

Food Chemistry 74 (2001) 21-33



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# Performance of a lipase-catalyzed transesterified palm kernel olein and palm stearin blend in frying banana chips

B.S. Chu<sup>a</sup>, H.M. Ghazali<sup>a</sup>, O.M. Lai<sup>a,\*</sup>, Y.B. Che Man<sup>a</sup>, S. Yusof<sup>a</sup>, M.S.A. Yusoff<sup>b</sup>

<sup>a</sup>Faculty of Food Science and Biotechnology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor DE, Malaysia <sup>b</sup>Chemistry and Technology Division, Palm Oil Research Institute of Malaysia, PO Box 10620, Kuala Lumpur, Malaysia

Received 25 July 2000; received in revised form 4 December 2000; accepted 4 December 2000

#### Abstract

The frying performance of an enzymatically transesterified palm stearin and palm kernel olein (1:1 by weight) blend was compared with its control (physical mixture or no enzyme added) and a commercial plastic frying shortening (CS). The samples were used as deep-fat frying media at 180°C for banana chips for seven consecutive days. The samples were then analysed for iodine value (IV), free fatty acid (FFA) content, peroxide value (PV), thiobarbituric acid (TBA) value, p-anisidine value (AV), total polar compounds (TPC), fatty acid composition, specific extinction,  $E_{1cm}^{1\%}$  at 233 and 269 nm, polymer contents, viscosity and colour indices. The fried banana chips were analysed for acceptability by sensory evaluations. Storage properties of the banana chips were also evaluated by trained sensory panellists and a modified TBA test. The transesterified blend was found to have significantly (P < 0.05) higher IV, FFA, PV, TBA value, AV, TPC,  $E_{1cm}^{1\%}$  at 233 and 269 nm values, polymer content, viscosity and colour indices compared to the control, indicating that the transesterified blend was more susceptible to oxidative deterioration during deep-fat frying. CS generally showed the largest changes in most of the parameters, basically due to its high polyunsaturated fatty acid levels. There was no significant difference (P > 0.05; for all the attributes tested) between the acceptability of the banana chips fried by the transesterified and control blends. However, the banana chips fried in CS had significantly (P < 0.05) lower scores in terms of flavour, aftertaste and overall acceptability. This might be due to the typical hydrogenation flavour of CS. In the storage stability study of the banana chips, it was found that the banana chips fried in the transesterified blend were significantly (P < 0.05) more rancid (lower score in sensory evaluations) and had a higher TBA value at the end of the storage time than the control. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Transesterified; Palm kernel olein; Palm stearin; Banana chips

#### 1. Introduction

Deep-fat frying is considered to be one of the oldest cooking methods for achieving the desired texture and flavour attributes of a variety of food products. During deep-fat frying, the frying fat/oil is continuously or repeatedly used at elevated temperatures in the presence of air, and hence suffers oxidative and thermal abuse. Such unavoidable chemical reactions cause formation of a range of volatile and non-volatile decomposition products,

E-mail address: lom@fsb.upm.edu.my (O.M. Lai).

such as peroxides, ketones, aldehydes, dimeric, polymeric and cyclic compounds (Fritsch, 1981; Melton, Jafar, Sykes, & Trigiano, 1994; Orthoefer, Gurkin & Liu, 1996). It has been reported that lipid oxidation can lead to changes in functional, sensory and nutritive values and even safety of the fried foods (Pearson, Gray, Wolzak & Horenstein, 1983; Wu & Nawar, 1983). Therefore, the frying performance and quality of the oil under frying conditions are of interest to oil processors, commercial frying operators and individual consumers. Generally, antioxidants are added to the frying medium to inhibit the oxidation process. Hydrogenated frying fats/oils, which are less susceptible to lipid oxidation, may be used to reduce the development of off-flavour arising from the unsaturated fatty acids (FA) (Applewhite, 1981).

<sup>\*</sup> Corresponding author. Tel.: +60-38948-6101, ext. 3437; fax: +60-38942-3552.

Frying shortenings are among the most popular frying media used in the snack and fast food industries, as well as in households. These shortenings are normally hydrogenated and contain trans FA which have been shown to correlate positively with the development of coronary heart disease (Ray & Bhattacharyya, 1996; Willett et al., 1993; Zock & Katan, 1992). For this reason, interest in the production of low- or zero-trans FA-containing frying shortenings has grown. One distinct approach is transesterification of a natural hard stock with liquid oil(s), which involves randomisation of FA in their triacylglycerol (TG) molecules. Palm stearin (PS), the solid fraction obtained from palm oil after crystallisation at a controlled temperature, is the most common hard stock used in the process (Lai, Ghazali & Chong, 1998a,b; Zainal & Yusoff, 1999). Since PS has a low iodine value (IV; Chong, 1994; ranging from 20 g of I<sub>2</sub>/100 g of oil for hard stearin to about 50 g of I<sub>2</sub>/100 g of oil for soft stearin), it possesses an additional advantage to the frying shortenings, whereby the frying shortenings will be more stable against oxidative deterioration during deepfat frying and extend the shelf life of the fried foods.

In this study, PS and palm kernel olein (PKO) were blended at a ratio of 1:1 by weight and the mixture was enzymatically transesterified with 1.0%w/w Lipozyme IM60 (Rhizomucor miehei) lipase. PKO is used in this study in order to utilize the advantageous properties and characteristics normally associated with lauric oils, most notably their ability to withstand the rigours of high-heat frying, and provides protection from undesirable deterioration of the blend. Frying shortenings containing substantial quantities of lauric oil allow a cleaner frying operation (Crosby, 1993). This study entailed an evaluation of frying performance of the lipase-catalysed transesterified PS/PKO blend and its control, in comparison with a commercial frying shortening during the intermittent deep-fat frying of banana chips. It is known that a transesterification process may lead to the partial production of tocopherol esters of long chain FA and may change the antioxidant properties of the transesterified blend (Aitzetmuller, 1996). Bearing in mind that it is impractical for industries to purify the fats and oils prior to transesterification, the PS and PKO used in this study had not been chromatographed to free them of the non-TG components especially the tocopherols.

The frying performance of various oils have been reported in many papers (Augustin, Heng & Idris, 1988; Raoux, Morin & Mordret, 1996; Tyagi & Vasishtha, 1996; Warner, Orr, Parrott & Glynn, 1994), but there have been limited reports on the frying performance of transesterified blends. Therefore, the objectives of this study were to assess the frying performance of the PS/PKO lipase transesterified blend and to study the oxidative stability of the fried banana chips produced.

#### 2. Materials and methods

#### 2.1. Materials

Refined, bleached and deodorised (RBD) PS (slip point 54.4°C, IV ca. 32.0 g of  $I_2/100$  g of oil) and RBD PKO (slip point 23.4°C, IV ca. 15.3 g of  $I_2/100$  g of oil) were purchased from Ngo Chew Hong Oils and Fats Pte. Ltd., Semenyih, Malaysia and donated by Cargill Specialty Oils and Fats Pte. Ltd., Port Klang, Malaysia, respectively. One imported commercial plastic frying shortening (CS) was purchased from a local supermarket in Kuala Lumpur, Malaysia, which contains partially hydrogenated soybean and cottonseed oil. Lipase used in this study was a commercially immobilised Rhizomucor miehei lipase (Lipozyme IM60) which was a gift from Novo Nordisk Ind. (Copenhagen, Denmark). The moisture content of the enzyme was ca. 2.5% w/w. The bananas (Musa paradisiaca, a triploid of seedless Musa balbisiana and Musa acuminata or pisang abu variety) were purchased from the local market in Serdang, Malaysia. Slightly under-ripe bananas (maturity index of 2, more greenish than yellowish colour) were used as this is the usual practice in the preparation of fried banana chips (Augustin et al., 1988). The peeled bananas were about 12-15 cm long and the diameter was 2.5-3.5 cm. All chemicals used were either analytical, high-performance liquid chromatograph (HPLC) or spectrophotometric grade.

