Antioxidant effect of supercritical CO₂ extracted *Nigella sativa* L. seed extract on deep fried oil quality parameters

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Abstract Effect of supercritical CO₂ extracted *Nigella sativa* L. seed extract (NE) on frying performance of sunflower oil and refined, bleached and deodorized (RBD) palm olein was investigated at concentrations of 1.2 % and 1.0 % respectively. Two frying systems containing 0 % *N. sativa* L. extract (Control) and 0.02 % butylated hydroxytoluene (BHT) were used for comparison. Physicochemical properties such as fatty acid composition (FAC), Peroxide Value (PV), Anisidine Value (AV), Totox Value (TV), Total Polar Content (TPC), C_{18:2}/C_{16:0} ratio and viscosity of frying oils were determined during five consecutive days of frying. Results have shown that *N. sativa* L. extract was able to improve the oxidative stability of both frying oils during the frying process compared to control. The stabilizing effect of antioxidants were in the order of BHT > NE. RBD palm olein was found to be more stable than sunflower oil based on the ratio of linoleic acid (C_{18:2}) to palmitic acid (C_{16:0}) and fatty acid composition.

Keywords Natural antioxidants · *Nigella sativa* L. extract · Fatty acid composition · Deep fat frying · Physicochemical properties

Introduction

Since food habits are based on baked and deep fried foods worldwide, oxidative-resistant oils are required. Conventionally existing cooking oils cannot fulfill this necessity as they may result in serious health disorders because of the

generation of harmful oxidation products (Ramadan 2013). Scientists have extensively reported on physical and chemical changes that take place during frying and on the wide range of decomposition products appeared in frying oils. To develop the delicious deep fried flavor, a small amount of oxidation is necessary in the frying oil containing the fried food. Nevertheless, as a result of oil further break down, due to the processes of oxidation, hydrolysis and polymerization, some compounds are formed that can result in off flavors and even may be toxic if they are formed in high concentrations (Mezouari and Eichner 2007). Oxidation reaction can be inhibited by antioxidants that naturally exist in the oils or can be added to increase the stability. Antioxidants are primarily applied in the oils to delay the accumulation of primary oxidation products and consequently to improve the oxidative stability (Mohdaly et al. 2010). There is an increase in consumer's concern for replacing synthetic antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), and gallates with natural antioxidants, which could present additional biological functions to the food products and prevent toxicity concerns (Chaiyasit et al. 2007). The use of antioxidants from plants and herbs in processed foods has achieved an increasing importance in food industry as an alternative to synthetic antioxidants. Antioxidants from natural sources are accompanied with health benefits since these oxygenated compounds contribute to a positive action against heart diseases, malaria, neurodegenerative diseases, AIDS, and cancer (Aruoma et al. 1997). Natural antioxidants allow food processors to produce stable products with clean labels and all-natural constituents (Ramadan et al. 2012). Due to these reasons, the market for natural antioxidant should rapidly grow. Studies have shown that the presence of natural antioxidants from various aromatic and medicinal plants is closely related to a decrease in chronic diseases such as DNA damage, mutagenesis, and carcinogenesis (Reddy et al. 2003). There is a growing interest in the

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study of plant extracts and essential oils for their antioxidant activity (Rasooli 2007). Many plant extracts exhibit various degrees of antioxidant activity in different fats and oils (Che Man and Tan 1999). No scientific study has been conducted on the effect of *N. sativa* L. extract (NE) in frying conditions. Previous studies had explored antioxidant activity of *Nigella* extract on chemical changes of different types of frying oils at accelerated oxidative reaction conditions (Lutterodt et al. 2010; Mariod et al. 2009; Singh et al. 2005). The results of these studies have shown that NE was able to stabilize the oil and the stabilization extent was comparable with synthetic antioxidants such as BHA or BHT. This study is aimed at evaluating the antioxidative property of NE in RBD palm olein and sunflower oil during deep fat frying of French fries.

Materials and methods

Materials

N. sativa L. seeds were purchased from a local market (Tehran, Iran). Carbon dioxide (purity 99.99 %), contained in a dip tube cylinder, was supplied by MOX Company (Petaling Jaya, Selangor, Malaysia). Refined, bleached and deodorized (RBD) palm olein and sunflower oil were purchased from a local market (Selangor, Malaysia). Fresh potato was purchased from a local market (Selangor, Malaysia). All chemicals and solvents used were either of analytical grade or GC grade purchased from Fisher Scientific Chemical (Loughborough, UK) and Merck (Darmstadt, Germany).

N. sativa L. extraction

N. sativa L. seeds were milled in a grinder (MX-335, Panasonic, Malaysia) for 2 min and then passed through 1–2 mm screens and preserved in hermetic bags at -20°C until analysis according to the method of Cheikh-Rouhou et al. (2007). Supercritical carbon dioxide (SC- CO_2) extraction was performed at pressure of 350 bar, temperature of 50°C for a duration of 60 min dynamic extraction time using supercritical fluid extractor (ABRP200, Pittsburgh, PA, USA). Ethanol (99.9 %) was used as modifier with a flow rate of 5 ml/min. The supercritical CO_2 flow rate was maintained at 15 g/min and the duration of static extraction time was fixed to 30 min.

Preliminary determination of NE concentration for frying study

To determine the concentration of NE to be studied in the frying oil, DPPH radical scavenging method was used according to Ramadan et al. (2006) method. Toluenic solution of DPPH (10^{-4} M) was freshly prepared. 10 mg of the oil

(sunflower oil and RBD palm olein) containing different concentrations of NE (0.02, 0.05, 0.1, 0.2, 0.4, 0.8, 0.9, 1, 1.1, 1.2 and 1.3 %) was sampled during the frying process in 100 μl toluene at room temperature and was mixed with 390 μl of DPPH toluenic solution, the mixture was then vortexed for 20 s at ambient temperature. After 60 min, the decrease in absorbance at 515 nm was measured in a 1-cm quartz cell against a blank of pure toluene using spectrophotometer Model U2000 (Hitachi Ltd., Tokyo, Japan). The radical scavenging activity toward DPPH radical was evaluated from differences in the absorbance of toluenic DPPH solution with or without sample. The percentage of inhibition was calculated according to the following equation:

$$\% \text{inhibition} = 100(A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}}$$

Antioxidant activity of test compounds or extracts were expressed as IC_{50} which is defined as concentration of test material required to cause a 50 % decrease in initial DPPH concentration. IC_{50} of the sample was expressed in mg/ml and calculated through the linear regression analysis.

