

Available online at www.sciencedirect.com



Food Chemistry

Food Chemistry 105 (2007) 1382-1389

www.elsevier.com/locate/foodchem

Frying quality and stability of high-oleic *Moringa oleifera* seed oil in comparison with other vegetable oils

S.M. Abdulkarim^a, K. Long^b, O.M. Lai^c, S.K.S. Muhammad^a, H.M. Ghazali^{a,*}

^a Department of Food Science, Faculty of Science and Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

^b Malaysian Agricultural Research and Development Institute, P.O. Box 12301, 50774 Kuala Lumpur, Malaysia

^c Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

Received 6 June 2006; received in revised form 16 February 2007; accepted 3 May 2007

Abstract

The performance of the high-oleic *Moringa oleifera* seed oil (MoO) in deep-frying was evaluated by comparing its frying stability with other conventional frying oils [canola (CLO), soybean (SBO), and palm olein (PO)]. The oils were used as a frying media to fry potato chips for 6 h a day up to a maximum of 5 days. Standard methods for the determination of used frying oil deterioration such as changes in color, viscosity, free fatty acids (FFA), peroxide value (PV), *p*-anisidine value (*p*-AV), iodine value (IV), specific extinction $(E_{lm})^{\%}$ 233 and 269 nm) and total polar compounds (TPC) were used to evaluate the oils. At the end of the frying period, the change in percent FFA from the initial to final day of frying were as follows SBO (60.0%), PSO (65.0%), MoO (66.6%) and CLO (71.4%) and the change in *p*-AV and TOTOX value of MoO were found to be significantly lower (P < 0.05) than the rest of the oils tested, followed by PO, with the highest values obtained in CLO and SBO. The levels of conjugated dienes and trienes ($E_{lm})^{\%}$ at 233 and 269 nm) throughout the frying period were lowest in MoO and PO followed CLO, with highest levels found in SBO. The rate of darkening and increase in viscosity were proportional to the frying time for all the oils. PO darkened earlier followed by CLO. At the end of frying period, TPC was significantly (P < 0.05) lower in MoO (20.78%) and PSO (21.23%), as compared to CLO (28.73%) and SBO (31.82%).

Keywords: High-oleic Moringa oleifera seed oil; Oxidative stability and frying quality

1. Introduction

The edible oil extracted from the *Moringa oleifera* seed (Lowell, 1999) resembles olive oil in its fatty acid composition (Ramachandran, Peter, & Gopalakrishnan, 1980). In Haiti, the oil is used as a general culinary and salad oil (Price, 1986). In Africa and some parts of Asia, particularly India, the oil has been reportedly used for cooking purposes (Dahot & Memon, 1985; Dietz, Metzler, & Zarate, 1994). Recent studies include the frying stability of cold pressed and solvent-extracted *M. oleifera* seed oil from India (Tsaknis & Lalas, 2002), the physico-chemical prop-

erties of the seed oil from a Malaysian variety of *M. oleifera* extracted using solvent and aqueous enzymatic methods (Abdulkarim, Long, Lai, Muhammad, & Ghazali, 2005), the application of enzymes to enhance oil recovery during aqueous extraction of *M. oleifera* seed oil (Abdulkarim, Long, Lai, Muhammad, & Ghazali, 2006), and the enhancement of the oxidative stability of soybean and sunflower oils through blending with Moringa oleifera seed oil (Anwar, Hussain, Iqbal, & Bhanger, 2007). Apart from resembling olive oil in fatty acid composition and in being oleic acid-rich, the oil has also a pleasant peanut-like flavor, based on a comparative analysis using an eNose (Abdulkarim et al., 2005).

All edible oils and fats consist of triglycerides with a variety of fatty acids that differ in chain-length (number

^{*} Corresponding author. Tel.: +60 (0) 89468345; fax: +60 (0) 89423552. *E-mail address:* hasanah@putra.upm.edu.my (H.M. Ghazali).

of carbon atoms in molecule), degree of saturation (number of double bond in carbon chain), position of double bond within the carbon chain, and geometry of each double bond (cis and trans isomers). Oleic acid is the most abundant monounsaturated fatty acid in all the common edible oils (Gunstone, 2000). Compared with polyunsaturated fatty acids, oleic acid is more stable towards oxidation both at ambient storage temperatures and at the high temperatures that prevail during the cooking and frying of food. Therefore, oils with high amounts of oleic acid are slower to develop oxidative rancidity during shelf life or undergo oxidative decomposition during frying than those oils that contain high amounts of polyunsaturated fatty acids. Modified oils containing high-oleic acid, low-linoleic and low-linolenic acids produced by various methods including genetic modification (Anon, 1998), and have been shown to be more stable to deterioration during deep-frying than regular oils.

The physical and chemical changes occurring in frying oils and the many compounds formed in deteriorated frying oils have been extensively reported. Although these compounds often are used to measure degradation, many of the existing methods are based on measuring nonspecific compounds that may or may not relate to oil degradation or fried-food quality. In fact, the frying industry is still searching for the ultimate criteria to evaluate frying stability of oils and fried-food flavor quality and stability (Warner, 2002). From a practical point of view, commercial and industrial frying oil operators want to know the answer to one question: when should frying oil be discarded or how does one know when the frying oil needs to be dumped? Unfortunately, there is no simple answer. A specific method may be ideal for one operation but completely useless in another. The determination of the end point of frying oil is therefore dependent on good judgment and knowledge of the particular frying operation, as well as on type of frying oil and the analytical measurements used (Fritsch, 1981). Quality evaluation of frying fats may be carried out in many ways. Although sensory evaluation of foods is the most important quality assessment, taste evaluations are not practical for routine quality control. It is always preferred to have a quantitative method for which rejection point could be established by sensory means (Fritsch, 1981). Due to the complexity of the problem, there is no single procedure, that will yield reliable results in all situations. Determination of total polar materials in a frying fat provides the most reliable measure of the extent of deterioration in most cases. In this paper, the oxidative stability of *M. oleifera* seed oil during frying was determined using quantitative methods and its frying performance was compared with other vegetable oils.