## 2.2. Sample preparation

PS was melted at 60°C in an oven prior to use. A total of 30 kg of 1:1 (by weight) PS/PKO mixture was prepared. The mixture was transesterified batch wise, using an orbital shaker (Certomat U, B. Braun, Germany) at 200 rpm for 6 h. Each batch contained 500 g of PS/PKO mixture with 1.0% w/w of Lipozyme IM60 lipase as the biocatalyst. After the reaction process, the lipase was filtered out using a three layered cheese cloth (Ghazali, Maisarah, Yusof & Yusoff, 1995). The lipase was reused in the following three batches. It was reported that the immobilised lipase was stable for repeated use up to five times (Rosu, Uozaki, Iwasaki & Yamane, 1997). To confirm that the transesterification reaction had taken place, the transesterified blend was injected into an HPLC system (Shimadzu LC-10 AD liquid chromatograph and RID-6A Shimadzu refractive index detector, Kyoto, Japan). All of the transesterified mixture (30 kg) was then poured into the metal vessel of a deodoriser to removed the free fatty acids (FFA). The mixture was neutralised and deodorised by distillation at 160°C and a pressure of 30 X  $10^{-3}$  torr for 1.5 h (Idris, Abdullah, & Halim, 1992). The FFA in the mixture after distillation was  $0.056\pm0.001\%$  (% FFA of undistilled mixture was  $3.872 \pm 0.052\%$ ). Removal of FFA in the transesterified blend before frying and storage experiments was very important because the FFA might increase the degree of oxidation of the fat. The same procedures were carried out for the control blend except lipase was not added.

## 2.3. Preparation of banana chips and frying experiment

Banana rounds 1.5 mm thickness were cut using a mechanical slicer (Italimport SRL, Model 90915, China). The banana rounds were soaked in distilled water at room temperature, prior to use, to wash off the dirt and prevent Maillard reactions which cause browning on the surface of the banana rounds. They were then lightly blotted with tissue paper before weighing into 100 g batches for frying (Che Man & Tan, 1999). Frying experiments were carried out in various frying systems comprising the lipase transesterified PS/PKO blend, PS/PKO control blend and CS. Frying experiments were conducted in duplicate.

For each frying system, 4.5 kg of frying shortening was put into a Valentine batch fryer (Type T4, Valentine Equipment Ltd., Reading, UK). The temperature of the shortening was raised to 180°C during 20 min and the frying process was started 20 min after the temperature had reached 180°C. A batch of 100 g of banana rounds was placed in the fryer basket and fried for 3 min. The banana chips were allowed to drain for 20 s, after which the chips were dabbed with tissue paper for 1 min to remove excess oil. The chips were then quickly packed in glass bottles and labelled for sensory evaluations. The fryer was left uncovered during frying. At the end of the tenth frying, the fryer was switched off and shortening sample (100 g) was collected and stored in brown-colour amber bottles when the temperature of the shortening dropped to 60°C. The shortening sample was flushed with nitrogen and kept at 4°C before being analysed. The lid was placed on the fryer and the shortening was allowed to cool overnight. The frying experiments were carried out for 7 consecutive days and the same procedures were repeated (Che Man & Tan, 1999).

## 2.4. Analysis of the shortening

The PORIM test methods (PORIM, 1995) were used to determine the IV (method p3.2), FFA content (method p2.5), peroxide value (PV; method p2.3), p-anisidine value (AV; method p2.4), and specific extinction,  $E_{1cm}^{1\%}$  at 232 and 269 nm values (method p2.15). The total polar compound (TPC) content and direct method of determining the thiobarbituric acid (TBA) value were carried out according to the AOCS Official Methods (method Cd 20-91 and Cd 19-90, respectively; AOCS, 1989). The FA composition was determined by using a gas chromatograph model GC-17A (Shimadzu Co., Kyoto, Japan) equipped with a flame ionisation detector and a polar

capillary column model BPX70 (0.32 mm id, 30 m length, 0.25 µm film thickness), SGE Australia, Pty. Ltd., Ringwood, Australia. The colour of the shortenings was measured in a 1 in. cell in a Lovibond Tintometer (Salibury, UK) at 60°C and the viscosity of the shortenings was determined at 60°C using a Brookfield viscometer model DV-II+ (Stoughton, MA) with spindle number 3 at 30 rpm. Polymer content was analyzed according to the method described by Peled, Gutfinger and Letan (1975). The quality assessments of the shortenings were monitored across the 7 consecutive days of frying. The slip melting points (SMP) of the fresh shortenings were determined according to AOCS method Cc 3-25 (AOCS, 1989). The TG profiles of the fresh shortenings were determined by a Shimadzu LC-10 AD HPLC, equipped with a RID-6A refractive index detector (Kyoto, Japan) with a commercially packed RP-18 column (250×4 mm) with particle size of 5  $\mu$ m (E. Merck, Darmstadt, Germany). The TG were eluted using acetone/acetonitrile (63.5:36.5 v/v) as the mobile phase. The flow rate was 1 ml/min.

#### 2.5. Analysis of the fried banana chips

The sensory evaluation, using a nine-point hedonic scale (Peryam & Pilgrim, 1957), was carried out on the banana chips fried on the first day, as a tool to determine the acceptability of the chips against different frying systems. One hundred and ten panellists were selected randomly from the students and staff in the faculty. The banana chips, fried in different systems, were coded with a three-digit random number. The panellists were required to evaluate the organoleptic qualities of the chips namely colour, oiliness, flavour, crispiness, after-taste and overall acceptability, by giving a score ranging from 1 (dislike extremely) to 9 (like extremely).

For storage analysis, the fried banana chips, of each system of the first day of the frying operation, were kept in transparent bottles, separately. The bottles were then stored in a conventional oven at 60°C to stimulate lipid oxidation (Tangel, Leeder & Chang, 1977). The bottles were left uncapped to allow the oxidation to take place. The fried banana chips were sampled from the bottles at the start of the storage analysis (day 0) and at 2-day intervals for a period of 2 weeks. The banana chips sampled were analysed for rancidity by sensory evaluations and a modified distillation TBA test (Ke, Cervantes & Rables-Martinez, 1984). In the sensory evaluations, 12 trained sensory panellists were required to determine the intensity of rancid off-flavour of the banana chips throughout the storage periods. About 15 g of the banana chips from each system were put in amber-brown bottles with screw-caps, separately, and coded with three-digit random numbers. The bottles were placed in a 60°C conventional oven for 30 min to help the rancid odour develop in the headspace of the bottles. During the sensory evaluations, the panellists were instructed to open the bottles and take sniffs. By comparing with three given standards, the panellists were then required to evaluate the intensity of rancid-off flavour of the chips by giving a score ranging from 10 to 0 (10.0–8.0, no rancid-off flavour detected; 7.9–6.0, slight or detectable rancid-off flavour; 5.9–4.0, moderate intensity of rancid-off flavour; 3.9–2.0, strong or markedly disagreeable rancid-off flavour, and 1.9–0.0, extremely rancid). The three standards given were samples with scores of 9.0, 5.0 and 3.0. The standards were rated by their TBA values (which had been scaled up and correlated to intensity of rancid-off flavour in the banana chips).

#### 2.6. Statistical analysis

The SAS (SAS, 1989) software package was used to analyse all data obtained. Significant differences (P < 0.05) between means were also determined using Duncan's multiple range test. Each reported value is the mean of four analyses from two replications.