Frying experiment

Frying experiment was carried out according to Che Man and Tan (1999) method using two types of frying oils namely, sunflower oil and RBD palm olein with and without antioxidants (BHT and NE). The frying performance for different types of frying oils was consisted of control (without antioxidant, System I), standard (0.02 % BHT, System II) and NE (System III) with concentrations of 1 and 1.2 % for palm olein and sunflower oil, respectively. The frying process was performed in triplicate for each system for each of the frying oils. The oil (2 kg) was put into a Philips batch fryer, model HD 6121 (Philips Malaysia Sdn. Bhd). The temperature was brought up to 60°C before addition of antioxidants to frying oils. The oil was stirred for 10 min to ensure dissolution of antioxidant. In the case of control, the oil also was held for 10 min at 60°C , even though no antioxidant was added. Temperature was then raised to 180°C during 20 min and the frying was started 20 min after the temperature had reached 180°C . A batch of 100 g raw potato chips was fried for 2.5 min at 17.5 min intervals for a period of 3.5 h per day for five consecutive days which is equivalent to 10 fryings per day and 50 times frying for five consecutive days. The fryer was left uncovered during the frying period. At the end of the tenth frying, the fryer was switched off and the temperature was allowed to drop to 60°C . Samples containing 120 g of oil were collected in amber bottles at 60°C for further analyses. All samples were stored under nitrogen at 4°C . The lid of the fryer was put on and the oil was allowed to cool overnight.

Frying was continued the next day while fresh oil was not added to the frying vessel.

Peroxide (PV), Anisidine (AV) and Totox (TV) Values

AOAC (2000) standard method (965.33) was used for determination of peroxide value. 5 g of oil was used for determination using acetic acid-chloroform (60:40, v/v) and saturated potassium iodide solutions. Titration was performed using 0.01 N sodium thiosulphate.

Anisidine value (AV) was determined according to the AOCS (1980) standard method (Ca Sa-40/93). 1.5 g of oil sample was dissolved and made up to volume with iso-octane in a 25 mL volumetric flask. The absorbance (A_b) of the solution was measured at 350 nm against the solvent as blank. Exactly 5 ml of the fat solution was transferred to a test tube and 5 ml of the solvent to another test tube. 1 ml of the p-anisidine reagent (0.25 % W/V solution in glacial acetic acid) was added to each of the tubes. The tubes were shaken to homogenize the solution and after exactly 10 min the absorbance (A_s) of the solution in the first test tube (sample solution) was measured at 350 nm using the solution in the second test tube (solvent solution) as blank. The analysis was performed in triplicate.

$$P-AV = [25(1.2 A_s - A_b)] / W$$

Totox (TV) value was expressed as $2PV + AV$ (Shahidi & Wanasundara 1997).

Total polar compounds (TPC)

The AOAC (2000) standard method (982.27) was used to determine the total polar compounds. A chromatographic column (21 mm i.d., 450 mm long with stopcock and ground glass joint) was filled with 30 ml of a mixture of light petroleum ether and diethyl ether (87:13, V/V). Glass wool was put at the end of the column. 25 g of silica gel was dissolved in 80 ml of the solvent mixture and poured into the column. The elution solvent was removed from the column until its level reached to 10 cm above the silica gel level. About 4 g of sea sand was added to the top layer of silica gel to fix the gel. For TPC determination, 2.5 g of the oil sample was dissolved in 20 ml of the solvent mixture containing light petroleum ether and diethyl ether (87:13, V/V) at room temperature ($30 \pm 2^\circ\text{C}$). It was then made up to volume (50 ml) with the solvent mixture and 20 ml of the solution was poured into the column and drained off to the level of the sand layer. The non-polar compounds were removed with 150 ml of the solvent mixture. The following equation was used for calculation of TPC. Determination was performed in triplicate.

$$\%TPC = (m - m_1)100$$

Where m_1 , is the mass (g) of non-polar fraction and m , is the mass (g) of the sample contained in 20 ml of the solution added to the column.

Apparent Viscosity

The apparent viscosity of samples was determined using a rheological measurement (Rheostress 600, Haake, Karlsruhe, Germany). Oscillatory tests (mechanical spectra) were performed using a cone sensor (C35/2° Ti; 222–1,632; 35 mm diameter, 2° angle), with 0.1 mm gap and a measuring plate cover (MPC 35; 222–1549). Measurement was performed at 25 °C at various shear rates (from 10:00 to 40:00 s^{-1}) and duration of 60 s, whereby the temperature is commonly considered during product utilization. The equipment was driven through the Haake software, Rheowin Job Manager Version 3.12. The flow curves giving viscosity η (mPas.) as a function of shear rate $\dot{\gamma}$ (s^{-1}) were characteristic of shear thinning behavior. Determination was performed in triplicate.

Fatty acid composition (FAC)

Fatty acid methyl esters (FAME) were prepared by dissolving 50 μL of the oil in 950 μL of hexane followed by 50 μL of 1 M sodium methoxide for esterification using the method of Cocks & Van Rede (1966). Fatty acid composition was determined using an Agilent 6,890 N GC (Wilmington, USA) equipped with a flame ionization detector (FID) and a polar capillary column of BPX-70 (0.25 mm $\times$ 30 m $\times$ 0.25 μm , SGE international Pty, Victoria, Australia). The carrier gas (Helium) flow rate was maintained at 6.8 ml/min. The oven temperature was programmed to two stages, first from 50 to 180 °C at the rate of 4 °C/min and then the temperature was raised to 200 °C at the rate of 1 °C/min. The same condition was performed for the FAME standard. The identification of fatty acid methyl esters was performed by comparing the retention times with those of standards. The percentage of each fatty acid was calculated from the peak areas as the ratio of partial area to the total area. Determination was performed in triplicate for all samples.