2. Materials and methods

2.1. Materials

M. oleifera seed oil was solvent-extracted (Abdulkarim et al., 2005) and refined to obtain good grade oil so that it

can be compared with market samples of refined palm olein, and canola and soybean oils. Degumming and bleaching were carried out on the crude oil extract according to the method described by Greyt and Kellens (2000). Briefly, the crude oil was degummed by mixing it with 3% (v/w) hot (approx. 80 °C) distilled water in a 21 beaker and vigorous stirring with a magnetic stirrer for 30 min. The wet gum that agglomerated was removed from the lighter oil by centrifugation at 9820g for 20 min at ambient temperature. The degummed oil was then heated to 50 °C and phosphoric acid was added at a ratio of 500:1 w/v and mixed for 5 min after which 10% w/w of bleaching earth was added. The temperature of the oil was raised to 95 °C under vacuum and 45 min allowed for the bleaching to occur. The oil was then allowed to cool down and then filtered to separate the oil from the bleaching earth. Further refining was carried out in a deodorizer (Binder Crystallization and Degumming apparatus, Charleroi, Belgium) at 260 °C under vacuum for 2 h to remove fatty acids and volatile odoriferous components. Three different types of commercial oils namely, refined, bleached and deodorized palm olein, and canola and soybean oils were purchased from a local supermarket. Fresh China potatoes were purchased from a local vegetable market. Chemicals and solvents are either analytical or HPLC grade purchased from BDH Laboratories (Poole, England) and Merck (Darmstadt, Germany).

2.2. Methods

2.2.1. Frying test design

Laboratory scale frying test was carried out initially on three commercial oils namely; palm olein (PO),Canola oil (CLO) and soybean oil (SBO) and the same test carried out using refined Moringa oil (MoO). Several batches of potato chips were fried at intervals of 15 min up to a total of 6 h per day for a total of 5 days.

2.2.2. Initial oil analysis

AOCS recommended methods (AOCS, 1989) were used to determine FFA content (method Ca 5a-40/93), iodine value (method Cd 1-25/93) and peroxide value (method Cd 8-53). While PORIM test methods (PORIM, 1995), were used to determine *p*-anisidine values (method p2.4), and specific extinction (method p2.15). Viscosity was determined at 40 °C using Brookfield DV-II viscometer version 5 with temperature control (Stoughton, Massachusetts, USA). A sample adaptor No. 13, and spindle No. SC418 were used. Colour was determined using a Lovibond tintometer Model E (Salisbury, England) according to PORIM test method (p4.1). FA composition was determined according to the methods of Cocks and van Rede (1966) using a gas chromatograph model GC-14A (Shimadzu Co., Kyoto, Japan) equipped with a flame ionization detector and polar capillary column model $BP \times 70$ $(0.32 \text{ mm} \times 60 \text{ m} \text{ length}, 0.25 \mu\text{m} \text{ film thickness}, \text{SGE}$ Incorporated USA). Total polar compounds were determined according to IUPAC standardized method (IUPAC,

Table 1

2000) using Sep-Pak Vac 6cc (C18-1g) cartridges (Waters corporation, Milford, MA, USA).

2.2.3. Frying protocol

The protocol includes intermittent frying at 185 ± 5 °C with total heating/frying time of 30 h over 5 days period. One and a half kilograms of each oil sample to be tested was used for the frying. Fresh China potato was cut into 7–8 cm length of shoestring size (0.5 cm \times 0.5 cm) and fried in 150 g batches (Warner & Knowlton, 1997) in a 21 Philips fryer Model HD-6121 (Philips Malaysia Sdn. Bhd.) for 6 h each day. On the first day of frying, the oil was conditioned by heating to 185 ± 5 °C and held for 30 min (Petukhov, Malcolmson, Przybylski, & Armstrong, 1999) and the potato chips fried until bubbling of the oil ceased (estimated time of 2-3 min). Batches of potato chips were fried 15 min apart for the total of 6 h. Each day fresh oil was added to make up oil to the initial level in the fryer, to replenish the used oil before frying commenced (Warner & Knowlton, 1997; Petukhov et al., 1999).

2.2.4. Sampling of oil for analysis

Samples of oil for analysis were taken each morning after the oil had cooled overnight at 20 °C and before replenishment. Six samples of oil were collected each at day 0, day 1, day 2, day 3, day 4, and day 5. Day 0 oil was collected after the oil conditioning before the start of the frying. All the oil samples collected were analyzed using the same procedure used for the initial oil analysis.

2.2.5. Statistical analysis

Values represented are the means and standard deviations for three replicates. Statistical analysis was carried out by Student's *t*-test using SPSS Version 11.0 software and ANOVA using SAS system Version 8e. Significance was defined at P < 0.05 using Duncan's multiple range test.

3. Results and discussion

3.1. Fatty acid composition

The fatty acid compositions of the oils used in the frying experiment are shown in Table 1. The most prominent fatty acids in the oils are palmitic (37.7%, 8.9%, 11.3%), oleic (45.6%, 57.4%, 24.8%) and linoleic (10.8%, 22.8%, 53.5%) for PO, CLO, and SBO, respectively. MoO has the highest amount of oleic acid (74.5%) of all the oils with only 6.1%and 0.7% palmitic and linoleic acids, respectively. The total monounsaturated acids in MoO is very high (78.1%) compared to the other oils with 46.3%, 58.6%, and 25.1% for PO, CLO, and SBO, respectively. High amounts of monounsaturated fatty acids in oils are desirable because of the health benefits (Mensink & Katan, 1990). Oils with high amounts of monounsaturated (oleic type) fatty acids are associated with decreased risk of coronary heart disease. Due to this, successful attempts were made to produce canola, sunflower, safflower, peanut and soybean plants

