

eISSN 1889-9594

www.food.actapol.net/

# EFFECT OF HEATING AT FRYING TEMPERATURE ON THE QUALITY CHARACTERISTICS OF REGULAR AND HIGH-OLEIC ACID SUNFLOWER OILS

M. Abbas Ali<sup>1,2</sup>, Ali Hassan Ali Najmaldien<sup>1</sup>, Razam Abd Latip<sup>3</sup>, Noor Hidayu Othman<sup>3</sup>, Fadzilah Adibah Abdul Majid<sup>1</sup>, Liza Md. Salleh<sup>1</sup>

<sup>1</sup>Department of Bioprocess Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia UTM Skudai, 81310 Johor, Malaysia

<sup>2</sup>Department of Chemistry, Rajshahi University of Engineering and Technology Rajshahi-6204, Bangladesh <sup>3</sup>Sime Darby Research Sdn. Bhd.

42700 Banting, Selangor, Malaysia

### ABSTRACT

Background. Understanding of oil deterioration during heating/frying process is important as oils are normally kept hot at commercial food outlets during intermittent frying cycles. An increased level of consumer awareness toward fat composition and its impact on human health could have an effect on selection of fats in the food industry. The rate of quality deterioration during heating depends on fatty acid composition and also the content and composition of minor components. Therefore, the use of more stable frying oils would be desirable. The present study compares the heat stability at frying temperature of regular sunflower oil (RSFO) with that of high-oleic acid sunflower oil (HSFO).

**Material and methods.** Heating test was carried out at  $185 \pm 5^{\circ}$ C for the samples RSFO and HSFO using electric fryer for 8 h/day for 3 consecutive days. The samples were collected every 4 h. The changes in physicochemical properties of the samples were monitored by analytical and instrumental methods.

Results. In this study, refractive index, free fatty acid content, peroxide value, p-anisidine value, TOTOX value and polar compounds of the oils all increased, whereas  $C_{18:2}/C_{16:0}$  ratio decreased as heating progressed. The percentage of linoleic acid tended to decrease, whereas the percentages of palmitic, stearic and oleic acids increased. The sample HSFO exhibited better heating performance compared to RSFO. However, a higher amount of free fatty acids was found in HSFO compared to RSFO at the end of heating trial. Moreover, heating process decreased the total tocopherol content and higher reduction was detected in RSFO.

**Conclusion.** In conclusion, the heating caused the formation of comparatively lower amounts of some degradative products in HSFO compared to RSFO indicating a lower extent of quality deterioration of HSFO.

Key words: frying oil, sunflower oil, fatty acids, oxidative stability, polar compounds

<sup>&</sup>lt;sup>™</sup>radwiya44@yahoo.com

## INTRODUCTION

Deep-fat frying is one of the most popular procedures for food preparation since it is rapid and develops desirable flavours and textures. However, using frying oils repeatedly can produce constituents that not only compromise food quality but also can promote the formation of compounds with adverse nutritional implications and potential hazards to human health. The quality and stability of frying oils are therefore of concern to food technologists, nutritionists, and consumers [Sanibal and Mancini-Filho 2004]. The choice of frying oil should be made according to its performance in the frying process. Therefore, the use of more stable frying oils would be desirable. To overcome the problem of poor stability of traditional soybean, sunflower and rapeseed oils, ways of reducing the unstable polyunsaturated fatty acid (PUFA) content were sought. Technology is now available to alter the fatty acid composition of oilseeds by genetic modification or traditional breeding [Wilson et al. 1989] in order to increase the stability during heating or frying. Safflower and sunflower oils have been modified to improve their oxidative stability by increasing oleic acid levels to 70-90% [Fuller et al. 1971]. Decreasing linolenic acid and increasing oleic acid in canola oil have been found to give greater frying stability [Warner et al. 1994]. The composition of oleic, linoleic and linolenic acids in oil has been an effect of the oxidative stability [Min and Boff 2001]. Sunflower oil has approximately 70% linoleic acid [Meydani et al. 1991] and is highly susceptible to lipid oxidation [Jeleń et al. 2000]. Heating speeds up the oxidative reaction, which is a major concern for deep fat frying operations [Muik et al. 2005]. Ashton et al. [2001] reported that high oleic sunflower oil may decrease the risk of coronary heart disease by decreasing LDL cholesterol susceptibility to oxidation. Genetic modification of sunflower oil, to decrease linoleic acid and increase oleic acid, could increase the oxidative stability during frying, as well as improve the health benefits.

Few studies have been conducted on the deteriorative changes of genetically modified vegetable oils, especially sunflower oil during heating [Romero et al. 1998, Normand et al. 2006]. The objective of this study was to compare the effects of heating at frying temperature on the quality characteristics of regular and high-oleic acid sunflower oils.