Statistical analysis

The frying experiment was consisted of two frying oils (sunflower oil and RBD palm olein) each of which including three systems (I, II and III). The frying experiment was performed in triplicate for both frying oils and each frying system. Data obtained from the physicochemical measurements were subjected to one way analyses of variance (ANOVA) to determine

the significance of difference among the samples. The significance of difference among the mean values was determined using Tukey's test. A probability of $p < 0.05$ was considered significant. All the measurements are reported as the mean $\pm$ standard deviation of triplicate analysis. All the analyses were carried out using the statistical software, MINITAB 15 (Minitab Inc., state college, PA, USA).

Results and discussion

Preliminary determination of antioxidant activity

DPPH radical scavenging test has been used to measure the antiradical action of antioxidants since it has a high correlation with the physicochemical characteristics of frying oil (Ramadan 2010). IC_{50} was chosen as an indicator to see the changes in the antioxidant capacity of both frying oils after addition of NE. Accordingly, in order to see the changes in physicochemical characteristics of frying oil, IC_{50} could be the best option to determine and to select the best concentration of the extract which has no significant ($p < 0.05$) difference in terms of IC_{50} with that of synthetic antioxidant, BHT (0.02 %). The IC_{50} of frying oils (RBD palm olein and sunflower oil) containing different concentrations of NE (0.02, 0.05, 0.1, 0.2, 0.4, 0.8, 0.9, 1, 1.1, 1.2 and 1.3 %) was measured prior to the frying experiment and was compared with the frying oil containing 0.02 % BHT. By comparing the results, the concentration of NE with no significant ($p > 0.05$) different IC_{50} from that of the oil containing standard BHT (with the maximum allowance level of 0.02 %) was monitored. The preliminary results obtained allowed us to suggest that antiradical measurement could be used to quantify the oxidative and hydrolytic deterioration of vegetable oils during deep frying (Ramadan 2010). Table 1 shows the IC_{50} of different concentrations of NE in sunflower oil and RBD palm olein. According to the results, concentrations of 1 % and 1.2 % for palm olein and sunflower oil respectively was determined to have no significant ($p > 0.05$) different IC_{50} from that of the oil containing 0.02 % BHT. Inasmuch as,

the extracts from the SC- CO_2 are not pure antioxidants, the IC_{50} was used to estimate the antioxidant capacity of the extract in the frying oil so that it would be possible to compare it with pure synthetic antioxidant (BHT) in terms of antioxidant activity.

Fatty acid composition (FAC)

Fatty acid composition of sunflower oil and RBD palm olein are presented in Tables 2 and 3 showing the changes in the quantity of fatty acids as affected by frying process through five days of frying. The major fatty acids identified for sunflower oil were oleic acid (C18:1) and linoleic acid (C18:2) whereas, the major fatty acids recognized were palmitic acid (C16:0) and oleic acid (C18:1) for palm olein. In all frying systems there was a decrease in relative amounts of oleic acid (C18:1) and linoleic acid (C18:2) while there was an increase in the amounts of palmitic acid (C16:0) and stearic acid (C18:0). Particularly, during the frying process, polyunsaturated fatty acids were decreased and total saturated fatty acids increased (Orthoefer and List 2006).

In sunflower oil, the decrease in C18:2 across five days of frying were 7.7, 4.01 and 4.51 % in systems I, II and III respectively. Results showed that the system containing NE had lower decrease in the amount of C18:2 compared to control which shows that lower oxidation of polyunsaturated fatty acid had occurred and the oil is more stable in comparison to the control frying system. However, the frying system containing NE (III) had shown a higher decrease in the relative amount of C18:2 compared to the frying system containing BHT (II) which reveals that it is less stable in comparison to system II. In RBD palm olein, the decrease in C18:2 across five days of frying were 6.03, 2.72 and 3.22 % in systems I, II and III respectively. The same trend was observed in RBD palm olein with system containing NE showing a lower decrease in relative amount of C18:2 compared to control and higher decrease compared to the frying system containing BHT. The reason for higher antioxidant power of BHT in frying oil compared to NE could be because of the thermolability of NE active compounds in the frying condition.

Table 1 The DPPH radical scavenging activity (IC_{50}) of *N. sativa* L. extract defined as mg/ml in RBD palm olein and sunflower oil

Type of Oil	Control	BHT (0.02 %)	NE Concentrations (%)										
			0.02	0.05	0.1	0.2	0.4	0.8	0.9	1	1.1	1.2	1.3
Palm Olein	12.48 $\pm$ 0.04 ^a	9.60 $\pm$ 0.02 ^f	12.31 $\pm$ 0.02 ^{ab}	12.16 $\pm$ 0.12 ^{ab}	11.94 $\pm$ 0.07 ^b	11.66 $\pm$ 0.17 ^b	11.14 $\pm$ 0.05 ^c	10.49 $\pm$ 0.22 ^d	10.17 $\pm$ 0.21 ^e	9.65 $\pm$ 0.04 ^f	9.30 $\pm$ 0.09 ^g	9.13 $\pm$ 0.06 ^h	8.89 $\pm$ 0.12 ⁱ
Sunflower	15.76 $\pm$ 0.00 ^a	12.83 $\pm$ 0.08 ⁱ	15.68 $\pm$ 0.02 ^{ab}	15.51 $\pm$ 0.04 ^{ab}	15.43 $\pm$ 0.01 ^b	15.11 $\pm$ 0.24 ^c	14.79 $\pm$ 0.07 ^d	13.65 $\pm$ 0.08 ^e	13.50 $\pm$ 0.05 ^f	13.30 $\pm$ 0.07 ^g	13.15 $\pm$ 0.07 ^h	12.74 $\pm$ 0.08 ⁱ	12.46 $\pm$ 0.02 ^j

Values given are the mean $\pm$ standard deviation of three replications. Values with different small letters are significantly ($p < 0.05$) different. NE, *N. sativa* L. extract

Table 2 Fatty acid composition of sunflower oil for three frying systems during the frying process