| Fatty acid composition of oils used in the frying test | | | | | |
|--|------|------|------|------|--|
| Fatty acid | РО | CLO | SBO | MoO | |
| C _{12:0} | 0.2 | _ | _ | _ | |
| C _{14:0} | 0.7 | 0.1 | 0.1 | 0.1 | |
| C _{16:0} | 37.7 | 8.9 | 11.3 | 6.1 | |
| C _{16:1} | 0.6 | 0.2 | 0.1 | 1.8 | |
| C _{18:0} | 3.7 | 2.2 | 3.9 | 5.1 | |
| C _{18:1} | 45.6 | 57.4 | 24.8 | 74.5 | |
| C _{18:2} | 10.8 | 22.8 | 53.5 | 0.7 | |
| C _{18:3} | 0.2 | 6.8 | 5.5 | - | |
| C _{20:0} | 0.4 | 0.6 | 0.5 | 3.0 | |
| C _{20:1} | 0.1 | 1.0 | 0.2 | 1.8 | |
| C _{22:0} | _ | _ | _ | 5.4 | |
| C _{24:0} | _ | _ | _ | 1.5 | |

that produce oils with an increased monounsaturated (oleic) acid content (Corbett, 2003).

3.2. Changes in color and viscosity

Table 2 shows changes in color and viscosity for MoO, PO, CLO, and SBO for the 5 days of frying. Color change in frying oils is a visual indication of the extent of oil deterioration caused by oxidation. Increase in the color intensity is due to accumulation of nonvolatile decomposition products such as oxidized triacylglycerols and FFA. All the oils darkened during the frying trial, and the rate of darkening is proportional to the frying time. The initial rate of darkening was higher in PO than in MoO, CLO and SBO. PO showed a rapid darkening after day 1, but the rate slowed down and became steady throughout the rest of the frying trial. While in MoO, CLO and SBO the rate of darkening was the same throughout the frying days. Even though the initial color of CLO was lighter than the other oils, it was found to be the darkest at the end of the frying trial followed by SBO, MoO and PO.

The viscosity of all the oils increased with frying days. 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. The changes in viscosity in all the oil samples had a positive and high correlation with changes in percent TPC during the frying period, with correlation coefficient, of 0.9966, 0.9826, 0.9796, and 0.9809, for MoO, PO, CLO, and SBO, respectively. Colour and viscosity are the most common physical parameters used to evaluate the extent of frying oil deterioration in commercial and household frying. They are the most obvious changes that can be observed even for the non-expert.

3.3. Changes in free fatty acid content (FFA)

The amount of FFA in fats and oils can be used to indicate the extent of its deterioration due to hydrolysis of TAG and/or cleavage and oxidation of fatty acid double bonds. Although the initial FFA values of the oils were

 Table 2

 Changes in color and viscosity during frying

| Characteristics Day PO | | РО | CLO | SBO | MoO |
|------------------------|---|--------------------------|--------------------------|----------------------------|----------------------------|
| Color (Lovibond) | | | | | |
| Red unit | 0 | $1.13\pm0.05\mathrm{D}$ | $0.10\pm0.00\mathrm{E}$ | $0.40\pm0.00{ m D}$ | $0.10\pm0.00\mathrm{E}$ |
| | 1 | $2.15\pm0.05\mathrm{C}$ | $0.67\pm0.05\mathrm{D}$ | $0.90\pm0.00{ m D}$ | $1.80\pm0.00\mathrm{D}$ |
| | 2 | $2.70\pm0.00\mathrm{BC}$ | $1.10\pm0.00\mathrm{C}$ | $1.23\pm0.06\mathrm{D}$ | $3.80\pm0.10\mathrm{C}$ |
| | 3 | $3.23\pm0.06\mathrm{AB}$ | $2.20\pm0.10\mathrm{B}$ | $2.10\pm0.00\mathrm{C}$ | $5.10\pm0.05\mathrm{B}$ |
| | 4 | $3.50\pm0.00\mathrm{A}$ | $2.33\pm0.06\mathrm{B}$ | $3.37\pm0.05\mathrm{B}$ | $6.30\pm0.55\mathrm{A}$ |
| | 5 | $3.73\pm0.05 \mathrm{A}$ | $3.40\pm0.00A$ | $4.50\pm0.00\mathrm{A}$ | $6.30\pm0.15A$ |
| Yellow unit | 0 | $7.00\pm0.00\mathrm{D}$ | $1.10\pm0.00\mathrm{F}$ | $3.00\pm0.00F$ | $1.00\pm0.00\mathrm{F}$ |
| | 1 | $11.10\pm0.00\mathrm{C}$ | $4.15\pm0.05\mathrm{E}$ | $6.00\pm0.05\mathrm{E}$ | $5.00\pm0.25\mathrm{E}$ |
| | 2 | $17.10\pm0.00\mathrm{B}$ | $8.50\pm0.00\mathrm{D}$ | $10.15\pm0.05\mathrm{D}$ | $10.00\pm0.15\mathrm{D}$ |
| | 3 | $17.30\pm0.00\mathrm{B}$ | $10.15\pm0.12\mathrm{C}$ | $14.00\pm0.00\mathrm{C}$ | $14.20\pm0.20\mathrm{C}$ |
| | 4 | $17.40\pm0.00\mathrm{B}$ | $18.23\pm0.15\mathrm{B}$ | $15.90\pm0.15\mathrm{B}$ | $15.40\pm0.25B$ |
| | 5 | $18.07\pm0.06\mathrm{A}$ | $24.0\pm0.20\mathrm{A}$ | $18.00\pm0.10\mathrm{A}$ | $16.80\pm0.10\mathrm{A}$ |
| Viscosity, C_p | 0 | $90.0\pm0.76\mathrm{F}$ | $79.2\pm1.20\mathrm{F}$ | $74.4 \pm 0.15 \mathrm{E}$ | $51.7\pm0.68F$ |
| 1 | 1 | $92.9\pm0.25\mathrm{E}$ | $84.7\pm0.15\mathrm{E}$ | $81.4 \pm 0.55 \mathrm{D}$ | $54.9\pm0.58\mathrm{E}$ |
| | 2 | $96.1 \pm 1.15 \text{D}$ | $92.5\pm0.75\mathrm{D}$ | $87.8 \pm 1.00 \mathrm{C}$ | $59.2 \pm 1.05 \mathrm{D}$ |
| | 3 | $99.9\pm0.51\mathrm{C}$ | $101.5\pm1.00\mathrm{C}$ | $93.6 \pm 1.15B$ | $63.8\pm0.92\mathrm{C}$ |
| | 4 | $105.5\pm0.32\mathrm{B}$ | $107.1\pm1.21\mathrm{B}$ | $94.7\pm0.95\mathrm{AB}$ | $66.5\pm0.66\mathrm{B}$ |
| | 5 | $108.7\pm1.55A$ | $110.9\pm2.15A$ | $95.9\pm0.65\mathrm{A}$ | $70.3 \pm 1.25 \mathrm{A}$ |