#### 3. Results and discussion

## 3.1. Physicochemical properties of the fresh oils

Table 1 shows some physico-chemical properties of the fresh transesterified PS/PKO blend and its control, as well as CS. On comparing the TG composition of the transesterified blend with its control, TG with carbon numbers ranging from C<sub>32</sub> to C<sub>36</sub> and C<sub>48</sub> and C<sub>50</sub> were reduced significantly (P < 0.05), while TG with carbon numbers ranging from C<sub>40</sub> to C<sub>46</sub> increased significantly (P < 0.05) after transesterification. The lipase had utilised the low and high carbon number TG to produce TG that had intermediate carbon numbers. The rearrangement of the FA from the higher melting point TG to lower also caused a marked reduction in SMP. This was in accordance with Lai et al.'s (1998a) findings. Low IV was an advantage for both transesterified and control blends (31.4 and 29.0 g of I<sub>2</sub>/100 g of oil, respectively) and hence they might have a better oxidative stability during frying and storage. TG with carbon number C<sub>54</sub> constituted about 73.0% of the TG in CS. CS was made of partially hydrogenated soybean oil and cottonseed oil (from the label) and it has the highest IV (89.1 g of  $I_2$ ) 100 g of oil) but lowest SMP (45.3°C).

There was no significant (P > 0.05) change in FA composition in the PS/PKO blend after transesterification, although some of the FA decreased a little due to hydrolysis. Two main FA in the PS/PKO blends were palmitic (C16:0) and lauric (C12:0) acids which were contributed mainly by the PS and PKO, respectively. Both transesterified and control blends were of good quality, as indicated by their low FFA, PV and TBA

values (Table 1). The results also show that CS had higher oxidation values than the transesterified and control blends. It should be noted that CS is a Malaysian imported product while PS and PKO are locally produced. The higher oxidation values of CS were probably the result of the greater degree of handling, transportation and storage of CS compared to the PS and PKO. High levels of C18:2 and C18:3 acids in CS could also lead to instability to oxidation. Nevertheless, CS was still of good quality as a frying shortening. As stated on the label, CS contained tertiary butylhydroxyquinone (TBHQ) as an antioxidant while the PS and PKO had no added antioxidants, as confirmed by the companies.

## 3.2. Changes in IV and FFA content

Table 2 shows the changes in IV and FFA contents of the frying media (oil) during 7 consecutive days of frying. The IV indicates degree of unsaturation of fats and oils. A decrease in IV can be attributed to the destruction of double bonds by oxidation, scission and polymerization (Cuesta, Sanchez-Muniz & Hernandez, 1991). The changes of IV over 7 frying days for the transesterified blend was larger (8.6 g of  $I_2/100$  g of oil) than the control  $(7.7 \text{ g of } I_2/100 \text{ g of oil})$ . The control also had a longer induction period, since there were no significant (P > 0.05) changes of IV in the control for the first 3 frying days. This meant that the control was less susceptible to oxidation than the transesterified blend although they initially had a similar IV. This is quite surprising because both the transesterified and control blends had similar TG and FA compositions. Results showed that the transesterified blend had lost its stability against oxidation during frying. The transesterification process might reposition the unsaturated FA in the TG molecules from position sn-2, which was reported to be more stable against oxidation (Martin, Lavillonniere, Nour & Sebedio, 1998; Neff & List, 1999) to position sn-1 or 3.

Another possible reason for this observation was the lost of antioxidative activity of antioxidants such as tocopherols in the non-TG components of the transesterified blend. Tocopherols, despite their small quantity in the oil, play a very significant role in inhibiting oxidation. For example, crude palm oil contains about 600–1000 ppm of tocopherols and the RBD palm oil even less (Chong, 1994). The tocopherol content of the PS/PKO mixture in this study decreased after transesterification (tocopherol contents of the blend before and after the reaction were 532 and 468 ppm, respectively), while the control blend remained unchanged (524 ppm). The tocopherols and tocotrienols in the PS and PKO are initially in the free state, which contained a free OHgroup. During transesterification, the OH-groups of the tocopherols might be transesterified to FA to form tocopherol esters. This may change the antioxidant

Table 1 Characteristics of the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristics  | Control            | Transesterified blend | CS                 |
|--|--------------------|-----------------------|--------------------|
| Triacylglycerol (TG) composition in carbon number, % (peak area) |                    |                       |                    |
| $C_{28}$   | 0.17b              | 0.23a                 | -                  |
| $C_{30}$   | 0.88b              | 1.29a                 | =                  |
| $C_{32}$   | 3.95b              | 2.78a                 | -                  |
| $C_{34}$   | 6.27b              | 4.84a                 | =                  |
| $C_{36}$   | 9.48b              | 7.60a                 | -                  |
| $C_{38}$   | 5.86b              | 4.63a                 | =                  |
| $C_{40}$   | 6.89b              | 9.59a                 | -                  |
| $C_{42}$   | 1.47b              | 2.33a                 | -                  |
| $C_{44}$   | 5.81b              | 8.36a                 | =                  |
| $C_{46}$   | 2.85b              | 5.53a                 | =                  |
| $C_{48}$   | 19.5b              | 16.5a                 | =                  |
| $C_{50}$   | 19.4b              | 17.2a                 | 2.27c              |
| $C_{52}$   | 11.3a              | 11.6a                 | 24.5b              |
| C <sub>54</sub>  | 5.16a              | 5.97a                 | 73.3b              |
| Fatty acid (FA) composition, % (peak area)                       |                    |                       |                    |
| C8:0   | 2.32a              | 2.53a                 | _                  |
| C10:0  | 1.81a              | 1.90a                 | _                  |
| C12:0  | 21.2a              | 21.9a                 | 0.20b              |
| C14:0  | 6.60a              | 6.56a                 | 0.23b              |
| C16:0  | 37.2a              | 35.0a                 | 14.4b              |
| C18:0  | 3.49a              | 3.54a                 | 12.2b              |
| C18:1  | 22.7a              | 22.8a                 | 37.7b              |
| C18:1 trans  | _                  | _                     | 5.69               |
| C18:2  | 4.60a              | 5.61a                 | 25.7b              |
| C18:2 trans  | _                  | _                     | 1.66               |
| C18:3  | 0.08a              | 0.10a                 | 2.24b              |
| Slip melting point (SMP), °C                                     | $50.07 \pm 0.05$ b | $47.00 \pm 0.10a$     | $45.30 \pm 0.05c$  |
| Iodine value (IV), g of $I_2/100$ g of oil                       | $29.0 \pm 1.12a$   | $31.4 \pm 0.41a$      | $89.4 \pm 0.19b$   |
| Free fatty acid (FFA) content, %                                 | $0.060 \pm 0.005a$ | $0.056 \pm 0.001a$    | $0.078 \pm 0.0011$ |
| Peroxide value (PV), meq/kg                                      | $0.79 \pm 0.05a$   | $0.55 \pm 0.05a$      | $0.91 \pm 0.01b$   |
| Thiobarbituric acid (TBA) value, moles malonaldehyde/kg oil      | $2.13 \pm 0.37a$   | $3.54 \pm 0.61a$      | $5.72 \pm 0.25b$   |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analysis from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different.