System	Day	Fatty Acid (%)							
		C16:0	C18:0	C18:1	C18:2	C20:0	C22:0	C18:2/C16:0	TU
I Control	0	6.33±0.15 ^{Fa}	2.91±0.21 ^{Ba}	36.52±0.41 ^{Aa}	52.25±0.32 ^{Aa}	0.53±0.00 ^{Fa}	0.60±0.02 ^{Ca}	8.25±0.15 ^{Aa}	88.77±0.73 ^{Aa}
	1	7.26±0.18 ^{Ea}	3.27±0.29 ^{Ba}	36.21±0.22 ^{ABa}	51.06±0.21 ^{Ba}	0.59±0.00 ^{Ea}	0.68±0.03 ^{Ca}	7.03±0.14 ^{Ba}	87.27±0.43 ^{ABa}
	2	8.54±0.12 ^{Da}	3.32±0.19 ^{Ba}	35.92±0.38 ^{ABa}	50.11±0.17 ^{Ca}	0.63±0.02 ^{Da}	0.75±0.02 ^{BCa}	5.86±0.06 ^{Ca}	86.03±0.55 ^{Ba}
	3	9.77±0.19 ^{Ca}	4.18±0.14 ^{Aa}	35.12±0.17 ^{Ba}	48.78±0.24 ^{Da}	0.71±0.00 ^{Ca}	0.80±0.04 ^{Ba}	4.99±0.07 ^{Da}	83.90±0.41 ^{Ca}
	4	10.48±0.17 ^{Ba}	4.36±0.29 ^{Aa}	36.19±0.49 ^{ABa}	46.29±0.17 ^{Ea}	0.84±0.00 ^{Ba}	0.92±0.02 ^{Aa}	4.41±0.05 ^{Ea}	82.48±0.66 ^{CDa}
	5	12.34±0.15 ^{Aa}	4.57±0.28 ^{Aa}	35.80±0.41 ^{ABa}	44.55±0.29 ^{Fa}	0.88±0.00 ^{Aa}	0.97±0.01 ^{Aa}	3.61±0.02 ^{Fa}	80.35±0.70 ^{Da}
II BHT (0.02 %)	0	6.31±0.21 ^{Da}	2.90±0.09 ^{Ca}	36.68±0.42 ^{Aa}	52.35±0.21 ^{Aa}	0.51±0.00 ^{Ab}	0.58±0.00 ^{Ba}	8.30±0.24 ^{Aa}	89.03±0.63 ^{Aa}
	1	7.20±0.19 ^{Ca}	3.29±0.08 ^{Ba}	36.16±0.76 ^{Ca}	51.62±0.22 ^{ABa}	0.52±0.00 ^{Ab}	0.61±0.02 ^{Ba}	7.17±0.22 ^{Ba}	87.78±0.53 ^{ABa}
	2	7.49±0.19 ^{Cb}	3.53±0.05 ^{Ba}	36.42±0.05 ^{Ba}	50.85±0.33 ^{Bab}	0.57±0.00 ^{Ba}	0.65±0.01 ^{Bb}	6.79±0.13 ^{Bb}	87.27±0.39 ^{ABa}
	3	8.61±0.12 ^{Bb}	3.72±0.08 ^{ABa}	35.63±0.35 ^{Fa}	50.02±0.58 ^{Bab}	0.63±0.01 ^{Cb}	0.68±0.00 ^{ABa}	5.81±0.15 ^{Cb}	85.65±0.94 ^{Ba}
	4	8.99±0.19 ^{Bb}	3.83±0.09 ^{Aa}	35.99±0.07 ^{Da}	48.99±0.24 ^{Cb}	0.68±0.00 ^{Db}	0.74±0.07 ^{ABa}	5.45±0.09 ^{Cb}	84.98±0.31 ^{Bb}
	5	9.79±0.28 ^{Ab}	3.96±0.04 ^{Aa}	35.65±0.49 ^{Ea}	48.34±0.17 ^{Cb}	0.75±0.02 ^{Eb}	0.78±0.01 ^{Ab}	4.93±0.12 ^{Db}	83.99±0.66 ^{Bb}
III NE (1.2 %)	0	6.33±0.14 ^{Ea}	2.91±0.05 ^{Ba}	36.70±0.29 ^{Aa}	52.39±0.24 ^{Aa}	0.53±0.00 ^{Ca}	0.59±0.04 ^{Ca}	8.27±0.14 ^{Aa}	89.09±0.53 ^{Aa}
	1	6.77±0.15 ^{EDa}	3.09±0.14 ^{ABa}	36.24±0.11 ^{ABa}	52.15±0.32 ^{ABa}	0.57±0.00 ^{BCc}	0.64±0.02 ^{BCa}	7.70±0.12 ^{Ba}	88.39±0.43 ^{ABa}
	2	7.06±0.12 ^{Db}	3.57±0.29 ^{ABa}	35.76±0.46 ^{ABa}	51.45±0.22 ^{Bb}	0.66±0.04 ^{Ba}	0.68±0.00 ^{Bab}	7.28±0.09 ^{Cc}	87.21±0.69 ^{ABa}
	3	8.44±0.25 ^{Cb}	3.63±0.26 ^{ABa}	35.39±0.36 ^{Ba}	50.39±0.11 ^{Cb}	0.69±0.02 ^{ABab}	0.70±0.04 ^{ABa}	5.97±0.16 ^{Db}	85.78±0.48 ^{Ba}
	4	9.15±0.22 ^{Bb}	3.75±0.46 ^{Aa}	35.18±0.33 ^{Ba}	49.46±0.29 ^{Db}	0.72±0.04 ^{ABb}	0.75±0.02 ^{ABa}	5.40±0.10 ^{Eb}	84.64±0.63 ^{BCab}
	5	10.51±0.17 ^{Ab}	3.89±0.21 ^{Aa}	35.28±0.36 ^{Ba}	47.88±0.41 ^{Eb}	0.77±0.01 ^{Ab}	0.79±0.02 ^{Ab}	4.55±0.03 ^{Fc}	83.16±0.77 ^{Cab}

Values given are the mean of nine determinations of three replications ± standard deviation; TU, Total Unsaturated fatty acids; NE, *N. sativa* L. Extract. BHT: butylated hydroxytoluene. Values within each column with different upper case letter are significantly ($p < 0.05$) different. Values between different systems with different lower case letter are significantly ($p < 0.05$) different.

Generally, the decrease in the relative amount of C18:2 is due to oxidation of unsaturated fatty acids into the primary and secondary oxidation products which result in a decrease in the percentage of unsaturated fatty acids (Nazemroaya et al. 2009).