#### MATERIAL AND METHODS

#### Material

Refined regular sunflower (RSFO) and high oleic acid sunflower (HSFO) oils (Yee Lee Edible Oils Sdn. Bhd., Malaysia) were purchased from a local supermarket. The oils were kept in the refrigerator below 4°C for storage. Chemicals and solvents used were of analytical grade. *p*-Anisidine and silica gel were products of Merck (Darmstadt, Germany). Standards of fatty acid methyl esters were purchased from Supelco Chemical Co. (Bellefonte, PA, USA). All other chemicals and solvents were from J.T. Baker (Phillipsburg, USA) or RCI Labscan Ltd. (Pathumwan, Thailand) unless otherwise stated.

#### Heating protocol and oil sampling

Heating test was performed for RSFO and HSFO using 2.5 liters domestic electric fryer (Philips HD--6159, Malaysia). The fryer was switched on for 15 min before counting the heating time each day to heat oil up to the desired heating temperature ( $185 \pm 5^{\circ}$ C). Two and a half liters of each oil sample to be tested were used for the heating and two heating cycles at  $185 \pm 5^{\circ}$ C of 4 h were carried out. Heating session lasted continuously for 8 h/day for 3 consecutive days for each of oil samples. The fryer was left uncovered throughout the heating operation; after heating switched off and the lid was put. The volume of oil was not replenished during the heating operation. Oil samples were collected every 4 h and cooled to the room temperature before stored at -16°C for analyses. Initial physico-chemical analyses of the fresh samples were also carried out.

#### Fatty acid composition

Fatty acid composition of the oils was determined as their methyl esters prepared by the PORIM [1995] test method p3.4. In this method, the sample was first dissolved in n-hexane before methylation using sodium methoxide. The solution was then diluted with distilled water and allowed to settle for 5 min. The upper layer of fatty acid methyl ester (FAME) was collected and decanted for GC analysis. The FAMEs were quantified using an auto-system XL gas chromatograph (Perkin Elmer Incorporate, Massachusetts, USA) equipped with a SP-2340 (Supelco Inc., Bellefonte, PA, USA) fused silica capillary column (60 m × 0.25 mm i.d × 0.20 µm film thickness) and a flame ionization detector. Nitrogen was used as carrier gas with a flow rate of 20 ml/min at 20 psi. Initial oven temperature was set to 100°C, raised to 170°C at 20°C/min, then programmed to 230°C at 10°C/min, and finally heated to 250°C at 30°C/min. The detector and injector temperatures were both maintained at 250°C. Methyl esters were quantified by comparing the retention times and peak area of the unknowns with known FAME standard mixtures.

#### Standard physicochemical analyses

Refractive index (method Cc 7-25), free fatty acid content (method Ca 5a-40) and peroxide value (method Cd 8-53) were determined according to American Oil Chemists' Society official methods [AOCS 1987]. Determination of *p*-anisidine value (method p2.4) of the sample was carried out by means of a Jenway 6305 Spectrophotometer (Barloworld Scientific Ltd., UK) according to the PORIM [1995] test method.

#### Viscosity measurement

Viscosity of the oils was measured by using a Brookfield DV–II+ viscometer (Brookfield Engineering Laboratories Inc., Middleboro, USA). One milliliter of oil was placed on the plate of the viscometer with spindle S-42; the viscosity of the sample was read in cP (centipoise) directly from the viscometer, which was maintained at 40°C.

#### Polar compounds

Total polar compounds were determined by means of mini column method [Dobarganes et al. 2000]. Briefly, about 1.0 g of oil was diluted in light petroleum ether/diethyl ether (90:10, v/v) and made up to 10 ml with the same solvent mixture. Five milliliters of the solution were applied to a silica gel (Merck grade 60, 70-230 mesh) glass column (150 mm  $\times$  10 mm i.d). The nonpolar fraction was eluted with 60 ml of light petroleum ether/diethyl ether (90:10, v/v) while the polar fraction was eluted with 50 ml of diethyl ether. The solvent was removed by a rotary evaporator; afterwards the flask was flushed under a stream of nitrogen for complete dryness. The completeness of fractionation was evaluated by analytical thin-layer chromatography in the elution system light petroleum ether:diethyl ether:acetic acid (70:40:1; v:v:v).

#### **Total tocopherol**

Tocopherol of the samples was analysed using HPLC as described in AOCS (1987) Official Method Ce 8-89. Briefly, oil sample was dissolved with n-hexane (Merck, Darmstadt, Germany) before being injected into the HPLC. The HPLC (Agilent 1100 series, Agilent Technologies, Wilmington, USA) was fitted with a  $250 \times 4$  mm column, packed with 5 µm of silica (Jones chromatography). A fluorescence detector (Agilent Model G1321A, Massachusetts, USA) was used at 292 and 330 nm for excitation and emission wavelengths, respectively. Mobile phase consisted of iso-propanol (Merck, Darmstadt, Germany) in n-hexane (0.5:99.5, v/v) with a flow rate of 1.4 ml/min. Total tocopherol was determined by comparing the retention times of standard ones.