Table 2
Changes in iodine value (IV) and free fatty acid (FFA) content during frying in the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristics       | Day | Control                      | Transesterified blend | CS                          |
|-----------------------|-----|------------------------------|-----------------------|-----------------------------|
| IV, g of I2/100 g oil | 0   | 29.0±1.12aA                  | 31.4±0.41aA           | 89.4±0.19bA                 |
| , ,                   | 1   | $28.2 \pm 0.10$ aA           | $29.3 \pm 0.07$ aAB   | $89.1 \pm 0.15$ bA          |
|                       | 2   | $27.5 \pm 0.44$ aA           | $28.5 \pm 0.22aB$     | $88.4 \pm 0.77 \text{bAB}$  |
|                       | 3   | $26.4 \pm 0.27 aA$           | $28.1 \pm 0.74aB$     | $87.2 \pm 0.44$ bBC         |
|                       | 4   | $24.7 \pm 0.29$ bB           | $27.4 \pm 0.90 aBC$   | $86.6 \pm 0.20$ cBC         |
|                       | 5   | $24.0 \pm 0.15 aBC$          | $25.3 \pm 0.56 aCD$   | $85.7 \pm 0.52 bCD$         |
|                       | 6   | $22.2 \pm 0.15 bCD$          | $23.4 \pm 0.18aD$     | $84.5 \pm 0.42$ cDE         |
|                       | 7   | $21.3 \pm 0.10 \text{bD}$    | $22.8 \pm 0.15 aD$    | $83.7 \pm 0.44$ cE          |
| FFA content, %        | 0   | $0.060 \pm 0.005$ aA         | $0.056 \pm 0.001$ aA  | $0.078 \pm 0.001 \text{bA}$ |
|                       | 1   | $0.087 \pm 0.002 aAB$        | $0.079 \pm 0.002 aB$  | $0.101 \pm 0.004$ bB        |
|                       | 2   | $0.116 \pm 0.001$ bBC        | $0.096 \pm 0.001 aC$  | $0.107 \pm 0.001 \text{cB}$ |
|                       | 3   | $0.152 \pm 0.001$ bC         | $0.125 \pm 0.002 aD$  | $0.119 \pm 0.001 aC$        |
|                       | 4   | $0.197 \pm 0.001 aD$         | $0.192 \pm 0.005 aE$  | $0.146 \pm 0.001 \text{bD}$ |
|                       | 5   | $0.217 \pm 0.001 \text{bDE}$ | $0.248 \pm 0.009 aF$  | $0.187 \pm 0.007 bE$        |
|                       | 6   | $0.243 \pm 0.002$ bEF        | $0.277 \pm 0.002$ aG  | $0.174 \pm 0.001 cF$        |
|                       | 7   | $0.263 \pm 0.004 abF$        | $0.329 \pm 0.001$ aH  | $0.216 \pm 0.001 bG$        |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc.) are significantly (P < 0.05) different.

activity of the antioxidants. On the other hand, in the control blend, the tocopherols appeared in the non-esterified form with free OH-groups and its stability against oxidation during deep-fat frying remained unchanged. Deodorization and distillation at high temperature (160°C) further decreased the tocopherol levels of the transesterified (from 468 to 397 ppm) and control (from 524 to 445 ppm) blends. CS had the smallest change in IV over time (5.7 g of  $I_2/100$  g of oil) although it was suspected to have more active methylene groups which were prone to oxidative deterioration. This maybe mainly due to the antioxidant added.

The FFA are formed as a result of cleavage and oxidation of the double bonds of the FA, as well as the hydrolysis of the TG molecules. Although the FFA content determined by titration does not differentiate between acids formed by oxidation and those formed by hydrolysis (Fritsch, 1981), it was nevertheless measured as free acids which contribute to the development of rancid off-flavours in the frying fats and the fried foods (Che Man & Tan, 1999). Acidity, also, is identified to be one of the factors that contribute to increased smoking during frying (Augustin, Lee & Yau, 1987). The changes of FFA content for the transestrified blend, control and CS over 7 frying days are 0.27, 0.20 and 0.14%, respectively. The transesterified blend had a slightly higher level of FFA, at the end of the frying experiments, than the control. It was noted that, although CS had the highest initial FFA, the amount of FFA formed in the frying media was the lowest, even though it is known that the initial FFA tend to catalyse the hydrolysis of the oil (Tyagi & Vasishtha, 1996). It was reported that the FFA content is not a reliable measurement of oil deterioration (Fritsch, 1981). During deep-fat frying, the rate of FFA formation may vary over time within the same frying operation (Stevenson, Vaisey-Genser & Eakin, 1984). However, in this study, there was a good correlation between the FFA and TPC for all samples except the transesterified blend, which gave a lower correlation coefficient, r value. The r value = 0.7803, 0.9914 and 0.9817, P < 0.05, for transesterified blend, control and CS, respectively. Similar results were reported in previous studies (Melton et al., 1994; Smith, Clifford, Hamblin & Creveling, 1986). Therefore, the FFA content, as a measurement of degradation in frying oils, is controversial (Melton et al., 1994). In fact, whether or not the FFA levels are indicative of frying oil degradation, and also related to the fried food quality, most likely depends on the type of fat/oil used for frying and the frying practices utilised (Melton et al., 1994).

## 3.3. Changes in PV and TBA value

The changes in PV and TBA values of the frying shortenings over the frying days are presented in Table 3. For all shortenings, the PV increased drastically and then fell slightly on the last two frying days. Decomposition of the peroxides to produce carbonyl and aldehydic compounds under deep-fat frying operations is one of the reasons why PV decreased (Perkin, 1967). As with the results obtained for IV and FFA content, the control was found to have significantly (P < 0.05) smaller changes in PV compared to the transesterified blend, indicating that the transesterified blend was more susceptible to the production of peroxides. In CS, which was rich in polyunsaturated FA, oxidation of free radicals obtained from abstraction of protons from methylene-interrupted fatty molecules caused the formation of peroxides. These peroxides decompose much faster by means of labile hydrogen obtained from the active methylene group of another molecule (Tyagi & Vasishtha, 1996). This may explain why CS had significantly (P < 0.05)higher PV initially (day 1 and 2) and then decomposed to give significantly (P < 0.05) lower PV after day 2 compared to the transesterified and control blends.

The TBA test measures the secondary oxidation products, mainly malondialdehydes, present in the oil. The TBA values of all shortenings increased significantly (P < 0.05) throughout the frying days. In general, once again, the transesterified blend had higher levels of TBA value than the control. It was clear also that the transesterified blend had a higher rate of increment. Higher PV and TBA values in the transesterified blend further confirmed that the transesterified blend was more susceptible to primary and secondary oxidation than the control. CS had the highest TBA values for all frying days. A rapid decrease of PV in CS at the early stage of frying caused a rapid increase in TBA value on day 2 of the frying operations. Decomposition of peroxides at a higher rate gives rise to more free malondialdehydes which are responsive to the TBA reagent.

### 3.4. Changes in AV and TPC

Table 4 shows the AV and TPC value in the short-enings over the frying days. The changes of AV of the transesterified blend, control and CS after the frying operations were 40.4, 32.6 and 81.9, respectively. The AV method determines the amount of aldehydes (2-alkenals and 2,4-dienals) produced in the oil as a result of oxidation (PORIM, 1995). The transesterified blend was more susceptible to oxidation than the control, as indicated by their AV, although they both initially contained a similar amount of linoleic acid (Table 1). CS which contained the highest amount of linoleic acid is probably the cause of the biggest change in AV.