The rate of increase in the relative amount of C16:0 were found to be 6.01, 3.48 and 4.18 % in systems I, II and III respectively in sunflower oil. The frying system containing NE had shown lower increase in C16:0 compared to control whereas, it had shown higher increase in comparison to the frying system containing BHT which shows higher stability in comparison to control and lower stability compared to the frying system containing BHT. In fact, the increase in relative amount of C16:0 is due to the breaking of double bonds in unsaturated fatty acids as a result of oxidation during the frying process. The rate of increase in the relative amount of C16:0 were found to be 5.73, 4.34 and 4.55 % in systems I, II and III respectively in RBD palm olein. The same as sunflower oil, the system containing NE showed lower increase in C16:0 compared to the control and higher increase in comparison to the system containing BHT. In fact, addition of NE to frying oil had reduced the oxidation of unsaturated fatty acids and minimized the increase in C16:0. However, BHT could be more effective in reducing the breaking of double bonds and oxidation compared to NE. The high amount of unsaturation in NE (~85 %) could be a reason for its lower

stability in frying condition. From the results, it can be concluded that the rate of oxidation is decreased in the presence of antioxidants (NE and BHT). Palm olein which contains lower percentage of linoleic acid (C18:2) and higher palmitic acid (C16:0) has shown higher stability towards oxidation during the frying process. In case of palm olein, interaction between the polyphenol compounds from NE and existing tocopherols and tocotrienols in RBD palm olein may have resulted in synergistic antioxidant effects and consequently higher stability of the oil (Mohd Nor et al. 2009).

The ratio of C18:2/C16:0 is used to indicate the degree of oxidative deterioration of frying oils. The ratio of linoleic acid to palmitic acid has been suggested as a valid indicator of the level of polyunsaturated fatty acid (PUFA) deterioration (Normand et al. 2001). The ratio of C18:2/C16:0 is presented in Tables 2 and 3. In all frying systems, the rate of C18:2/C16:0 has been decreased during the five consecutive days of frying. Considering the rate of C18:2/C16:0 as an indicator for the degree of oxidative deterioration, it can be concluded that system containing NE (III) showing lower decrease in C18:2/C16:0 ratio and therefore has more stability as compared to the control and higher decrease in comparison to the system containing BHT (II) in both frying oils.

By comparing relative percentage of fatty acids during the frying process, a clear reduction of unsaturated fatty acids was

Table 3 Fatty acid composition of RBD Palm Olein for three frying systems during the frying process

System	Day	Fatty Acid (%)							TU
		C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:2/C16	
I Control	0	0.30±0.02 ^{Ba}	0.97±0.00 ^{Da}	37.41±0.04 ^{Ea}	4.27±0.02 ^{Da}	45.60±0.04 ^{Aa}	11.33±0.02 ^{Aa}	0.30±0.00 ^{Aa}	56.93±0.07 ^{Aa}
	1	0.35±0.01 ^{Ba}	1.09±0.01 ^{Ca}	38.30±0.28 ^{Da}	4.34±0.01 ^{CDa}	45.29±0.29 ^{Aa}	10.11±0.11 ^{Ba}	0.26±0.00 ^{Ba}	55.40±0.41 ^{Ba}
	2	0.34±0.05 ^{Ba}	1.15±0.04 ^{Ba}	39.27±0.15 ^{Ca}	4.34±0.01 ^{CDa}	45.52±0.11 ^{Aa}	9.10±0.01 ^{Ca}	0.23±0.00 ^{Ca}	54.62±0.12 ^{Ba}
	3	0.41±0.02 ^{ABa}	1.15±0.01 ^{Ba}	39.53±0.05 ^{Ca}	4.36±0.02 ^{Ca}	45.48±0.09 ^{Aa}	8.89±0.02 ^{Ca}	0.22±0.00 ^{Da}	54.37±0.12 ^{Ba}
	4	0.46±0.04 ^{ABa}	1.22±0.02 ^{Bab}	40.85±0.28 ^{Ba}	4.86±0.02 ^{Ba}	44.74±0.09 ^{Aa}	7.44±0.12 ^{Da}	0.18±0.00 ^{Ea}	52.18±0.22 ^{Ca}
II BHT (0.02 %)	5	0.50±0.01 ^{Aa}	1.52±0.00 ^{Aa}	43.14±0.42 ^{Aa}	4.97±0.02 ^{Aa}	43.72±0.67 ^{Ba}	5.30±0.05 ^{Ea}	0.10±0.00 ^{Fa}	49.02±0.73 ^{Da}
	0	0.30±0.04 ^{Ba}	0.96±0.01 ^{Ba}	36.60±0.24 ^{Db}	4.19±0.02 ^{Aa}	45.61±0.071 ^{Aa}	11.59±0.02 ^{Aa}	0.31±0.00 ^{Aa}	57.20±0.09 ^{Aa}
	1	0.32±0.02 ^{Ba}	0.98±0.04 ^{Ba}	37.74±0.48 ^{Ca}	4.21±0.24 ^{Aa}	44.83±0.36 ^{Aa}	10.98±0.17 ^{Bab}	0.29±0.00 ^{Bb}	55.81±0.53 ^{ABa}
	2	0.38±0.01 ^{ABa}	1.07±0.07 ^{Ba}	38.89±0.31 ^{Ba}	4.31±0.14 ^{Aa}	44.76±0.24 ^{Ab}	9.76±0.39 ^{Cab}	0.25±0.00 ^{Cab}	54.52±0.63 ^{Ba}
	3	0.43±0.05 ^{ABa}	1.20±0.05 ^{ABa}	39.32±0.39 ^{Ba}	4.23±0.15 ^{Aa}	43.70±0.19 ^{Bb}	9.65±0.19 ^{CDb}	0.24±0.00 ^{Cb}	53.35±0.39 ^{BCa}
III NE (1 %)	4	0.47±0.02 ^{Aa}	1.28±0.01 ^{Aa}	40.63±0.19 ^{Aa}	4.25±0.12 ^{Ab}	43.64±0.53 ^{Ba}	8.98±0.18 ^{Db}	0.22±0.00 ^{Db}	52.62±0.72 ^{Ca}
	5	0.45±0.02 ^{Aa}	1.34±0.04 ^{Ab}	40.94±0.31 ^{Ab}	4.25±0.26 ^{Ab}	43.44±0.28 ^{Ba}	8.87±0.12 ^{Db}	0.21±0.00 ^{Db}	52.31±0.41 ^{Cb}
	0	0.31±0.04 ^{Ba}	0.54±0.62 ^{Aa}	36.52±0.14 ^{Eb}	4.33±0.04 ^{Aa}	45.92±0.08 ^{Ab}	11.88±0.45 ^{Aa}	0.32±0.01 ^{Aa}	57.80±0.53 ^{Aa}
	1	0.33±0.01 ^{Ba}	0.97±0.02 ^{Aa}	37.28±0.26 ^{Da}	4.35±0.08 ^{Aa}	45.26±0.18 ^{ABa}	11.16±0.33 ^{ABb}	0.29±0.00 ^{Bb}	56.42±0.52 ^{ABa}
	2	0.35±0.02 ^{ABa}	1.10±0.01 ^{Aa}	38.45±0.09 ^{Ca}	4.39±0.07 ^{Aa}	44.71±0.01 ^{Bb}	10.57±0.22 ^{Bb}	0.27±0.00 ^{Cb}	55.28±0.24 ^{Ba}
	3	0.40±0.01 ^{ABa}	1.14±0.02 ^{Aa}	39.84±0.19 ^{Ba}	4.36±0.00 ^{Aa}	43.89±0.33 ^{BCb}	9.76±0.11 ^{BCb}	0.24±0.00 ^{Db}	53.65±0.45 ^{Ca}
	4	0.39±0.02 ^{ABa}	1.16±0.01 ^{Ab}	40.61±0.15 ^{Aa}	4.34±0.02 ^{Ab}	43.54±0.45 ^{Ca}	9.29±0.08 ^{Cb}	0.22±0.00 ^{DEb}	52.83±0.53 ^{CDa}
	5	0.44±0.04 ^{Aa}	1.31±0.00 ^{Ab}	41.07±0.33 ^{Ab}	4.37±0.01 ^{Ab}	43.52±0.25 ^{Ca}	8.66±0.24 ^{Cb}	0.21±0.00 ^{Eb}	52.18±0.49 ^{Db}