#### **Statistical analysis**

Results were expressed as the means and standard deviation (SD). Significant differences between means of two oil samples were assessed with Student's *t* test. Significant differences between means of same sample were determined by Duncan's multiple range test using SPSS 11.5 software package. Differences were considered statistically significant at p < 0.05.

#### **RESULT AND DISCUSSION**

#### Changes in fatty acids composition (FAC)

Fatty acids composition of the samples is presented in Table 1. Linoleic acid (62.29%) was major in RSFO followed by oleic (26.23%) and palmitic (6.36%) acids. Stearic acid was detected in trace amount in RSFO. HSFO was characterized by a high content of oleic acid (86.65%) followed by linoleic acid (5.72%), and palmitic (3.66%) and stearic (3.13%) acids at lesser concentration. It has been shown that heating of oil causes a fast decrease in more USFA than less unsaturated or saturated fatty acids [Warner and Mounts 1993]. In this study, the percentage of linoleic acids tended to decrease, whereas the percentage of palmitic, stearic and oleic acids, increased, probably due to PUFA degradation. A similar trend was found by Sebedio et al. [1990] in soybean oil during frying frozen potatoes. The decrease in C<sub>18:2</sub> could be explained by the oxidation of unsaturated fatty acid (USFA), which changes to primary and secondary

Ali M.A., Najmaldien A.H.A., Latip R.A., Othman N.H., Majid F.A.A., Salleh L.M., 2013. Effect of heating at frying temperature on the quality characteristics of regular and high-oleic acid sunflower oils. Acta Sci. Pol., Technol. Aliment. 12(2), 159-167.

Oil sample	Heating time h	C <sub>14:0</sub>	C <sub>16:0</sub>	C <sub>16:1</sub>	C <sub>18:0</sub>	C <sub>18:1</sub>	C <sub>18:2</sub>	Trans C <sub>18:2</sub>	C <sub>18:3</sub>	C <sub>20:0</sub>	SFA	MUFA	PUFA	C <sub>18:2</sub> /C <sub>16:0</sub>
RSFO	0	$\begin{array}{c} 0.08 \\ \pm 0.00 \end{array}$	6.36 ±0.00	0.08 ±0.00	3.58 ±0.00	26.23 ±0.02	62.29 ±0.01	0.73 ±0.00	0.18 ±0.00	0.47 ±0.00	10.50	26.31	63.20	9.91
	4	0.09 ±0.00	6.75 ±0.01	0.09 ±0.00	$\begin{array}{c} 3.80 \\ \pm 0.00 \end{array}$	27.45 ±0.06	60.46 ±0.04	0.71 ±0.00	0.19 ±0.01	0.46 ±0.01	11.10	27.54	61.36	9.06
	8	$\begin{array}{c} 0.09 \\ \pm 0.00 \end{array}$	7.09 ±0.00	0.09 ±0.00	3.99 ±0.01	28.35 ±0.06	59.02 ±0.07	0.72 ±0.00	0.19 ±0.00	$\begin{array}{c} 0.46 \\ \pm 0.00 \end{array}$	11.63	28.44	59.93	8.42
	12	$\begin{array}{c} 0.10 \\ \pm 0.00 \end{array}$	7.39 ±0.01	0.09 ±0.00	4.13 ±0.01	28.94 ±0.12	57.99 ±0.00	0.72 ±0.01	0.19 ±0.00	0.44 ±0.00	12.06	29.03	58.90	7.94
	16	$\begin{array}{c} 0.10 \\ \pm 0.00 \end{array}$	7.67 ±0.00	0.10 ±0.00	4.36 ±0.01	29.84 ±0.10	56.57 ±0.12	0.73 ±0.00	0.20 ±0.01	$\begin{array}{c} 0.43 \\ \pm 0.00 \end{array}$	12.56	29.94	57.50	7.47
	20	$\begin{array}{c} 0.11 \\ \pm 0.00 \end{array}$	7.96 ±0.03	0.10 ±0.00	4.48 ±0.02	$30.34 \pm 0.08$	55.66 ±0.14	0.74 ±0.00	0.20 ±0.01	$\begin{array}{c} 0.43 \\ \pm 0.00 \end{array}$	12.98	30.44	56.60	7.08
	24	$\begin{array}{c} 0.11 \\ \pm 0.00 \end{array}$	8.22 ±0.03	$\begin{array}{c} 0.10 \\ \pm 0.00 \end{array}$	4.62 ±0.01	$31.05 \pm 0.10$	54.22 ±0.17	1.07 ±0.14	0.20 ±0.00	$\begin{array}{c} 0.41 \\ \pm 0.01 \end{array}$	13.36	31.15	55.49	6.73
HSFO	0	$\begin{array}{c} 0.04 \\ \pm 0.00 \end{array}$	3.66 ±0.00	0.10 ±0.00	3.13 ±0.00	86.65 ±0.02	5.72 ±0.00	0.13 ±0.01	0.26 ±0.00	$\begin{array}{c} 0.30 \\ \pm 0.00 \end{array}$	7.13	86.75	6.11	1.60
	4	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	3.74 ±0.07	0.10 ±0.00	3.18 ±0.04	86.70 ±0.03	5.55 ±0.15	0.09 ±0.00	0.26 ±0.00	$\begin{array}{c} 0.33 \\ \pm 0.00 \end{array}$	7.30	86.80	5.90	1.51
	8	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	3.89 ±0.08	$\begin{array}{c} 0.10 \\ \pm 0.00 \end{array}$	3.31 ±0.07	87.12 ±0.39	4.84 ±0.55	0.09 ±0.00	0.26 ±0.00	0.34 ±0.01	7.59	87.22	5.19	1.24
	12	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	$\begin{array}{c} 4.05 \\ \pm 0.08 \end{array}$	0.10 ±0.00	3.44 ±0.06	87.66 ±0.12	3.98 ±0.30	0.11 ±0.01	0.26 ±0.00	0.34 ±0.01	7.88	87.76	4.29	0.99
	16	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	4.38 ±0.08	$0.11 \\ \pm 0.00$	3.71 ±0.07	91.12 ±0.17	3.09 ±0.06	0.25 ±0.18	0.26 ±0.00	0.36 ±0.02	8.50	91.23	3.60	0.70
	20	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	4.37 ±0.11	0.10 ±0.00	3.70 ±0.09	87.54 ±0.06	3.62 ±0.15	$\begin{array}{c} 0.00 \\ \pm 0.00 \end{array}$	0.25 ±0.00	0.36 ±0.02	8.48	87.64	3.87	0.83
	24	$\begin{array}{c} 0.05 \\ \pm 0.00 \end{array}$	4.44 ±0.00	0.10 ±0.00	3.77 ±0.01	87.41 ±0.20	3.57 ±0.16	0.02 ±0.00	0.25 ±0.00	$\begin{array}{c} 0.37 \\ \pm 0.01 \end{array}$	8.63	87.51	3.84	0.81