Since the polar materials in frying oil contain compounds that linearly relate to the quality of the oil usage over time (Blumenthal, 1996; Melton et al., 1994), TPC appears as the most reliable indicator of fat and oil deterioration. The TPC in all samples increased significantly (P < 0.05) after seven consecutive frying days. The changes in TPC for

Table 3
Changes in peroxide value (PV) and thiobarbituric acid (TBA) value during frying in the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristics                       | Day | Control                   | Transesterified blend | CS                        |
|---------------------------------------|-----|---------------------------|-----------------------|---------------------------|
| PV, meq/kg                            | 0   | 0.79±0.05aA               | 0.55±0.05aA           | 0.91±0.01bA               |
|                                       | 1   | $6.35 \pm 0.05$ bB        | $12.9 \pm 0.06$ aB    | $18.1 \pm 0.01 \text{cB}$ |
|                                       | 2   | $18.3 \pm 0.09 \text{bC}$ | $25.4 \pm 0.06 aC$    | $31.8 \pm 0.03$ cC        |
|                                       | 3   | $30.3 \pm 0.05 \text{bD}$ | $33.9 \pm 0.36 aD$    | $16.5 \pm 0.41$ cB        |
|                                       | 4   | $35.8 \pm 0.51$ bE        | $40.7 \pm 0.09$ aE    | $15.8 \pm 0.02$ cBD       |
|                                       | 5   | $44.5 \pm 0.90 aF$        | $45.1 \pm 0.06$ aF    | $15.8 \pm 0.53$ bBD       |
|                                       | 6   | $54.6 \pm 0.89 \text{bG}$ | $49.2 \pm 0.29 aG$    | $15.4 \pm 0.05$ cDE       |
|                                       | 7   | $48.0 \pm 0.37$ bH        | $45.1 \pm 0.03$ aF    | $15.2 \pm 0.08$ cE        |
| TBA value, moles malonaldehyde/kg oil | 0   | $2.13 \pm 0.37aA$         | $3.54 \pm 0.61$ aA    | $5.72 \pm 0.25 \text{bA}$ |
|                                       | 1   | $3.56 \pm 0.24 \text{bB}$ | $5.18 \pm 0.24 aB$    | $8.80 \pm 0.12$ cB        |
|                                       | 2   | $5.38 \pm 0.12 bC$        | $7.52 \pm 0.01aC$     | $14.5 \pm 0.25 cC$        |
|                                       | 3   | $9.30 \pm 0.50 aD$        | $9.72 \pm 0.01 aD$    | $15.3 \pm 0.12 \text{bD}$ |
|                                       | 4   | $11.42 \pm 0.12aE$        | $12.4 \pm 0.49aE$     | $15.6 \pm 0.35 bD$        |
|                                       | 5   | $12.9 \pm 0.24 aF$        | $12.9 \pm 0.01aE$     | $17.3 \pm 0.25$ bE        |
|                                       | 6   | $13.2 \pm 0.50 \text{bF}$ | $16.1 \pm 0.08 aF$    | $18.5 \pm 0.23 cF$        |
|                                       | 7   | $15.0 \pm 0.73$ bG        | $17.3 \pm 0.12aG$     | $21.0 \pm 0.12$ cG        |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc) are significantly (P < 0.05) different.

Table 4 Changes in *p*-anisidine value (AV) and total polar compounds (TPC) during frying of the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristics | Day | Control                   | Transesterified blend | CS                        |
|-----------------|-----|---------------------------|-----------------------|---------------------------|
| AV              | 0   | 0.63±0.55aA               | 0.71±0.19aA           | 0.93±0.06aA               |
|                 | 1   | $2.75 \pm 0.02 \text{bB}$ | $7.54 \pm 0.20 aB$    | $13.1 \pm 0.10$ cB        |
|                 | 2   | $9.09 \pm 0.02 bC$        | $13.6 \pm 0.39 aC$    | $27.2 \pm 0.58$ cC        |
|                 | 3   | 15.4±0.25bD               | $20.6 \pm 0.05 aD$    | $40.7 \pm 0.09$ cD        |
|                 | 4   | $21.5 \pm 0.12$ bE        | $26.9 \pm 0.12aE$     | 51.3±0.34cE               |
|                 | 5   | $27.6 \pm 0.52 aF$        | $31.6 \pm 0.40 aF$    | 59.2±1.26bF               |
|                 | 6   | 32.1±0.21bG               | $38.1 \pm 0.62aG$     | $69.6 \pm 0.50$ cG        |
|                 | 7   | $33.3 \pm 0.04 aG$        | $41.1 \pm 0.60 aH$    | $82.8 \pm 0.95$ cH        |
| TPC, %          | 0   | $5.74 \pm 0.12 aA$        | 5.95±0.06aA           | $8.23 \pm 0.14 \text{bA}$ |
|                 | 1   | $9.63 \pm 0.16 aB$        | $9.75 \pm 0.21aB$     | $12.4 \pm 0.27$ bB        |
|                 | 2   | $12.8 \pm 0.47 bC$        | $14.7 \pm 0.13 aC$    | $17.8 \pm 0.19$ cC        |
|                 | 3   | $15.9 \pm 0.31 \text{bD}$ | $18.1 \pm 0.25aD$     | 21.2±0.41cD               |
|                 | 4   | $19.4 \pm 0.11$ bE        | $22.3 \pm 0.45 aE$    | $27.2 \pm 0.28$ cE        |
|                 | 5   | $23.7 \pm 0.57 bF$        | $27.1 \pm 0.14aF$     | $32.5 \pm 0.47 cF$        |
|                 | 6   | $27.1 \pm 0.15$ bG        | $30.8 \pm 0.37aG$     | $37.5 \pm 0.17$ cG        |
|                 | 7   | $31.0 \pm 0.23$ bH        | $35.8 \pm 0.69 aH$    | 44.4±0.65cH               |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean±standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc) are significantly (P < 0.05) different.

the transesterified blend, control and CS were 29.9, 25.2 and 36.1%, respectively. Higher TPC, in the transesterified blend, once again revealed that the transesterified blend was less stable against oxidation than the control. The fresh CS (day 0) had the highest TPC among the shortenings, mainly due to the presence of mono- and

diacylglycerols added as emulsifier, as stated on its label. A level of 27% polar compounds has been suggested as the limit beyond which the frying oil should be discarded (Billek, Guhr & Waibel, 1978; White, 1991). The transesterified and control blends achieved this limit on days 5 and 6, respectively, while CS achieved the cut-off point more rapidly, that is on day 4. The TPC was reported to have good correlation with a number of analyses such as IV, dielectric constant and C18:2/C16:0 ratio (Augustin, Asap & Heng, 1987). In this study, the TPC correlated well (P < 0.05) with IV and AV (r value of TPC with IV and AV for the transesterified blend, control and CS = -0.9823, -0.9941, -0.9938 and 0.9940, 0.9878, 0.9919, respectively, P < 0.05).

## 3.5. Changes in FA composition and C18:2/C16:0 ratio

C18:2 and C16:0 are usually used as an indicator of the extent of fat deterioration because the C18:2 is more susceptible to oxidation, while the C16:0 is more stable against oxidation. The FA composition and C18:2/C16:0 ratio of the shortenings during the frying operations are shown in Table 5. Both the transesterified and control blends initially contained a trace amount of linolenic acid (C18:3) but this virtually disappeared after the second frying day due to oxidation. For all samples, there were decreases in the C18:2 and C18:3 acids but increases in C18:1 and C16:0 with the frying time. The C18:2 and C18:3 were oxidised and hydrolysed to form other oxidation products. The decrease in C18:2 in the transesterified blend at the end of frying operations was larger than the control. This was followed by a significant (P < 0.05)lowering in C18:2/C16:0 ratio in the transesterified