Values given are the mean of nine determinations of three replications ± standard deviation; TU, Total Unsaturated fatty acids; NE, *N. sativa L.* Extract. BHT: butylated hydroxytoluene. Values within each column with different upper case letter are significantly ($p<0.05$) different. Values between different systems with different lower case letter are significantly ($p<0.05$) different

observed, with the consequent increase in the saturated fatty acids amount (Tables 2 and 3). The decrease was particularly noticeable in polyunsaturated fatty acids, presumably by oxidation. The rate of decrease was significantly ($p<0.05$) lower in system containing NE (III) compared to control showing that lower oxidation has occurred. However, there was no significant ($p>0.05$) difference in the rate of decrease in unsaturated fatty acids in comparison to the system containing BHT for both frying oil.

Peroxide (PV), Anisidine (AV) and Totox (TV) Values

Peroxide value test is extensively used for the measurement of oxidative rancidity in fats and oils (Mohdaly et al. 2010). Changes in PV of sunflower oil and RBD palm olein during five days of deep frying for three frying systems are presented in Table 4. It is clear that the PV rose and fell during the frying process. In fact, the PV increases as oxidation begins but eventually the rate of hydroperoxide decomposition is more rapid than the rate of hydroperoxide formation and therefore the peroxide value reaches to a maximum and then decreases. In palm olein, frying system I (Control), there was a sharp increase in the peroxide value from day 0 to day 1 of the frying process after which increased with the time of frying until day 3 and then decreased for the last two days of the frying

process. The decrease in peroxide value after day 3 of the frying may be attributed to the instability of peroxides during long heating treatments (Fritsch 1981). In frying system II (BHT), there was an increase in peroxide value until day 4 of the frying process after which decreased at the last day of frying process. In system III (NE), the same trend as system II was observed in the way that the peroxide value increased from day 0 to day 4 of the frying period after which decreased at day 5. This result shows that addition of NE was able to significantly ($p<0.05$) reduce the formation of hydroperoxides as a result of oxidation compared to control during the frying process. This is also expected from the fatty acid composition of both frying systems in the way that system III (NE) which contains more amount of C18:2 compared to system I (control) at the end of the frying process, had less oxidation of C18:2 (linoleic acid) which is shown by lower peroxide value of the oil. However, there was a significant difference ($p<0.05$) in formation of hydroperoxides in the system containing NE (III) in comparison to the system containing BHT (II), revealing that more oxidation has occurred in system containing NE. In sunflower oil, there was an increase in peroxide value of system I (Control) from day 0 to day 2 of the frying period and then a decrease until the end of the frying (day 5). This decrease is due to instability of peroxides under the heating conditions and their reaction to