Table 1. Fatty acids composition (%) of regular and high oleic acid sunflower oils during heating operation

Each value in the table represents the mean of two replicates  $\pm$ SD.

oxidation products during the heating process. Before heating, both samples contained *trans*  $C_{18:2}$  (0.73% in HSFO and 0.13% in RSFO), whilst no any *trans*  $C_{18:1}$  was detected. *Trans* isomers in the fresh oils are supposed to be produced in the deodorization process of crude oils [Tsuzuki et al. 2010]. It is worth mentioning that the amount of *trans*  $C_{18:2}$  in HSFO during the corresponding heating times, was greater than that in

RSFO. A high amount of PUFA detected in the RSFO makes it more susceptible to the oxidative deterioration. As shown in Table 1, the value of the  $C_{18:2}/C_{16:0}$  ratio in fresh RSFO was high than in HSFO due to the large percentage of linoleic acid in RSFO. The ratio  $C_{18:2}/C_{16:0}$  has been suggested as a valid indicator of the level of PUFA deterioration [Normand et. al. 2001]. Our results in the present study indicate that this ratio decreased in both samples during the heating process. The reduction (from the initial) in  $C_{18.2}/C_{16.0}$  ratio was 3.18 units for RSFO; being higher than that found in HSFO (0.79). This indicated higher rate of oxidative degradation of RSFO.

# Changes in standard physicochemical parameters

Refractive index (RI) values of the oils were increased significantly (P < 0.05) with the increasing heating times (Table 2). RI increases with an increase in polymerization, molecular cohesiveness among the components of increased chain length, saturation of carbon-carbon double bonds, moisture in food and opaqueness and turbidity [Kress Rogers et al. 1990]. R1 values of the HSFO at corresponding heating times were lower compared to RSFO. The highest amount of increment was found in RSFO (0.0046 unit from initial) compared to RSFO (0.0025 unit from initial). As shown in Table 2, there was no significant difference (P < 0.05) in the initial free fatty acid (FFA) content between RSFO and HSFO. The FFA level of the oils were significantly increased (P < 0.05) with increasing heating time. At the end of heating, the amount of FFA was found to be higher in HSFO (0.81%) than that of RSFO (0.54%). Normand et al. [2006] observed the

greater rate of formation of FFA in HSFO compared with RSFO during 72 h of frying. Warner et al. [1994] found that the higher the oleic acid content of the oil was, the higher the FFA content in the heated oil. Likewise, in this study HSFO showed the faster rate of FFA accumulation after 4 h of heating. The highest FFA value detected in HSFO at the end of heating is still far below the accepted limit of 2% [Matthaus 2006]. Using FFA content as an indicator of frying oil degradation and of fried food quality is still controversial. In practice, FFA levels may not affect frying performance or have significant adverse effects on health or sensory evaluation [Xin-Qing et al. 1999].