Table 5
Changes in fatty acid (FA) composition during frying of the control, transesterified blend and commercial sample (CS)

|                       | Day | C8:0 | C10:0 | C12:0 | C14:0 | C16:0 | C18:0 | C18:1 <i>c</i> | C18:1 <i>t</i> | C18:2 <i>c</i> | C18:2 <i>t</i> | C18:3 | C18:2/C16:0 |
|-----------------------|-----|------|-------|-------|-------|-------|-------|----------------|----------------|----------------|----------------|-------|-------------|
| Control               | 0   | 2.32 | 1.81  | 21.2  | 6.60  | 37.2  | 3.49  | 22.7           | _              | 4.60           | _              | 0.08  | 0.124       |
|                       | 1   | 2.27 | 1.79  | 21.0  | 6.76  | 37.7  | 3.29  | 22.8           | _              | 4.50           | _              | Trace | 0.119       |
|                       | 2   | 2.33 | 1.86  | 21.5  | 6.85  | 37.8  | 3.09  | 22.2           | _              | 4.41           | _              | -     | 0.116       |
|                       | 3   | 2.33 | 1.82  | 21.4  | 6.87  | 38.1  | 3.12  | 22.2           | _              | 4.12           | _              | -     | 0.108       |
|                       | 4   | 3.44 | 2.13  | 22.3  | 6.86  | 37.2  | 2.99  | 21.2           | _              | 3.94           | _              | _     | 0.105       |
|                       | 5   | 2.21 | 1.78  | 21.5  | 6.88  | 38.2  | 3.34  | 22.2           | _              | 3.85           | _              | -     | 0.103       |
|                       | 6   | 2.28 | 1.72  | 20.8  | 6.88  | 39.1  | 3.25  | 22.2           | _              | 3.70           | _              | _     | 0.095       |
|                       | 7   | 2.17 | 1.74  | 21.1  | 6.96  | 39.5  | 3.28  | 22.0           |                | 3.37           |                | _     | 0.085       |
| Transesterified blend | 0   | 2.53 | 1.90  | 21.9  | 6.56  | 35.0  | 3.54  | 22.8           | =              | 5.61           | =              | 0.10  | 0.160       |
|                       | 1   | 2.38 | 1.82  | 21.4  | 6.59  | 35.4  | 3.65  | 23.6           | _              | 5.14           | _              | Trace | 0.145       |
|                       | 2   | 2.50 | 1.87  | 21.7  | 6.70  | 35.6  | 3.58  | 23.0           | _              | 5.04           | _              | Trace | 0.141       |
|                       | 3   | 2.29 | 1.85  | 22.2  | 6.99  | 36.3  | 3.45  | 22.6           | _              | 4.27           | _              | -     | 0.117       |
|                       | 4   | 2.47 | 1.96  | 22.9  | 6.97  | 36.3  | 3.21  | 22.1           | _              | 4.18           | _              | _     | 0.115       |
|                       | 5   | 2.52 | 1.96  | 22.9  | 7.02  | 36.8  | 3.27  | 21.8           | _              | 3.81           | _              | _     | 0.104       |
|                       | 6   | 2.28 | 1.81  | 22.0  | 7.05  | 38.0  | 3.21  | 22.2           | _              | 3.53           | _              | _     | 0.093       |
|                       | 7   | 2.48 | 1.89  | 22.4  | 7.02  | 37.1  | 3.21  | 21.9           |                | 3.50           |                | _     | 0.092       |
| CS                    | 0   | _    | _     | 0.20  | 0.23  | 14.4  | 12.16 | 37.7           | 5.69           | 25.7           | 1.66           | 2.24  | 1.90        |
|                       | 1   | _    | _     | 0.19  | 0.23  | 14.5  | 11.87 | 37.8           | 5.64           | 25.9           | 1.64           | 2.33  | 1.90        |
|                       | 2   | -    | -     | 0.27  | 0.25  | 14.5  | 12.22 | 37.2           | 5.59           | 25.1           | 1.61           | 2.27  | 1.84        |
|                       | 3   | _    | _     | 0.62  | 0.35  | 14.6  | 11.54 | 36.4           | 5.53           | 24.9           | 1.52           | 2.10  | 1.81        |
|                       | 4   | _    | _     | 0.24  | 0.19  | 14.7  | 13.24 | 38.3           | 5.41           | 24.7           | 1.23           | 2.05  | 1.76        |
|                       | 5   | -    | _     | 0.44  | 0.31  | 15.0  | 12.12 | 39.0           | 5.42           | 24.1           | 0.94           | 1.69  | 1.67        |
|                       | 6   | -    | _     | 0.40  | 0.29  | 15.8  | 12.08 | 38.9           | 5.35           | 23.8           | 0.72           | 1.15  | 1.55        |
|                       | 7   | _    | _     | 0.88  | 0.45  | 16.4  | 11.11 | 38.4           | 5.24           | 23.1           | 0.47           | 0.98  | 1.44        |

blend compared to the control. In CS, the C18:2 had a larger change than the C18:3. The *trans* C18:1 was found to decrease in the frying systems at the end of the frying operations. This was in accordance to Smith's et al. (1986) findings in partially hydrogenated soybean oil. The C18:2/C16:0 of CS decreased with frying time. It should be noted that the C18:2/C16:0 ratio calculated here included both the *cis* and *trans* forms of C18:2.

## 3.6. Changes in specific extinction, $E_{lcm}^{1\%}$ at 233 and 269 nm

Oxidation of polyunsaturated FA produces conjugated diene and triene which are accompanied by increased ultraviolet absorption at 232 and 269 nm, respectively (PORIM, 1995). The magnitude of changes in these absorption is not readily related to the degree of oxidation because the effects upon the various unsaturated FA vary in quality and magnitude. However, the changes in the ultraviolet spectrum of a given substance can be used as a relative measurement of oxidation (Gray, 1978). It was apparent that the specific extinction is a very sensitive means to measure the difference of lipid oxidation (Du Plessis & van Niekerk, 1981).

The changes in  $E_{\rm 1cm}^{1\%}$  at 233 and 269 nm during frying for the transesterified blend, control and CS are shown in Table 6. For all samples, both  $E_{\rm 1cm}^{1\%}$  at 233 and 269 nm increased throughout the frying days and their changes paralleled each other. The levels of conjugated diene were much higher than the conjugated triene in all

samples. This was mainly because the samples contained higher levels of linoleic acid than linolenic acid (Table 1). More conjugated dienes were formed in the transesterified blend during the frying compared to the control, as indicated in the  $E_{1\text{cm}}^{1\%}$  at 233 nm even though both blends had no significant difference (P > 0.05) in their linoleic acid levels. This may be due to the transesterified blend losing its stability against oxidation. CS showed significantly (P < 0.05) larger changes in both  $E_{\text{lcm}}^{1\%}$  at 233 and 269 nm than the rest. This is mostly due to CS consisting of higher levels of linoleate or other polyunsaturated FA compared to the transesterified and control blends. It was noted that, for all samples, the rate of increment decreased after day 3. This might be due to the conjugated dienes being transformed into polymer compounds.

## 3.7. Changes in polymer compounds and viscosity

Table 7 shows the changes in polymer compounds and viscosity in different frying systems for seven consecutive days. For all shortenings, the polymer content increased slowly, followed by a more marked increment after the fifth day. The same changing trend of polymer compounds was observed in the previous study (Che Man & Tan, 1999). The formation of polymer compounds is generally believed to require the presence of conjugated dienes (Augustin, Asap & Heng, 1987; White, 1991). It has been reported that there is a nonlinear relationship