Mean values within each column followed by different letters (A, B, C, etc.) are significantly ($P \le 0.05$) different.

different (0.10, 0.17, 0.19 and 0.22% for CLO, MoO, PO and SBO, respectively), at the end of the frying period (5 days), the total change in FFA values from the initial to final day of frying were found to be the lowest in SBO (60.0%), followed by PO (65.0%), and MoO (66.6%) with the highest percentage found in CLO (71.4%) (Table 3).

Petukhov et al. (1999) evaluated the frying performance of genetically modified low-linolenic (LLCO) and higholeic canola (HOCO) oils and compared them with regular (RCO) and hydrogenated canola oils. Using FFA, contents of dienoic acids (CDA) and polar components as deterioration markers, they found out that after 5 days frying, lower levels of CDA were found initially in LLCO than the other three oils. LLCO and RCO had significantly greater rates of CDA accumulation than HOCO and hydrogenated canola oils. Initial amounts of polymers were significantly higher in the hydrogenated canola oil than in the LLCO. They concluded that the genetically modified LLCO and the HOCO showed slight improvement in frying performance over the RCO. In a similar study, Warner and Mounts (1993) evaluated the frying stability of soybean and canola oils with modified fatty acid composition and found that FFA and polar compounds during frying were significantly less in the low-linolenic soybean and canola oils than the corresponding unmodified oils after 5 h of frying.

In most deep fat frying operations, the amount of FFA produced by hydrolysis is too small to affect the quality of the food. Generally, the adverse effects are due to oxidation of unsaturated fatty acids. Because the determination of

| Chemical changes in oils during frying | | | | | | |
|--|-----|------------------------------|-----------------------------|-----------------------------|-----------------------------|--|
| | Day | РО | CLO | SBO | MoO | |
| FFA content (%) | 0 | $0.19\pm0.02aD$ | $0.10\pm0.00 \text{bC}$ | $0.22\pm0.02\mathrm{aD}$ | $0.17 \pm 0.00 aD$ | |
| | 1 | $0.25 \pm 0.02 b CD$ | $0.11 \pm 0.01 \mathrm{cC}$ | $0.34\pm0.02\mathrm{aC}$ | $0.23\pm0.01\text{bD}$ | |
| | 2 | $0.30\pm0.01\mathrm{aC}$ | $0.16\pm0.01 \mathrm{bC}$ | $0.39\pm0.01\mathrm{aC}$ | $0.31\pm0.01aC$ | |
| | 3 | $0.35 \pm 0.00 \mathrm{bcC}$ | $0.23\pm0.00\mathrm{dB}$ | $0.44\pm0.01\mathrm{aBC}$ | $0.39 \pm 0.01 abBC$ | |
| | 4 | $0.41\pm0.01\mathrm{bB}$ | $0.28\pm0.01\mathrm{cB}$ | $0.50\pm0.01\mathrm{aAB}$ | $0.45\pm0.02abAB$ | |
| | 5 | $0.55\pm0.01aA$ | $0.35\pm0.01\text{bA}$ | $0.54\pm0.01 aA$ | $0.51\pm0.01 aA$ | |
| IV (g I ₂ /100 g oil) | 0 | $56.8\pm0.52\mathrm{A}$ | $109.9\pm2.05A$ | $116.9 \pm 1.02 \mathrm{A}$ | $65.9\pm0.50\mathrm{A}$ | |
| | 1 | $56.6 \pm 0.15 A$ | $108.0\pm1.00\mathrm{A}$ | $115.9\pm0.52\text{AB}$ | $65.2 \pm 0.44 \mathrm{AB}$ | |
| | 2 | $55.8 \pm 0.22 \text{AB}$ | $105.8\pm0.51\mathrm{B}$ | $115.3 \pm 1.01 \text{AB}$ | $64.7\pm0.71\mathrm{BC}$ | |
| | 3 | $54.9\pm0.10\mathrm{B}$ | $104.1\pm0.90\mathrm{C}$ | $114.7\pm0.81\mathrm{BC}$ | $63.8\pm0.69\mathrm{C}$ | |
| | 4 | $54.2 \pm 0.44 \mathrm{B}$ | $103.4\pm1.01\mathrm{C}$ | $113.5\pm0.21\mathrm{C}$ | $62.6\pm0.62\mathrm{C}$ | |
| | 5 | $53.7\pm0.27\mathrm{B}$ | $103.0\pm0.71\mathrm{C}$ | $111.7 \pm 0.83 \mathrm{D}$ | $62.2\pm0.53\mathrm{C}$ | |

Mean values within each row followed different letters (a, b, c, etc.) are significantly (P < 0.05) different. Mean values within each column followed by different letters (A, B, C, etc.) are significantly (P < 0.05) different.

| Table 3 | | | | |
|------------------|----|------|--------|--------|
| Chemical changes | in | oils | during | frying |

FFA by titration does not differentiate between acids formed by oxidation and those by hydrolysis, the increase in FFA is a poor measure of frying fat deterioration if used alone. However, it can be a good indicator of the extent of fat abuse if used in conjunction with other methods. The correlation coefficient (R^2) between FFA and total polar compound (TPC) were high for individual oils: 0.9544, 0.9607, 0.9747 and, 0.9790 for PO, CLO, SBO and MoO, respectively.

