) Influence of pomegranate (Punica granatum) peels extract on the stability of sunflower oil during deep–fat frying process. Electron J Food Plants Chem 1:14–19

Aralaguppi MI, Barragi JC (2006) Physico-chemical and excess properties of the binary mixtures of methyl cyclohexane + ethanol + propan-1-ol + propanol, + butane-1- ol + 2-methyl-1-propanol or 3- methyl -1- propanol or 3- methyl-1- butanol at T = 298.15, 303.15 and 308.15 K. J Chem Therm 38:434–442

Augustin MA, Asap T, Heng LK (1987) Relationships between measurements of fat deterioration during heating and frying in RBD olein. J Am Oil Chem Soc 64:1670–1675

Azuma K, Ippousshi K, Higasio H, Terao J (1999) Evaluation of antioxidative activity of vegetable extracts in linoleic acid–emulsion and phospholipids bilayers. J Sci Food Agric 79:1–7

Barthel G, Grosch W (1974) Peroxide value determination and comparison of some methods. J Am Oil Chem Soc 51:540–544

Benedito J, Garcia-Perez JV, Dobarganes MC, Mulet A (2007) Rapid evaluation of frying oil degradation using ultrasonic technology. Food Res Intl 40:406–414

Billek C, Cuhr C, Waibel J (1978) Quality assessments of used frying fats: a comparison of four methods. J Am Oil Chem Soc 55:728–733

Blumenthal MM (1996) Frying technology. In: Hui YH (ed) Bailey's industrial oil & fat products edible oil & fat products: products and application technology. Wiley-Interscience, New York, pp 429–483

Clark WL, Serbia GW (1991) Safety aspects of frying fats and oils. J Food Technol 45(2):44–89

Codex (1995) General Standard for Food Additives (GSFA) Codex STAN 192–1995, Preamble

de Guzman R, Tang H, Salley S, Ng KYS (2009) Synergistic effect of antioxidants on the oxidative stability of soya bean oil- and poultry fat-based biodiesel. J Am Oil Chem Soc 86:459–467

Ernest S, Kavitha P (2011) Acoustical and excess thermodynamical parameters of sesame oil in different organic solvents. J Chem Environ Pharm Res 2

Farag RS, El-Baroty GS, Amany B (2003) The influence of phenolic extracts obtained from the olive plants (*cvs. Picual and Kronakii*) on stability of sunflower oil. J Food Sci Technol 38:81–87

Firestone D (ed) (1998) Method no: Ce1-62. Official methods and recommended practices of the American Oil Chemists Society, 5th edn. AOCS press, USA

Frankel EN, Huang SW (1994) Improving the oxidative stability of polyunsaturated vegetable oils by blending with high-oleic sunflower oil. J Am Oil Chem Soc 71:255–259

Frega N, Mozzon M, Lercka G (1999) Effects of free fatty acids on oxidative stability of vegetable oil. J Am Oil Chem Soc 76:325–329

Fritch CW (1981) Measurements of frying fat deterioration: a brief review. J Am Oil Chem Soc 58:272–274

Gere A (1982) Studies of the changes in edible fats during heating and frying. Die Nahrung 26:923–932

Harish B, Sharma K, Kaur B, Sarkar BC, Singh C (2006) Thermal behavior of pure rice bran oil, sunflower oil and their model blends during deep fat frying. Grasas Aceites Int J Fats oils 57(4): 376–381

Innawong B, Parameswarakumar M, Marcy JE (2004) The determination of frying oil quality using a chemosensory system. Lebensm Wiss Technol 37:35–41

Izbaim BD, Faiz B, Moudden A, Taifi N, Aboudaoud I (2010) Evaluation of the performance of frying oils using an ultrasonic technique. Grasas Aceites Int J Fats oils 61(2):151–156

Izbaim BD, Faiz B, Moudden A, Hammine A (2009) Use of ultrasonic for the quality assessment of frying oil. J Int Signal Syst Control Eng Appl 2(2):35–39