Table 6 Changes in specific extinction,  $E_{1 \text{ cm}}^{1\%}$  at 233 and 269 nm during frying in the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Specific extinction                | Day | Control                   | Transesterified blend | CS                         |
|------------------------------------|-----|---------------------------|-----------------------|----------------------------|
| $E_{1 \text{ cm}}^{1\%}$ at 233 nm | 0   | 1.58±0.09aA               | 1.61±0.01aA           | 6.18±0.29bA                |
|                                    | 1   | $1.72 \pm 0.06$ bA        | $2.32 \pm 0.02 aB$    | $9.76 \pm 0.18$ cB         |
|                                    | 2   | $2.28 \pm 0.05$ bB        | $3.21 \pm 0.03 aC$    | $10.79 \pm 0.30$ cBC       |
|                                    | 3   | $3.35 \pm 0.02 aC$        | $4.02 \pm 0.01 aD$    | $11.80 \pm 0.71$ bC        |
|                                    | 4   | $4.11 \pm 0.05 aD$        | $4.71 \pm 0.01aE$     | $13.81 \pm 0.01$ bD        |
|                                    | 5   | $4.46 \pm 0.02$ bE        | $5.45 \pm 0.07 aF$    | $14.35 \pm 0.32$ cD        |
|                                    | 6   | $5.26 \pm 0.01 aF$        | $5.86 \pm 0.01aG$     | $16.54 \pm 0.39$ bE        |
|                                    | 7   | $4.60 \pm 0.05$ bE        | $5.79 \pm 0.05 aG$    | $15.96 \pm 0.09$ cE        |
| $E_{1 \text{ cm}}^{1\%}$ at 269 nm | 0   | $0.19 \pm 0.05$ bA        | $0.47 \pm 0.04$ aA    | $0.83 \pm 0.05$ cA         |
|                                    | 1   | $0.45 \pm 0.02aB$         | $0.51 \pm 0.01$ aA    | $1.82 \pm 0.02$ bB         |
|                                    | 2   | $0.36 \pm 0.01aB$         | $0.59 \pm 0.01aB$     | $2.56 \pm 0.35 bC$         |
|                                    | 3   | $0.45 \pm 0.02$ bB        | $0.75 \pm 0.01aC$     | $3.02 \pm 0.01 \text{cCD}$ |
|                                    | 4   | $0.65 \pm 0.01 \text{bC}$ | $0.80 \pm 0.02 aCD$   | $3.44 \pm 0.04$ cDE        |
|                                    | 5   | $0.72 \pm 0.04 bC$        | $0.89 \pm 0.02 aE$    | $3.60 \pm 0.03$ cE         |
|                                    | 6   | $0.75 \pm 0.02 aCD$       | $0.85 \pm 0.01 aDE$   | $3.85 \pm 0.10 bEF$        |
|                                    | 7   | $0.84 \pm 0.04 aD$        | $1.01 \pm 0.01 aF$    | $4.27 \pm 0.07 bF$         |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc.) are significantly (P < 0.05) different.

Table 7
Changes in polymer content and viscosity during frying of the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristic     | Day | Control                   | Tranesterified blend | CS                  |
|--------------------|-----|---------------------------|----------------------|---------------------|
| Polymer content, % | 0   | $0.01 \pm 0.00 aA$        | $0.01 \pm 0.00$ aA   | 0.02±0.01aA         |
| •                  | 1   | $0.56 \pm 0.03$ bB        | $0.63 \pm 0.01aB$    | $0.60 \pm 0.26$ cB  |
|                    | 2   | $0.86 \pm 0.04 aC$        | $0.95 \pm 0.02 aC$   | $0.85 \pm 0.12aB$   |
|                    | 3   | $1.17 \pm 0.01 aD$        | $1.23 \pm 0.02aD$    | $1.42 \pm 0.03 bC$  |
|                    | 4   | $1.26 \pm 0.01 \text{bD}$ | $1.39 \pm 0.04 aDE$  | $1.64 \pm 0.01 cC$  |
|                    | 5   | $1.40 \pm 0.02aE$         | $1.47 \pm 0.02 aE$   | $1.98 \pm 0.09 bC$  |
|                    | 6   | $2.06 \pm 0.04 aF$        | $2.23 \pm 0.07 aF$   | $3.40 \pm 0.07 bD$  |
|                    | 7   | $3.27 \pm 0.11$ bG        | $3.73 \pm 0.13aG$    | $5.45 \pm 0.03$ cE  |
| Viscosity, cP      | 0   | $2.25 \pm 0.05$ aA        | $2.35 \pm 0.15$ aA   | $2.40 \pm 0.10$ aA  |
|                    | 1   | $2.30 \pm 0.10$ aA        | $2.45 \pm 0.05 aAB$  | $2.65 \pm 0.15 aAB$ |
|                    | 2   | $2.85 \pm 0.15 aA$        | $2.95 \pm 0.15$ aBC  | $3.15 \pm 0.05 aB$  |
|                    | 3   | $2.95 \pm 0.45 aAB$       | $3.10 \pm 0.30 aC$   | $3.95 \pm 0.15 aC$  |
|                    | 4   | $3.10 \pm 0.30 aAB$       | $3.25 \pm 0.25 aC$   | $4.10 \pm 0.30 aC$  |
|                    | 5   | $3.80 \pm 0.30 aBC$       | $3.95 \pm 0.25 aD$   | $4.50 \pm 0.30 aCD$ |
|                    | 6   | $4.10 \pm 0.30 aC$        | $4.25 \pm 0.20 aD$   | $5.85 \pm 0.15$ bE  |
|                    | 7   | $5.45 \pm 0.25 aD$        | $5.95 \pm 0.05 aE$   | $7.20 \pm 0.20 bF$  |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc.) are significantly (P < 0.05) different.

between  $E_{1\text{cm}}^{1\%}$  at 233 nm and polymer content in frying systems (Augustin, Asap & Heng, 1987). At the initial frying stage, only small amounts of conjugated dienes were formed and this caused a negligible increase in the polymer compounds. As the frying operations continued, more and more conjugated dienes were formed and finally the equilibrium rate of transforming the conjugated dienes into polymer compounds was achieved (Peled et al., 1975). This caused a drastic increment in the polymer compounds.

The reduction in  $E_{1\text{cm}}^{1\%}$  at 233 nm (Table 6) gave rise to the increase of polymer compounds in the samples. The greatest change in absorbance at 233 nm in CS may be

related to the highest rate of polymer formation and yielded the highest level of polymer compounds at the end of frying among the shortenings. The transesterified blend had significantly (P < 0.05) higher polymer levels at the end of frying operation than the control because it contained more conjugated dienes which readily turned into polymers.

The viscosity of all the shortenings increased over the frying days. The higher the viscosity of a heated oil, the larger the degree of deterioration. The changes in viscosity agreed well with the polymer compounds. The correlation coefficients, r values for the transesterified blend, control and CS, were 0.9786, 0.9764 and 0.9895

(P < 0.05), respectively. The increase in the viscosity was due to the polymerisation, which resulted in formation of higher molecular weight compounds, such as carbon-carbon and/or carbon-oxygen-carbon bridges between the unsaturated FA (Gray, 1978). CS, which contained the highest level of linoleic and linolenic acids, had the highest viscosity.

## 3.8. Changes in colours

Table 8 shows the changes in colours, red and yellow units of the transesterified blend, control and CS over the frying days. Fresh CS made of soybean oil had significantly (P < 0.05) lower red and yellow units than the transesterified and control blends. For all samples, the red and yellow units increased significantly (P < 0.05) at the end of frying operations. The colour of the shortenings increased, probably for two reasons. First, the browning pigments from the bananas dissolved in the shortenings and second, oxidative deterioration occurred in the shortenings (Augustin et al., 1988; Fritsch, 1981). Formation of more polymeric or higher molecular weight compounds in the CS, throughout the frying days, resulted in the biggest changes in both red and yellow units (0.6 red unit and 2.5 yellow unit) compared to the transesterified and control blends. This could be explained by the good correlation between the red and yellow units of CS with the viscosity (the r values of red and yellow units with the viscosity were 0.9372 and 0.8622, respectively, P < 0.05). It should be noted, also, that CS contained phenolic antioxidants such as TBHQ. The oxidation of phenolic antioxidants in the presence of heat and metals results in the formation of quinonoid compounds (Augustin, Lee & Yau, 1987) which might lead to additional colour formation in CS. However, there was no significant difference (P > 0.05) in colour changes between the transesterified and its control, even though their viscosities were significantly different after the frying period. Therefore, evaluation of lipid oxidation, based on colour changes alone, might give an inaccurate result. It was also noted that, although the colour of the frying systems varied, the banana chips had a similar colour in all systems. This was in accordance with previous findings (Augustin, Lee & Yau, 1987).