3.4. Changes in iodine value (IV)

Table 3 shows the changes in IV of the oils during 5 consecutive days of frying. The IV indicates the degree of unsaturation of the oils. A decrease in IV can be attributed to the destruction of double bonds by oxidation and polymerization. Changes in IV over the 5 days frying period from the initial values for CLO; 109.9–103.0 was larger followed by that of SBO; 116.9–111.8. Lesser changes were found in PO; 56.8–53.7 and MoO; 65.9–62.2. MoO and PO had a longer induction period since there were no significant changes (P > 0.05) for the first two days of frying. In CLO and SBO, however, the changes in the IV were significant (P < 0.05) after the first day of frying, indicating shorter induction periods. This meant that MoO and PO were less susceptible to oxidation than CLO and SBO.

3.5. Changes in peroxide value (PV)

Table 4 shows the changes in the PV of the oils from day 0 to 5. There was an initial sharp increase in the PV for CLO from day 0 to day 1 after which the rate slows down, while MoO, PO and SBO showed a gradual increase throughout the frying time. The rate of change in PV with

Table 4 Changes in PV *p*-AV and TOTOX value during frying

time for the oils are as follows: MoO (0.62%/day), PO (0.67%/day), SBO (0.69%/day) and CLO (0.72%/day). Peak values for the PV (meq O_2/kg oil) were attained as follows; MoO (4.00 after day 3), PO (4.92 after day 4), CLO (5.08 after 2), and SBO (4.42 after day 2). Rapid increase in PV in SBO and CLO showed the oils to be very unstable to oxidative degradation. This was largely due to the high amounts of linolenic acid in the two oils. CLO has the highest percentage of linolenic acid and showed less stability to oxidation followed by SBO. The PV decreased in both oils after the peak was reached. The PV peak for the MoO and PO were reached after day 3 and 4, respectively as compared to day 2 in cases of CLO and SBO. This is because both MoO and PO contained significantly lesser amounts of C18:2 and C18:3 than CLO and SBO. MoO was found to have the least peak value of 4.00 compared to all the other oil.

PV alone is not a suitable parameter to assess the extent of fats and oils deterioration. Increase in the PV during frying period indicates increased formation of peroxides due to oxidation. However, peroxides are unstable under deep-frying conditions, at the frying temperatures and as oil deterioration continues the hydroperoxides decomposes forming carbonyl and aldehydic compounds causing the peroxide value to decrease (Shahidi & Wanasundara, 2002). This is the reason why the amount of peroxides in the oil cannot be used to estimate the extent of oil deterioration.

3.6. Changes in p-anisidine value (p-AV)

This method defined as 100 times the optical density measured at 350 nm in a 1 cm cell containing 1 g of oil in 100 ml of mixture of solvent and reagent is used to deter-

| Changes in PV, p-AV and TOTOX value during frying | | | | | | |
|---|-----|------------------------------|-----------------------------|----------------------------|------------------------------|--|
| | Day | PO | CLO | SBO | MoO | |
| PV, meqO ₂ /kg | 0 | $2.25\pm0.00\mathrm{bD}$ | $2.42\pm0.29\mathrm{bD}$ | $3.05\pm0.~30\mathrm{aC}$ | $2.15 \pm 0.00 \mathrm{bC}$ | |
| | 1 | $3.25 \pm 0.00 \mathrm{cC}$ | $4.75\pm0.00\mathrm{aB}$ | $3.75\pm0.00\mathrm{bB}$ | $2.95\pm0.00\mathrm{cB}$ | |
| | 2 | $3.75\pm0.00\mathrm{cB}$ | $5.08\pm0.30\mathrm{aA}$ | $4.42\pm0.29\mathrm{bA}$ | 3.80 ± 0.10 cA | |
| | 3 | $4.75\pm0.50\mathrm{aA}$ | $4.58\pm0.29aB$ | 4.25 ± 0.00 abA | 4.00 ± 0.12 bA | |
| | 4 | $4.92\pm0.29\mathrm{aA}$ | $3.25\pm0.00 \mathrm{bC}$ | $2.25\pm0.00 \mathrm{cD}$ | $3.55\pm0.07 \mathrm{bA}$ | |
| | 5 | $3.25\pm0.00aC$ | $2.75\pm0.00 \text{bD}$ | $2.25\pm0.00 \mathrm{cD}$ | $2.75\pm0.00\text{bB}$ | |
| <i>p</i> -AV | 0 | $19.97\pm0.03\text{bE}$ | $23.35\pm0.79\mathrm{aF}$ | $23.87 \pm 1.30 a E$ | $11.54\pm0.50 \text{cF}$ | |
| | 1 | $46.25\pm1.08 \text{cD}$ | $87.42\pm2.70\mathrm{bE}$ | $104.10\pm1.75\mathrm{aD}$ | $34.74 \pm 1.00 \text{dE}$ | |
| | 2 | 51.21 ± 1.00 cC | $99.23 \pm 1.00 \text{bD}$ | $133.53\pm1.29\mathrm{aC}$ | $47.51 \pm 1.10 \text{dD}$ | |
| | 3 | $62.74 \pm 1.50 \mathrm{bB}$ | $136.95\pm1.29\mathrm{aC}$ | $134.18\pm1.00\mathrm{aC}$ | 55.00 ± 2.12 cC | |
| | 4 | 63.13 ± 0.29 cA | $142.58\pm2.20aB$ | $139.19\pm1.52\text{bB}$ | $59.55 \pm 1.07 \text{dB}$ | |
| | 5 | $64.28\pm0.70\text{bA}$ | $146.64\pm1.90aA$ | $145.17\pm0.96aA$ | $63.25\pm0.60\text{bA}$ | |
| TOTOX value | 0 | $24.47\pm0.05\text{bE}$ | $28.19\pm0.91\mathrm{aE}$ | $29.97 \pm 1.52 \text{aD}$ | 15. 84 ± 0.52 cE | |
| (2PV + p-AV) | 1 | 52.75 ± 1.00 cD | $96.92\pm2.50 \mathrm{bD}$ | $111.60 \pm 1.75 aC$ | $39.74 \pm 1.20 \mathrm{dD}$ | |
| | 2 | 58.71 ± 1.06 cD | $109.30\pm1.08bC$ | $142.37\pm1.70\mathrm{aB}$ | $55.11 \pm 1.34 dC$ | |
| | 3 | 72.24 ± 1.42 cAB | $146.11\pm1.31\mathrm{aB}$ | $142.68\pm1.09\text{bB}$ | $63.00\pm2.52\mathrm{dB}$ | |
| | 4 | $72.97\pm0.49\mathrm{cA}$ | $149.08\pm2.29\mathrm{aAB}$ | $143.69\pm1.52\text{bB}$ | 66.65 ± 1.21 dA | |
| | 5 | $70.78\pm0.73\text{bB}$ | $152.14\pm1.89aA$ | $149.67\pm1.00aA$ | $68.78\pm0.63\text{cA}$ | |