Table 4 Peroxide, Anisidine and Totox value of sunflower oil and RBD palm olein

Frying system	Day	Characteristics					
		Peroxide value (meq hydroperoxide/kg oil)		Anisidine value		Totox value	
		SO	PO	SO	PO	SO	PO
System I (control)	0	7.56±0.04 ^{Aa}	0.93±0.06 ^{Aa}	10.32±0.07 ^{Aa}	0.92±0.02 ^{Aa}	25.45±0.02 ^{Aa}	2.79±0.14 ^{Aa}
	1	19.31±0.02 ^{Ba}	9.27±0.09 ^{Ba}	65.26±0.21 ^{Ba}	38.22±0.14 ^{Ba}	103.88±0.27 ^{Ba}	56.76±0.33 ^{Ba}
	2	21.87±0.59 ^{Ca}	11.08±0.11 ^{Ca}	74.47±0.47 ^{Ca}	43.51±0.41 ^{Ca}	118.21±1.66 ^{Ca}	65.67±0.64 ^{Ca}
	3	18.69±0.11 ^{Ba}	13.29±0.08 ^{Da}	87.51±0.50 ^{Da}	50.71±0.40 ^{Da}	124.89±0.27 ^{Da}	77.29±0.23 ^{Da}
	4	16.41±0.07 ^{Da}	11.41±0.19 ^{Ea}	98.25±0.28 ^{Ea}	58.10±0.10 ^{Ea}	131.08±0.43 ^{Ea}	80.93±0.48 ^{Ea}
System II (BHT)	5	14.33±0.30 ^{Ea}	9.71±0.09 ^{Fa}	120.56±1.12 ^{Fa}	63.19±0.04 ^{Fa}	149.23±0.51 ^{Fa}	82.61±0.24 ^{Fa}
	0	7.63±0.05 ^{Aa}	0.91±0.06 ^{Aa}	10.27±0.08 ^{Aa}	0.92±0.00 ^{Aa}	25.53±0.19 ^{Aa}	2.75±0.13 ^{Aa}
	1	11.36±0.11 ^{Bb}	5.36±0.29 ^{Bb}	58.44±0.04 ^{Bb}	31.55±0.32 ^{Bb}	81.16±0.26 ^{Bb}	42.27±0.26 ^{Bb}
	2	12.46±0.42 ^{Cb}	6.69±0.12 ^{Cb}	66.20±0.09 ^{Cb}	37.31±0.24 ^{Cb}	91.12±0.75 ^{Cb}	50.69±0.49 ^{Cb}
	3	14.69±0.17 ^{Db}	8.78±0.26 ^{Db}	79.03±1.15 ^{Db}	44.50±0.23 ^{Db}	108.42±0.79 ^{Db}	62.08±0.29 ^{Db}
System III (NE)	4	12.50±0.61 ^{Cb}	10.39±0.26 ^{Eb}	88.40±0.40 ^{Eb}	49.07±0.10 ^{Eb}	113.41±0.82 ^{Eb}	69.85±0.43 ^{Eb}
	5	11.52±0.20 ^{Bb}	9.42±0.22 ^{Da}	109.69±0.43 ^{Fb}	57.63±0.24 ^{Fb}	132.74±0.84 ^{Fb}	76.47±0.20 ^{Fb}
	0	7.62±0.01 ^{Aa}	0.92±0.04 ^{Aa}	10.34±0.01 ^{Aa}	0.92±0.02 ^{Aa}	25.58±0.01 ^{Aa}	2.77±0.12 ^{Aa}
	1	14.14±0.12 ^{Bc}	6.56±0.59 ^{Bb}	59.89±0.61 ^{Bb}	32.68±0.65 ^{Bb}	88.19±0.37 ^{Bc}	45.80±1.83 ^{Bb}
	2	15.61±0.38 ^{Bc}	8.20±0.12 ^{Cc}	69.51±0.50 ^{Cc}	38.44±0.27 ^{Cb}	100.75±0.28 ^{Cc}	54.86±0.02 ^{Cc}
	3	17.46±0.18 ^{Cc}	10.79±0.11 ^{Dc}	80.02±0.65 ^{Db}	47.21±0.09 ^{Dc}	114.95±0.29 ^{Dc}	68.79±0.12 ^{Dc}
	4	15.07±1.11 ^{Bab}	12.88±0.11 ^{Ec}	91.17±0.05 ^{Ec}	51.34±0.48 ^{Ec}	121.31±2.18 ^{Ec}	77.10±0.25 ^{Ec}
	5	13.68±0.08 ^{Ba}	10.60±0.10 ^{Db}	112.11±1.08 ^{Fb}	59.24±0.19 ^{Fc}	139.48±1.25 ^{Fc}	80.45±0.01 ^{Fc}

NE: *N. sativa* L. Extract; SO: Sunflower oil; PO: RBD palm olein; BHT: butylated hydroxytoluene; Values given are the mean of nine determinations of three replications ± standard deviation; Means within each column with different upper case letter are significantly ($p<0.05$) different; Means within each row with different lower case letter are significantly ($p<0.05$) different

form secondary oxidation products. In frying system II (BHT), there was an increase in PV from day 0 to day 3 and then a decrease from day 3 until day 5 of the frying process. In the frying system containing NE (system III) an increase in PV was observed from day 0 to day 3 of the frying process after which decreased until the end of the frying. The significantly ($p<0.05$) lower peroxide values for the system containing NE in both sunflower oil and palm olein compared to control could be due to the antioxidative properties of this additive. The high initial PV of NE could be the reason why it was not as effective as BHT in decreasing formation of hydroperoxides and stabilizing the frying oil which could be due to the decrease in effectiveness of phenolic compounds present in NE (Satue et al. 1995). According to Ramadan and Wahdan (2012) study, addition of *Nigella sativa* L. seeds oil to corn oil resulted in a significant decline in peroxide value of the oil during storage which shows the oxidative stability of the oil has been enhanced. Generally, a fat is considered rancid when the peroxide value is about 10 meq/Kg (Gunstone and Gunstone 1996). The oils with peroxide value between 1 and 5 meq/Kg are at low oxidation state and between 5 and 10 meq/Kg are at average oxidation state (O'Brien 2004). The results indicate that sunflower oil and palm olein have reached the oil's rancidity state and have exceeded the average

oxidation rate within first and second days of frying process for sunflower and palm olein oils respectively. However the rancidity has been delayed in systems containing antioxidants as a result of improvement in oxidative stability of the oils. Nevertheless, the deterioration of frying oils cannot be measured by peroxide value inasmuch as the peroxides which were initially formed are highly unstable and decompose easily to secondary oxidation products (Rossell 2001).

Changes in AV of palm olein and sunflower oil for three frying systems are shown in Table 4. There was an increase in anisidine value in all frying systems and in both frying oils with increase in frying time. The anisidine value increased due to decomposition of less stable primary oxidative products (hydroperoxides) to form further aldehydic compounds (Abdulkarim et al. 2007). In sunflower oil, the anisidine value was significantly ($p<0.05$) lower in the system containing NE compared to control which shows improved stability of the oil as a result of containing lower amount of decompositional products. however, there was no significant ($p>0.05$) difference between the anisidine value of systems II and III showing that they contain the same amount of decompositional products. In palm olein, anisidine value was significantly ($p<0.05$) lower in system containing NE (III) compared to control showing that NE was able to significantly ($p<0.05$) lower

the formation of decompositional products. Moreover, there was a significant difference ($p < 0.05$) in anisidine value of system containing NE (III) in comparison to the system containing BHT (II) at the end of the frying process (Day 5) which indicates the existence of lower amount of decompositional products and better oil quality in system II in comparison to system III. In other words, in system containing NE, there was a higher amount of peroxides compared to system containing BHT which led to a higher formation of products from peroxide decomposition. The anisidine value of palm olein was significantly higher on day 5 of the frying process (63.19) compared to the value of 55.00 which was reported by Che Man and Jaswir (2000) who studied the frying performance of palm olein with the same frying condition.