The peroxide values (PV) during the heating operation of the samples were increased up to the 16 h and then decreased until the end of the heating (Table 3). The results also indicated that the PVs in RSFO and HSFO were significantly different (P < 0.05) throughout the heating times. RSFO had highest peak value (50.46) compared to HSFO (27.80), might be attributed to decreasing amount of linoleic acids (more prone to oxidation) present in the RSFO. For peroxides, the data confirms the results showed in early studies [Tsaknis and Lalas 2002, Abdulkarim et al. 2007], with an increase in the peroxides until a maximum is reached, followed by a decrease of those compounds

Heating	Refrac	ctive index	FFA, %			
time h	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)		
0	$1.4743 \pm 0.00024^{\rm A}$	$1.4689 \pm 0.00005^{\mathrm{aA}}$	$0.16\pm\!0.01^{\rm A}$	0.16 ±0.02 <sup>A</sup>		
4	$1.4750 \pm \! 0.00012^{\rm B}$	$1.4692 \pm \! 0.00005^{\rm aB}$	$0.22\pm\!0.00^{\rm B}$	$0.22 \pm 0.00^{B}$		
8	$1.4759\ {\pm}0.00012^{\rm C}$	$1.4698 \pm 0.00008^{\mathrm{aC}}$	$0.25\pm\!0.00^{\rm B}$	$0.31 \pm 0.01^{aC}$		
12	$1.4769 \pm \! 0.00012^{\rm D}$	$1.4704 \pm \! 0.00021^{\rm aD}$	$0.33 \pm 0.00^{\circ}$	$0.42 \pm 0.01^{\mathrm{aD}}$		
16	$1.4774 \pm \! 0.00009^{\rm E}$	$1.4709 \pm \! 0.00005^{aE}$	$0.39\pm\!0.00^{\rm D}$	$0.51 \pm 0.03^{aE}$		
20	$1.4778 \pm \! 0.00023^{\rm F}$	$1.4711 \pm 0.00005^{aEF}$	$0.49\pm\!\!0.04^{\rm E}$	$0.67\pm\!\!0.02^{aF}$		
24	$1.4789 \pm \! 0.00009^{\rm G}$	$1.4714 \pm \! 0.00014^{aF}$	$0.54\pm\!0.04^{\rm F}$	$0.81 \pm 0.01^{aG}$		

Table 2. Refractive index and FFA value of regular and high oleic acid sunflower oils during heating operation

Each value in the table represents the mean of three replicates  $\pm$ SD.

For same oil, values within a column with the same uppercase letters are not significantly different at P < 0.05.

<sup>a</sup>For the same heating time, the value of refractive index or FFA of HSFO was significantly different from that of RSFO (Student t-test, P < 0.05).

Heating time h	Peroxide	e value	<i>p</i> -anisidi	ne value	TOTOX value		
	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)	
0	$4.60\pm\!\!0.15^{\scriptscriptstyle A}$	$3.14\pm\!0.02^{aA}$	$5.12\pm0.41^{\text{A}}$	$3.35\pm\!\!0.32^{aA}$	14.32	9.63	
4	$28.57\pm\!\!0.34^{\rm B}$	$8.00\pm\!\!0.48^{aB}$	$50.01 \pm 3.17^{\rm B}$	$36.96 \pm \! 0.62^{aB}$	107.15	52.96	
8	$49.22\pm\!0.80^{\rm E}$	$17.37\pm\!\!0.12^{aC}$	$61.12 \pm 2.38^{\circ}$	$53.77\pm\!\!1.06^{aC}$	159.56	88.51	
12	$35.18\pm\!\!0.22^{\rm D}$	$20.51 \pm 0.17^{aD}$	$75.87 \pm 0.15^{\rm D}$	$65.56\pm\!\!1.45^{aD}$	146.23	106.58	
16	$50.46 \pm 0.50^{\rm E}$	$27.80 \pm 1.14^{\mathrm{aF}}$	$89.72 \ {\pm} 0.93^{\rm E}$	$72.83 \pm \hspace{-0.5mm} 2.54^{aE}$	190.64	128.43	
20	$34.14\pm\!0.23^{\rm D}$	$25.22 \pm 1.93^{\mathtt{aE}}$	$93.58 \pm 0.69^{\rm F}$	$76.46\pm\!\!0.50^{aF}$	161.86	126.90	
24	$32.42\pm\!\!1.10^{\scriptscriptstyle C}$	$20.17\pm\!\!1.15^{aD}$	$94.90 \pm 1.00^{\rm G}$	$77.81 \pm 2.67^{aG}$	159.74	118.15	

**Table 3.** Peroxide value, *p*-anisidine value and TOTOX value of regular and high oleic acid sunflower oils during heating operation

<sup>a</sup>For the same heating time, peroxide value or *p*-anisidine value of HSFO was significantly different from that of RSFO (Student t-test, P < 0.05).