Mean values within each row followed different letters (a, b, c, etc.) are significantly (P < 0.05) different. Mean values within each column followed by different letters (A, B, C, etc.) are significantly (P < 0.05) different.

mine the secondary changes in oils. It determines the amounts of aldehyde (principally 2-alkenals and 2,4-alkadienals) in animal fats and vegetable oils. The method is used in combination with peroxide value to assess the extent of oxidative rancidity. Table 4 shows the changes in the p-AV of the oils from day 0 to 5. There was an increase in the *p*-AV in all the oils with increasing frying time. This happened because the less stable primary oxidative products (hydroperoxides) decompose further to form aldehvdic compounds. The change in p-AV of MoO was found to be significantly lower ($P \le 0.05$) than the rest of the oils tested, followed by PO, with the highest values obtained in CLO and SBO. This confirms the results of the PV that showed the two oils to be more susceptible to oxidation at high temperatures than PO and MoO. At the end of the 5 days frying period, the p-AV were found to be 63.25, 64.28, 145.17 and 146.64, for MoO, PO, SBO, and CLO, respectively.

3.7. Determination of total oxidation (TOTOX value)

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 & Wanasundara, 2002). The results of this analysis are shown in Table 4. After the fifth day of frying, the TOTOX value of MoO (68.78) was found to be significantly lower (P < 0.05) than PO (70.78), CLO (152.14) and SBO (149.67). The lower TOTOX value of MoO shows that the oil is more stable to oxidative rancidity than the rest of the oils used. The higher TOTOX values in CLO and SBO were due to the high percentages of polyunsaturated fatty acids in the two oils. They contain high amounts of linoleic and linolenic acids. In contrast MoO contained high amounts of monounsaturated (oleic) acid, while PO contained high amounts of saturated (palmitic) and monounsaturated (oleic) acids. This gives the latter oils their oxidative stability and hence lower TOTOX value.

3.8. Changes in specific extinction $(E_{l_{cm}})^{\%}$ at 233 and 269 nm)

Changes in the ultraviolet absorption at 233 and 269 nm are associated with the changes in the conjugated dienes and trienes that are produced due to the oxidation of polyunsaturated fatty acids. The resulting conjugated dienes exhibit an intense absorption at 233 nm; similarly the conjugated trienes absorb at 269 nm. The changes in $E_{l_{cm}}^{\%}$ at 233 and 269 nm during frying for PO, CLO, and SBO are shown in Table 5. The $E_{l_{cm}}^{\%}$ at 233 and 269 nm for all the samples increased with frying time throughout the frying days. The levels of conjugated dienes throughout the frying days. The levels of conjugated dienes throughout the frying days. The levels found in SBO. The levels of conjugated trienes are however lowest in MoO as compared to all the other oils. The low levels of both conjugated dienes and trienes in MoO are indications of good oxidative stability of the oil, and it is because of the high percentage of monounsaturated/oleic acid it contains. The higher the percentage of polyunsaturated acids in the oil, the higher the levels of conjugated dienes and trienes formed during frying. This was the reason why SBO and CLO, that contained high percentages of polyunsaturated acids (linoleic and linolenic), have accumulated more conjugated dienes and trienes. In contrast, PO and MoO that contain high percentages of saturated and monounsaturated acids, respectively, have lower levels of the conjugated dienes and trienes. The high percentage saturated fatty acid in PO is, however, considered less desirable due to the increased risk of coronary heart disease it presents whereas the high monounsaturated acid in MoO is desirable because it is associated with decreased risk (Corbett, 2003; Mensink & Katan, 1990).

Changes in the ultraviolet spectrum have been used as a relative measure of oxidation. Farmer and Sutton (2002) indicated that the absorption increase due to the formation of conjugated dienes and trienes is proportional to the uptake of oxygen and formation of peroxides during the early stages of oxidation. Correlation coefficients (R^2) between $E_{l_{cm}}^{|\%}$ at 233 nm and PV during the initial stage of oxidation were found to be positive and very high; 0.9850, 0.9817, 0.9976, and 0.9889 respectively for PO, CLO, SBO and MoO. Specific extinction is thus a very sensitive means of measuring differences of lipid oxidation. It was found that in all the samples, the levels of conjugated dienes are higher than trienes, this is indicated by the higher values of $E_{l_{cm}}^{1}$ at 233 nm. The rate of increment in the level of conjugated dienes is sharp during frying on day 1, 2, and 3, after which it decreased on day 4 and 5. Most of the dienes will be transformed into polymer compounds with increase in frying time.