Totox value not only describes the state of the oil with reference to the amount of peroxides but also considers the formation of decomposition products of the oxidation process. The results for totox values of palm olein and sunflower oil for three frying systems are shown in Table 4. The totox value for all systems increased during frying. In sunflower oil, the totox value of systems I, II and III were significantly ($P < 0.05$) different. The increment of totox values in frying systems was in the order of system I (Control) > system III (NE) > system II (BHT). In palm olein, the totox value for systems I, II and III were significantly ($P < 0.05$) different from each other during the frying process. Results had shown that addition of NE to the frying oil had significantly ($P < 0.05$) decreased the total amount of primary and secondary products as a result of significantly ($P < 0.05$) lower oxidation reaction compared to control which means that NE was able to stabilize the frying oil during the frying process in both frying oils. In fact, NE contains different carotenoids, tocopherols and polyphenol compounds (Ramadan et al. 2003) which may contribute to its antioxidative activity in frying oil at high temperature. The totox value was significantly ($P < 0.05$) higher for sunflower oil which indicates that it contains much amount of polyunsaturated fatty acids notably linoleic acid, leading to less stability compared to palm olein oil. Wai et al. (2009) have reported that the lower TOTOX value is an indication of the better quality of the oil.

Total polar components (TPC)

The amount of polar compounds is one of the most reliable criteria for estimating frying oil quality for human consumption. Total polar content is a chemical factor that shows the high temperature degradation of frying oil (Warner & Gupta 2003). The TPC content increased significantly ($p < 0.05$) with the frying time in all frying systems in both frying oils (Fig. 1). For sunflower oil, the system containing NE (III) showed a significantly ($p < 0.05$) lower polar content compared to control. However, it had no significant ($p > 0.05$) difference in polar content with system containing BHT (II) at the end of

the frying (Day 5). Nevertheless, both NE and BHT were able to increase the stability of sunflower oil in accordance with the significantly ($p < 0.05$) lower increase in the percentage of polar compounds at the end of the frying period (Day 5). This result was expected from the polyunsaturated fatty acid (mainly linoleic acid) content of the frying systems containing NE (III) and BHT (II) as they have shown a significantly ($p < 0.05$) higher amount of linoleic acid (C18:2) which reveals that less oxidation of polyunsaturated fatty acids could have occurred. In palm olein, also there was a significant ($p < 0.05$) increase in the content of TPC from day 0 until the end of the frying period (Day 5). From the results, it was clear that the increment of TPC content was significantly ($p < 0.05$) lower in system containing NE (III) compared to control. However, there was no significant ($p > 0.05$) difference in the polar content of system III (NE) and system II (BHT). Both NE and BHT were able to lower the TPC content during the frying period. Nevertheless, frying stability increased more in the presence of BHT than NE which might be due to the thermolability of NE active compounds at frying temperature. It has been recommended that frying oils containing more than 24–27 % TPC content should be discarded (Mariod et al. 2006). None of the frying oils, neither palm olein, nor sunflower oil had reached the TPC range at which the frying oil has to be discarded. Compared to palm olein, sunflower oil had formed more polar compounds during the frying process. In general, oils with higher level of unsaturated fatty acids produce more polar compounds compared to the more saturated ones (Takeoka et al. 1997). TPC is considered as a better indicator of frying oil deterioration because it is relevant to all the degraded products other than the initial triglycerides present in the fresh oil (Bansal et al. 2010).

Apparent viscosity

The changes in viscosity of frying oil are the sign of oil deterioration. During the frying process, viscosity is increased because of the polymerization and formation of high molecular weight compounds (Maskan 2003). There was a significant ($p < 0.05$) increase in the viscosity of sunflower oil and palm olein from day 0 to day 5 of the frying process (Fig. 2). In fact, as a result of heat proceeding during the frying process, oxidation has developed rapidly and resulted in the increase in viscosity of frying oil (Tyagi & Vasishtha 1996). It can be inferred from the results that the oxidation of unsaturated fatty acids occurred slower in system containing NE (III) compared to control and consequently, the increase in viscosity was slower in system III compared to control. However, there was no significant ($p > 0.05$) difference in the viscosity of system containing NE (III) in comparison to the system containing BHT at day 5 of the frying process. In sunflower oil, the increment order in viscosity was system I (Control) > III

Fig. 1 Changes in Total Polar Compound (%) of RBD palm olein (a) and sunflower oil (b) during five consecutive days of deep fat frying

(NE) > II (BHT), showing that both NE and BHT were able to decrease oxidation of unsaturated fatty acids.

Conclusion

Nigella sativa L. extract was able to significantly ($p < 0.05$) reduce peroxide value, polar compounds, viscosity and oxidation of unsaturated fatty acids. Moreover, the extent of frying oil stabilization was significantly ($p < 0.05$)

Fig. 2 Changes in viscosity (cP) of sunflower oil (a) and RBD palm olein (b) during five consecutive days of deep fat frying

different for NE compared to BHT with BHT being able to convey higher stability. The less ability of NE to stabilize and reducing oxidation of frying oil compared to synthetic antioxidant, BHT could be due to the volatility of NE active antioxidant constituents at frying temperature, high amount of polyunsaturated fatty acids present in the oil and high initial PV of NE. Palm olein which contains lower percentage of linoleic acid (C18:2) and higher oleic acid (C16:0) has shown higher stability towards oxidation during the frying process. As a result, *Nigella sativa* L. extract was able to stabilize both palm olein and sunflower oil and reduce the overall rate of oxidation at concentrations it was applied in this study and could be used in place of synthetic antioxidant, BHT with making the frying oil more safer for consumption. Applying NE as a natural

antioxidant could achieve consumer demand based on its natural origin and avoiding toxicity concerns.

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