Other explanations as in Table 2.

due to their reactions and degradations to other compounds. However, during the heating operation, PVs of the oils analysed exceeded the acceptable limit of 10 mEq O<sub>2</sub>/kg given by the Guidelines of the German Food Codex as the limit for edible fats and oils [Mariod et al. 2006]. Compared to PV, the p-anisidine value (p-AV) is a more reliable and meaningful test, because it measures the secondary oxidation products, which are more stable during the heating process [Al-Kahtani 1991]. p-AVs of the oils during 24 h of heating are shown in Table 3. As the heating time increased, p-AV of heated oils increased due to decomposition of oil hydroperoxides and similar trend for some vegetable oils was followed by other researchers [Abdulkarim et al. 2007]. *p*-AVs of RSFO were significantly (P < 0.05) different from those of HSFO during heating. At the end of the 24 h heating period, the *p*-AVs reached to 94.90 for RSFO and 77.81 for HSFO. Contact with air (oxygen) during frying, and unsaturation level in fatty acids are the factors that affect the *p*-AV level [Khan et al. 2011]. The HSFO containing lower amount of PUFA underwent the p-AV increases (74.46 units from the initial); being lower than that of the RSFO (89.78 units from the initial). This suggests that FAC affected the formation of secondary oxidation products from primary oxidation products in oil during heating. p-AV

is often used in the industry in conjunction with PV to calculate the so-called total oxidation or TOTOX value given as: TOTOX = 2PV + p-AV [Shahidi and Wanasundara 2002]. During heating process TOTOX values increased significantly (P < 0.05) with heating times and after the end of heating, the TOTOX values were found to be 159.74 for RSFO and 118.15 for HSFO (Table 3). A similar trend for some vegetable oils was followed by Abdulkarim et al. [2007] during frying. The lower TOTOX value of the HSFO indicated more stable to oxidative rancidity than the RSFO. The higher TOTOX value in RSFO was due to the high percentages of PUFAs in this oil.

Formation of total polar compounds (TPC) is strongly related with the primary and secondary oxidation that takes place during frying [Sibel and Sebnem 2011]. Despite the similar levels of TPC in the fresh oils, the TPC values increased significantly (P < 0.05) with different rates over 24 h of the heating periods (Table 4). After heating operation, the final TPC levels were: 24.40% in RSFO and 19.67% in HSFO. However, the total polar contents in both the samples did not exceed the limit 27% for used frying fats based on the German standard [Billek et al. 1978]. The faster increase in TPC levels observed for the sample RSFO can be attributed to its higher degree

Heating —	Total polar	compound, %	Viscosity, cP			
time h	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)		
0	4.65 ±0.32 <sup>A</sup>	$4.96\pm0.38^{\mathrm{A}}$	$28.37 \pm 0.22^{\text{A}}$	35.25 ±0.15 <sup>aA</sup>		
4	$6.94\pm\!0.23^{\rm B}$	$5.94\pm\!0.67^{\rm B}$	$31.13 \pm 0.15^{\rm B}$	$39.21 \pm 0.24^{aB}$		
8	$10.88\pm\!0.50^{\rm C}$	$7.29\pm\!0.58^{\mathrm{aC}}$	$41.75\pm\!0.35^{\rm C}$	$42.87 \pm 0.24^{aC}$		
12	$13.25 \pm 0.95^{\text{D}}$	$10.00\pm\!0.83^{\rm aD}$	$48.21 \pm \! 0.37^{\rm D}$	$49.05 \pm 0.32^{D}$		
16	$16.10\pm\!0.30^{\scriptscriptstyle E}$	$13.46\pm\!\!0.42^{\mathrm{aE}}$	$57.23 \pm 0.35^{\scriptscriptstyle E}$	$51.31 \pm 0.35^{aE}$		
20	$19.69\pm\!\!0.70^{\rm F}$	$15.24\pm\!0.33^{\mathrm{aF}}$	$61.83 \pm 0.26^{\rm F}$	$66.89 \pm 0.37^{aF}$		
24	$24.40 \pm 0.65^{G}$	$19.67 \pm 0.52^{aG}$	$82.98 \pm 0.79^{\rm G}$	$76.61 \pm 0.40^{aG}$		

Table 4. Total polar compound and viscosity of regular and high oleic acid sunflower oils during heating operation

<sup>a</sup>For the same heating time, the value of total polar compound or viscosity of HSFO was significantly different from that of RSFO (Student t-test, P < 0.05).

Other explanations as in Table 2.

of unsaturation. The viscosity of heated oils increased significantly (P < 0.05) with heating times (Table 4). Increase in viscosity was caused due to the formation of high molecular weight polymers. The more viscous the frying oil, the higher the degree of deterioration [Abdulkarim et al. 2007]. The treatment RSFO had lower initial viscosity as compared with HSFO. The viscosity increased from initial values of 28.37 and 35.25 to 82.98 and 76.61 cP for the RSFO and HSFO heating media, respectively. The viscosities of RSFO up to 12 h of heating time were lower than HSFO; afterwards the rate of viscosity for RSFO dramatically increased. These results clearly revealed the higher deteriorative effect of oxidation and polymerization of RSFO compared to HSFO.