3.9. Changes in total polar compound (TPC)

Determination of polar compounds in abused oils and fats is a well-accepted method due to its accuracy and reproducibility. It provides the most reliable measure of the extent of deterioration in frying oils and fats in most situations (Fritsch, 1981). The level of polar compounds is a good indicator of the quality of used frying oils and fats. giving information of the total amount of newly formed compounds having higher polarity than that of triacylglycerols. Table 5 shows the changes in the percent TPC during the frying period. TPC was found to increase with the frying time for all the oils. The rate of increase was gradual for MoO and PO and has a value of 20.78% and 21.23%, respectively at the end of the frying period. TPC in CLO and SBO (28.73% and 31.82%, respectively) were significantly (P < 0.05) higher than those of MoO and PO. A level of 24% total polar materials has been suggested as the limit beyond which frying oil should be discarded (Anonymous, 2000).

Among all the oils tested MoO was found to have the lowest percentage of TPC at the end of the frying period.

 Table 5

 Changes in specific extinction and total polar compounds during frying

| Characteristics | Day | РО | CLO S | SBO | MoO | |
|---------------------------|-----|------------------------------|------------------------------|------------------------------|------------------------------|--|
| Specific extinction | | | | | | |
| E^{\parallel} at 233 nm | 0 | $1.67\pm0.00\mathrm{bE}$ | $2.65\pm0.00\mathrm{aE}$ | $2.79\pm0.01\mathrm{aE}$ | $1.36\pm0.01\mathrm{cE}$ | |
| cm at 200 min | 1 | $2.43\pm0.00 \mathrm{dD}$ | $5.33 \pm 0.02 \mathrm{bD}$ | $6.56\pm0.01\mathrm{aD}$ | $2.91\pm0.02 \text{cD}$ | |
| | 2 | $3.11 \pm 0.01 dC$ | $7.19 \pm 0.03 \mathrm{bC}$ | $8.91\pm0.01\mathrm{aC}$ | $4.56\pm0.02 \text{cC}$ | |
| | 3 | $3.81\pm0.02 \mathrm{dB}$ | $8.34\pm0.01\mathrm{bB}$ | $9.78\pm0.02\mathrm{aB}$ | $5.12\pm0.01\mathrm{cB}$ | |
| | 4 | $4.24 \pm 0.01 \mathrm{dA}$ | $9.10\pm0.01\mathrm{bA}$ | $10.17\pm0.00\mathrm{aB}$ | $5.41 \pm 0.00 \mathrm{cB}$ | |
| | 5 | $4.27\pm0.01\text{dA}$ | $9.28\pm0.00\text{bA}$ | $10.64\pm0.06\mathrm{aA}$ | $6.07\pm0.03 \text{cA}$ | |
| $E_{1}^{\%}$ at 269 nm | 0 | $0.65\pm0.004 bC$ | $0.61\pm0.00 \text{bD}$ | $1.27\pm0.00\mathrm{aD}$ | $0.05\pm0.00\text{cE}$ | |
| 'cm | 1 | $0.96 \pm 0.00 \mathrm{cB}$ | $1.31 \pm 0.00 \mathrm{bC}$ | $1.90\pm0.02\mathrm{aC}$ | $0.29\pm0.00\text{dD}$ | |
| | 2 | $1.03\pm0.01\mathrm{cB}$ | $1.82\pm0.01\mathrm{bB}$ | $2.22\pm0.00\mathrm{aB}$ | $0.52\pm0.00 \text{dC}$ | |
| | 3 | $1.07\pm0.01\mathrm{cAB}$ | $1.96\pm0.01\mathrm{bB}$ | $2.24\pm0.00\mathrm{aAB}$ | $0.72\pm0.01\mathrm{dB}$ | |
| | 4 | $1.12\pm0.00\mathrm{bA}$ | $2.03\pm0.01\mathrm{aAB}$ | $2.30\pm0.01\mathrm{aA}$ | $0.77\pm0.01\mathrm{cAB}$ | |
| | 5 | $1.18\pm0.01\text{bA}$ | $2.11\pm0.01 aA$ | $2.34\pm0.01 a A$ | $0.89\pm0.01\text{bA}$ | |
| TPC (%) | 0 | $4.02\pm0.30\mathrm{aF}$ | $3.01 \pm 0.11 \mathrm{bF}$ | $4.72\pm0.\ 80\mathrm{aF}$ | $3.07\pm0.28bF$ | |
| | 1 | $6.04 \pm 0.52 \mathrm{bE}$ | $5.72\pm0.50\mathrm{bE}$ | $11.03 \pm 0.51 \mathrm{aE}$ | $5.90 \pm 1.05 \text{bE}$ | |
| | 2 | $10.84 \pm 1.00 \mathrm{bD}$ | $10.89\pm0.69\mathrm{bD}$ | $18.20 \pm 1.00 \mathrm{aD}$ | $10.23\pm1.00\text{bD}$ | |
| | 3 | $13.92 \pm 0.75 dC$ | $22.98 \pm 1.11 \mathrm{bC}$ | $24.18 \pm 1.20 \mathrm{aC}$ | $15.10 \pm 0.95 \mathrm{cC}$ | |
| | 4 | $17.10 \pm 0.98 \mathrm{cB}$ | $25.05\pm1.56\text{bB}$ | $27.01\pm0.50\mathrm{aB}$ | $18.23 \pm 1.55 \text{cB}$ | |
| | 5 | $21.28 \pm 1.25 \text{cA}$ | $28.73 \pm 1.05 \text{bA}$ | $31.82 \pm 1.75 aA$ | $20.78\pm0.75\text{cA}$ | |

Mean values within each row followed different letters (a, b, c, etc.) are significantly ($P \le 0.05$) different. Mean values within each column followed by different letters (A, B, C, etc.) are significantly ($P \le 0.05$) different.