Kalapathy U, Proctor A (2000) A new method for free fatty acid reduction in frying oil using silicate films produced from rice hull ash. J Am Oil Chem Soc 77:593–598

Kesavasamy R, Ponnuswamy V, Kannappan AN (2008) Molecular interaction studies in the ternary liquid mixture of pyridine + benzene + n, n-dimethylformamide. ARPN J Eng Appl Sci 3(4):41–45

Kimilu RK, Nyang'aya JA, Onyari JM (2011) The effects of temperature and blending on the specific gravity and viscosity of Jatropha methyl ester. ARPN J Eng Appl Sci 6:12

Kinsler LE, Rray AR (1989) Fundamentals of acoustics, 2nd edn. Wiley, Eastern New Delhi

Kishk YFM, Al-Sayed HM (2007) Free-radical scavenging and antioxidative activities of some polysaccharides in emulsions. LWT Food Sci Technol 40(2):270–277

Kowalski R (2007) GC analysis of changes in the fatty acid composition of sunflower and olive oils heated with quercetin, caffeic acid, protocatechuic acid. Symp A Q J Mod Foreign Lit 18:15–23

McClements DJ (1997) Ultrasonic characterization of food and drinks: principles, methods and applications. Crit Rev Food Sci 37: 1–46

Melton SL, Jafar S, Sykes D, Trigiano MK (1994) Review of stability measurements for frying oils and fried food flavor. J Am Oil Chem Soc 71:1301–1308

Min DB, Boff JF (2001) In: Akoh C, Min DB (eds) Food lipids lipid oxidation of edible oil. Marcel Dekker, New York, pp 335–363

Nawar WW (1996) Lipids. In: Fennema COR (ed) Food chemistry, 3rd edn. Marcel Dekker, New York, pp 225–319

Okoye IP, Onwe OJ, Aakarnta O (2009) The effect of the antioxidant quercetin on the oxidation stability of lubricating oil. J Sci Afr 8(2): 26–30

Pimpa B, Kanjanasopa D, Sophon (2009) Effect of addition of antioxidants on the oxidative stability of refined bleached and deodorized palm olein. J Kasetstart Nat Sci 43:370–377

Rehab Ali FM (2010) Improvement in the stability of fried sunflower oil by using different levels of pomposia (*Syzygium cumini*). EJEAF Chem 9(2):396–403

Priya C, Nithya S, Velraj AN (2010) Molecular interaction studies in liquid mixture using ultrasonic technique. J Adv Sci Technol 18:59–74

Paradis AJ, Nawar WW (1981) A gas chromatographic method for the assessment of used frying oils: comparison with other methods. J Am Oil Chem Soc 58:635–638

Romero A, Cuesta C, Sanchez MFJ (2000) Cyclic fatty acid monomers and thermoxidative alteration compounds formed during frying of frozen foods in extra virgin olive oil. J Am Oil Chem Soc 77:1169–1175

Rossell JB (ed) (2001) Frying improving quality Woodhead Publishing Limited. Cambridge UK Part II

Saeed R, Masood S, Nadeem (2012) Ionic-Interaction of Potassium Iodide in Edible Oils + DMF System by Viscosity. Method Int J Chem 4(4):28

Sarmento CMP, Ferriera SRS, Henseh (2006) Supercritical fluid extraction (SFE) of rice bran oil to obtain fractions enriched with tocopherols and tocotrienols. J Braz Chem Eng 23:243–249

Shaker ES (2006) Antioxidative effect of extracts from grape seed and peel on lipid oxidation in oils of sunflower. LWT J Food Sci Technol 39:883–892

Tyagi VK, Vasistha AK (1996) Changes in the characteristics and composition of oils during deep-fat frying. J Am Oil Chem Soc 73(4): 499–506

Valantina S, Sahayararaj P, Prema A (2010) Antioxidant stability in palm and rice bran oil using simple parameters. J RASAYAN Chem 3:44–50

White PJ (1991) Methods for measuring changes in deep-fat frying oils. J Food Technol 45(2):75–80