#### Changes in total tocopherol

Tocopherols are important biological antioxidants which has been associated with the reduction of heart disease, delay of Alzheimer's disease, and prevention of cancer. They have widely been used as antioxidants for frying fats and oils, margarines, fried snacks and so on [Akoh 2006]. They are susceptible to high temperature deterioration. The reduction of total tocopherol (TT) in RSFO and HSFO was evident as heating progressed (Table 5). The heating process decreased the TT content of the tested oils in a time-dependent manner. RSFO displayed a two-step drop of tocopherols from 494.50 to 185.50 ppm after 4 h and 15.53 ppm after 8 h, where it remained almost constant until the end of the heating test. In the case of HSFO, the tocopherols declined from 381.50 to 29.60 ppm after 4 h, and then varied within a narrow range of 24.40--17.90 ppm. The lowest percentage of reduction was found in the HSFO.

**Table 5.** Total tocopherol content of regular and high oleic acid sunflower oils during heating operation

Heating	Total tocopherol, ppm					
time h	regular sunflower oil (RSFO)	high oleic acid sunflower oil (HSFO)				
0	494.50 ±2.50	$381.50 \pm 7.50$				
4	$185.50\pm\!0.50$	$29.60 \pm 3.00$				
8	$15.53 \pm 0.78$	$24.40 \pm 1.00$				
12	4.31 ±0.11	23.15 ±3.85				
16	$4.38\pm\!0.11$	$25.55 \pm 0.45$				
20	$4.48\pm\!\!0.06$	$17.90 \pm 3.10$				
24	3.88 ±0.16	19.50 ±0.50				

Each value in the table represents the mean of two replicates  $\pm$ SD.

Ali M.A., Najmaldien A.H.A., Latip R.A., Othman N.H., Majid F.A.A., Salleh L.M., 2013. Effect of heating at frying temperature on the quality characteristics of regular and high-oleic acid sunflower oils. Acta Sci. Pol., Technol. Aliment. 12(2), 159-167.

# CONCLUSION

In this study, most of the chemical and physical degradation indicators suggested that the degradation was the fastest in RSFO as compared to HSFO. The oxidative and thermal stabilities of edible oils appear to be related to oleic and linoleic contents, decreased linoleic and increased oleic content result in increased oil stability. The  $C_{18:2}/C_{16:0}$  ratio decreased in all oil samples during the heating process. The highest decreased amount was observed for the RSFO. However, the formation of free fatty acids was higher in the HSFO. Further studies can be done to monitor the production of polar compounds and the effects of heating on minor oil components such as pigments and natural antioxidants.

#### REFERENCES

- Abdulkarim S.M., Long K., Lai O.M., Muhammad S.K.S., Ghazali H.M., 2007. Frying quality and stability of higholeic *Moringa oleifera* seed oil in comparison with other vegetable oils. Food Chem. 105, 1382-1389.
- Akoh C.C., 2006. Handbook of functional lipids. In: Nutraceuticals, aging, and food oxidation. Eds J.H. Lee, D.B. Min. CRC Press, Taylor & Francis, USA, 325-350.
- Al-Kahtani H., 1991. Survey of quality of used frying oils from restaurants. J. Am. Oil Chem. Soc. 68, 857-862.
- AOCS. 1987. Official Methods and Recommended Practices of the American Oil Chemists' Society. AOCS Press Champaign.
- Ashton E.L., Best J.D., Ball M.J., 2001. Effects of monosaturated enriched sunflower oil on the CHD risk factors including LDL size and copper-induced LDL oxidation. J. Am. Coll. Nutr. 20, 320-326.
- Billek G., Guhr G., Waibel J., 1978. Quality assessment of used frying fats: A comparison of four methods. J. Am. Oil Chem. Soc. 55, 728-732.
- Dobarganes M.C., Velasco J., Dieffenbacher A., 2000. Determination of polar compounds, polymerized and oxidized triacylglycerols and diacylglycerols in oils and fats. Pure Appl. Chem. 72, 1563-1575.
- Fuller G., Guadagni D.G., Weaver M.L., Notter G., Horvat R.J., 1971. Evaluation of oleic safflower oil in frying of potato chips. J. Food Sci. 36, 43-48.
- Jeleń H.H., Obuchowska M., Zawirska-Wajtasiak R., Wąsowicz E., 2000. Headspace solid-phase microextraction use for the characterization of volatile compounds in vegetable oils of different sensory quality. J. Agric. Food Chem. 48, 2360-2367.