This is an indication of high stability of the oil to changes in TAG that occur during the period of frying. In a related study, Warner and Knowlton (1997) determined the frying stability of corn oils that are genetically modified to contain 65% oleic acid. The high-oleic corn oil was evaluated in room odor test and by total polar compound content analysis. High-oleic corn oil had significantly lower total polar compound levels after 20 h of oil heating and frying at 190 °C compared to normal and hydrogenated corn oils.

4. Conclusions

The results of this study have shown that high-oleic *M. oleifera* seed oil to be more stable in the frying application compared to other oils used in this experiment. It showed improved frying performance over regular canola, soybean and palm olein. Apart from being more stable in high temperature frying application than the regular oils, it also has an added advantage of containing high-oleic (monounsaturated) acid content that has been linked to reduce risk of high cholesterol and heart disease.

Acknowledgement

The study was made possible by an 8th Malaysia Plan IRPA Grant awarded by the Malaysian government to H. M. Ghazali.

References

Abdulkarim, S. M., Long, K., Lai, O. M., Muhammad, S. K. S., & Ghazali, H. M. (2005). Some physico-chemical properties of *Moringa oleifera* seed oil extracted using solvent and aqueous enzymatic methods. *Food Chemistry*, 93, 253–263.

- Abdulkarim, S. M., Long, K., Lai, O. M., Muhammad, S. K. S., & Ghazali, H. M. (2006). Use of enzymes to enhance oil recovery during aqueous extraction of *Moringa oleifera* seed oil. *Journal of Food Lipids*, 13, 113–130.
- Anon (1998). US grower plant mid-oleic sunflower. Inform, 9, 92.
- Anonymous (2000). Recommendations of the 3rd international symposium on deep fat frying. European Journal of Lipid Science and Technology, 102, 594.
- Anwar, F., Hussain, A. I., Iqbal, S., & Bhanger, M. I. (2007). Enhancement of the oxidative stability of some vegetable oils by blending with *Moringa oleifera* oil. *Food Chemistry*, 103, 1181–1191.
- AOCS (1989). Official methods and recommended practices of the American Oil Chemists' Society (4th ed.). Champaign Illinois, USA.
- Cocks, L. V., & van Rede, C. (1966). Laboratory handbook for oil and fats analysts. London: Academic Press.
- Corbett, P. (2003). It is time for an oil change! Opportunities for high-oleic vegetables oils. *Inform*, 14, 480–481.
- Dahot, M. U., & Memon, A. R. (1985). Nutritive significance of oil extracted from *Moringa oleifera* seeds. *Journal of Pharmacology* (University of Karachi), 20, 75–79.
- Dietz, M., Metzler, R., & Zarate, C. (1994). Food security in the village: The case of oil seed processing. *Appropriate Technology*, 20, 9–11.
- Farmer, E. H., & Sutton, D. A. (2002). Peroxidation in relation to oleifenic structure. In C. C. Akoh & D. B. Min (Eds.), *Food lipids: Chemistry, nutrition, and biotechnology* (2nd ed., pp. 470). New York: Marcel Dekker, Inc.
- Fritsch, C. W. (1981). Measurement of frying fat deterioration, a brief review. Journal of the American Oil Chemists' Society, 58, 272–274.
- Greyt, W. D., & Kellens, M. (2000). Refining practice. In W. Hamm & R. J. Hamilton (Eds.), *Edible oil processing* (pp. 97). England: Sheffield academic press.
- Gunstone, F. D. (2000). Composition and properties of edible oils. In W. Hamm & R. J. Hamilton (Eds.), *Edible oil processing* (pp. 3–5). England: Sheffield Academic Press.
- IUPAC (2000). Determination of polar compounds, polymerized and oxidized triacylglycerols, and diacylglycerols in oils and fats: A technical report. *Pure and Applied Chemistry*, *72*, 1563–1575.
- Lowell, J. F. (1999). Moringa oleifera: Natural nutrition for the tropics. Dakar Senegal: Church World Service.

- Mensink, R. P., & Katan, M. B. (1990). Effect of dietary *trans*-fatty acids on high-density and low-density lipoprotein cholesterol levels in healthy subjects. *New England Journal of Medicine*, 323(7), 439–445.
- Petukhov, I., Malcolmson, L. J., Przybylski, R., & Armstrong, L. (1999). Frying performance of genetically modified canola oils. *Journal of the American Oil Chemists' Society*, 76, 627–632.
- PORIM (1995). *PORIM test methods*. Malaysia: Palm Oil Research Institute of Malaysia, Ministry of Primary Industries.
- Price, M. L. (1986). Vegetables from a tree! ECHO News, 8, 1-2.
- Ramachandran, C., Peter, K. V., & Gopalakrishnan, P. K. (1980). Drumstick (*Moringa oleifera*): A multipurpose Indian vegetable. *Economic Botany*, 34, 276–283.
- Shahidi, F., & Wanasundara, U. N. (2002). Methods for measuring oxidative rancidity in fats and oils. In C. C. Akoh & D. B. Min (Eds.),

Food lipids: Chemistry, nutrition, and biotechnology (2nd ed., pp. 465–482). New York: Marcel Dekker, Inc.

- Tsaknis, J., & Lalas, S. (2002). Stability during frying of Moringa oleifera seed oil variety "Periyakulam 1". Journal of Food Composition and Analysis, 15, 79–101.
- Warner, K. (2002). Chemistry of frying oils. In C. C. Akoh & D. B. Min (Eds.), *Food lipids: Chemistry, nutrition, and biotechnology* (2nd ed., pp. 205–221). New York: Marcel Dekker, Inc.
- Warner, K., & Knowlton, S. (1997). Frying quality and oxidative stability of high-oleic corn oils. *Journal of the American Oil Chemists' Society*, 74, 1317–1321.
- Warner, K., & Mounts, T. L. (1993). Frying stability of soybean and canola oils with modified fatty acid compositions. *Journal of the American Oil Chemists' Society*, 70, 983–988.