- Khan M.I., Asha M.R., Bhat K.K., Khatoon S., 2011. Studies on chemical and sensory parameters of coconut oil and its olein blends with sesame oil and palm olein during wheat flour-based product frying. J. Food Sci. Technol. 48, 175-182.
- Kress Rogers E., Gillat P.N., Rosel J.B., 1990. Development and evaluation of a novel sensor for the *in situ* assessment of frying oil quality. Food Contr. 1, 163-178.
- Mariod A., Matthäus B., Eichner K., Hussein I.H., 2006. Frying quality and oxidative stability of two unconventional oils. J. Am. Oil Chem. Soc. 83, 529-538.
- Matthaus B., 2006. Utilization of high-oleic rapeseed oil for deep fat frying of French fries compared to other commonly used edible oils. Eur. J. Lipid Sci. Technol. 108, 200-211.
- Meydani S.N., Lichtenstein A.H., White P.J., Goodnight S.H., Elson C.E., Woods M., Gorbach S.L., Schaefer E.J., 1991. Food use and health of soybean and sunflower oils. J. Am. Coll. Nutr. 10, 406-428.
- Min D.B., Boff J.F., 2001. Lipid oxidation of edible oil. In: Food lipids. Eds C. Akoh, D.B. Min. Marcel Dekker New York, 335-363.
- Muik B., Lendl B., Molina-Diaz A., Ayora-Canada M.J., 2005. Direct monitoring of lipid oxidation in edible oils by Fourier transform and Raman spectroscopy. Chem. Phys. Lipid 134, 173-182.
- Normand L., Eskin N.A.M., Przybylski R., 2001. Effects of tocopherols on the frying stability of regular and modified canola oils. J. Am. Oil Chem. Soc. 78, 369-373.
- Normand L., Eskin N.A.M., Przybylski R., 2006. Comparison of the frying stability of regular and high-oleic acid sunflower oils. J. Am. Oil Chem. Soc. 83, 331-334.
- PORIM., 1995. PORIM Test Methods. Palm Oil Research Institute of Malaysia, Ministry of Primary Industries Malaysia.
- Romero A., Cuesta C., Sánchez-Muniz F.J., 1998. Effect of oil replenishment during deep-fat frying of frozen foods in sunflower oil and high-oleic acid sunflower oil. J. Am. Oil Chem. Soc. 75, 161-166.
- Sanibal E.A.A., Mancini-Filho J., 2004. Frying oil and fat quality measured by chemical, physical, and test kit analyses. J. Am. Oil Chem. Soc. 81, 847-852.
- Sebedio J.L., Bonpunt A., Grandgirard A., Prevost J., 1990. Deep fat frying of frozen pre-fried french fries: influence of the amount of linolenic acid in the frying medium. J. Agric. Food Chem. 38, 1862-1867.
- Shahidi F., Wanasundara U.N., 2002. Food lipids: Chemistry, nutrition, and biotechnology. In: Methods for measuring oxidative rancidity in fats and oils. Eds C.C. Akoh, D.B. Min. Marcel Dekker New York, 465-482.

Ali M.A., Najmaldien A.H.A., Latip R.A., Othman N.H., Majid F.A.A., Salleh L.M., 2013. Effect of heating at frying temperature on the quality characteristics of regular and high-oleic acid sunflower oils. Acta Sci. Pol., Technol. Aliment. 12(2), 159-167.

- Sibel K., Sebnem S., 2011. Changes in total polar compounds, peroxide value, total phenols and antioxidant activity of various oils used in deep fat frying. J. Am. Oil Chem. Soc. 88, 1361-1366.
- Tsaknis J., Lalas S., 2002. Stability during frying of *Moringa oleifera* seed oil variety "Periyakulam 1". J. Food Comp. Anal. 15, 79-101.
- Tsuzuki W., Matsuoka A., Ushida K., 2010. Formation of *trans* fatty acids in edible oils during the frying and heating process. Food Chem. 123, 976-982.
- Warner K., Mounts T.L., 1993. Frying stability of soybean and canola oils with modified fatty acid compositions. J. Am. Oil Chem. Soc. 70, 983-988.

- Warner K., Orr P., Parrott L., Glynn M., 1994. Effects of frying oil composition on potato chip stability. J. Am. Oil Chem. Soc. 71, 1117-1121.
- Wilson R.F., Burton J.W., Kwanyuen P., 1989. Edible fats and oils processing. In: Basic principles and modern practices. Ed. D. Erickson. AOCS Press Champaign, 355-359.
- Xin-Qing X., Viet H.T., Martin P., Keith W., Philip S., 1999. Chemical and physical analyses and sensory evaluation of six deep-frying oils. J. Am. Oil Chem. Soc. 76, 1091-1099.

Accepted for print – Zaakceptowano do druku: 27.02.2013

Received - Przyjęto: 7.12.2012

For citation – Do cytowania

Ali M.A., Najmaldien A.H.A., Latip R.A., Othman N.H., Majid F.A.A., Salleh L.M., 2013. Effect of heating at frying temperature on the quality characteristics of regular and high-oleic acid sunflower oils. Acta Sci. Pol., Technol. Aliment. 12(2), 159-167.