#### 3.9. Evaluations on the banana chips

Table 9 shows the sensory evaluation of the fresh banana chips fried on the first day. The results show that there was no significant difference (P > 0.05) in terms of colour, appearance, and crispiness of the banana chips fried in different systems. The colour of the banana chips is more dependent on the sugar content of the banana while the appearance (oiliness) and crispiness are more related to the textural characteristics of the banana (Jackson, Bourne & Barnard, 1996) rather than types of frying oil. However, there were significant differences (P < 0.05) among the banana chips in terms of flavour and aftertaste, which affected the overall acceptability of the banana chips. Banana chips fried in CS were found to have a lower score in the flavour, aftertaste and overall acceptability, than the transesterified and control blends. This might be due to the hydrogenated CS imparting a typical hydrogenation flavour to the chips that affected the acceptance by the panellists (Warner et al., 1994). There were no significant differences (P > 0.05) in any organoleptic quality tested in the transesterified and control blends.

Table 8
Changes in colours (red and yellow units) during frying in the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Colour      | Day | Control                    | Transesterified blend | CS                        |
|-------------|-----|----------------------------|-----------------------|---------------------------|
| Red unit    | 0   | $0.35 \pm 0.05$ aA         | 0.30±0.00aA           | 0.10±0.00bA               |
|             | 1   | $0.40 \pm 0.00 aAB$        | $0.35 \pm 0.05 aAB$   | $0.15 \pm 0.05 \text{bA}$ |
|             | 2   | $0.40 \pm 0.00 aAB$        | $0.40 \pm 0.00 aABC$  | $0.30 \pm 0.00 aB$        |
|             | 3   | $0.46 \pm 0.05 aABC$       | $0.45 \pm 0.05 aCD$   | $0.40 \pm 0.00 aBC$       |
|             | 4   | $0.50 \pm 0.00 aBC$        | $0.50 \pm 0.00 a CDE$ | $0.45 \pm 0.05 aCD$       |
|             | 5   | $0.55 \pm 0.05 aCD$        | $0.55 \pm 0.05 aDEF$  | $0.50 \pm 0.00 aCD$       |
|             | 6   | $0.65 \pm 0.05 aD$         | $0.60 \pm 0.00 aEF$   | $0.55 \pm 0.05 aDE$       |
|             | 7   | $0.65 \pm 0.05 aD$         | $0.65 \pm 0.05 aF$    | $0.65 \pm 0.05 aE$        |
| Yellow unit | 0   | $1.35 \pm 0.05 aA$         | $1.40 \pm 0.00$ aA    | $0.70 \pm 0.00 \text{bA}$ |
|             | 1   | $1.45 \pm 0.05 aAB$        | $1.45 \pm 0.05 aAB$   | $1.25 \pm 0.05 aB$        |
|             | 2   | $1.55 \pm 0.05 aBC$        | $1.50 \pm 0.00 aABC$  | $2.05 \pm 0.05 bC$        |
|             | 3   | $1.60 \pm 0.00 aC$         | $1.55 \pm 0.05 aBCD$  | $2.35 \pm 0.05 bD$        |
|             | 4   | $1.75 \pm 0.00 \text{bD}$  | $1.60 \pm 0.00 aCDE$  | $2.65 \pm 0.05$ cE        |
|             | 5   | $1.75 \pm 0.05 aD$         | $1.65 \pm 0.05 aDE$   | $2.85 \pm 0.05 bF$        |
|             | 6   | $1.85 \pm 0.00 \text{bDE}$ | $1.70 \pm 0.00 aE$    | $3.00 \pm 0.05 cF$        |
|             | 7   | $1.90 \pm 0.00 aE$         | $1.80 \pm 0.00 aF$    | $3.15 \pm 0.05 bG$        |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc.) are significantly (P < 0.05) different.

Table 9
Sensory evaluation on the acceptability of the banana chips<sup>a</sup> fried in the control, transesterified blend and commercial sample (CS)<sup>b</sup>

| Frying medium         | Colour | Appearance (oiliness) | Flavour | Crispiness | Aftertaste | Overall acceptability |
|-----------------------|--------|-----------------------|---------|------------|------------|-----------------------|
| Transesterified blend | 6.45a  | 6.17a                 | 6.20a   | 4.95a      | 6.09a      | 5.48a                 |
| Control               | 6.23a  | 6.03a                 | 6.06a   | 5.06a      | 5.48ab     | 5.30a                 |
| CS                    | 6.13a  | 6.44a                 | 5.10b   | 5.29a      | 5.07b      | 4.18b                 |

<sup>&</sup>lt;sup>a</sup> First day fried banana chips.

Table 10 Changes in thiobarbituric acid (TBA) value and sensory evaluation of the rancid off-flavour of banana chips fried in the control, transesterified blend and commercial sample (CS)<sup>a</sup>

| Characteristics                | Day | Control                     | Transesterified blend      | CS                        |  |
|--------------------------------|-----|-----------------------------|----------------------------|---------------------------|--|
| TBA, mols malonaldehyde/kg oil | 0   | 2.45±0.05aA                 | 3.10±0.10aA                | 4.03±0.55aA               |  |
|                                | 2   | $2.60 \pm 0.10 \text{bAB}$  | $3.57 \pm 0.32 abAB$       | $4.53 \pm 0.07 aA$        |  |
|                                | 4   | $2.83 \pm 0.02 \text{bABC}$ | $3.50 \pm 0.10 \text{aAB}$ | $4.73 \pm 0.08$ cA        |  |
|                                | 6   | $2.89 \pm 0.09 \text{bABC}$ | $4.15 \pm 0.20 aB$         | $6.35 \pm 0.35$ cB        |  |
|                                | 8   | $2.98 \pm 0.02$ bBC         | $5.38 \pm 0.08 aC$         | $6.45 \pm 0.30 \text{cB}$ |  |
|                                | 10  | $3.25 \pm 0.15 bCD$         | $6.30 \pm 0.40 aCD$        | $9.05 \pm 0.15$ cC        |  |
|                                | 12  | $3.62 \pm 0.08 \text{bD}$   | $6.45 \pm 0.30 aD$         | $12.15 \pm 0.15$ cD       |  |
|                                | 14  | $4.60 \pm 0.15$ bE          | $9.15 \pm 0.45 aE$         | 15.15±0.45cE              |  |
| Sensory evaluation score       | 0   | 8.47aA                      | 8.46aA                     | 8.77aA                    |  |
|                                | 2   | 8.26aAB                     | 7.89aAB                    | 8.53aAB                   |  |
|                                | 4   | 7.91bAB                     | 7.31aBC                    | 7.74abB                   |  |
|                                | 6   | 7.48aB                      | 7.40aBC                    | 6.52bC                    |  |
|                                | 8   | 6.48abC                     | 6.61aCD                    | 5.59bCD                   |  |
|                                | 10  | 6.44aC                      | 6.16abDE                   | 5.46bD                    |  |
|                                | 12  | 6.23aC                      | 5.59aEF                    | 4.33bE                    |  |
|                                | 14  | 5.29aD                      | 5.18aF                     | 4.30bE                    |  |

<sup>&</sup>lt;sup>a</sup> Each value in the table represents the mean  $\pm$  standard deviation of four analyses from two replications. Means within each row with different letters (a, b or c) are significantly (P < 0.05) different. Means within each column with different letters (A, B, C etc.) are significantly (P < 0.05) different.

Table 10 shows the changes in TBA value of the banana chips fried in different shortenings, and the sensory evaluation results of the banana chips in terms of rancid off-flavour developed during storage. For all samples, the TBA value increased significantly (P < 0.05) after 4 days of storage at 60°C. Generally, in all samples, oxidatively deteriorated products, which gave rise to high TBA values, also caused reduction in the sensory evaluation score. Judging from the TBA results, the banana chips fried in the control blend had a significantly (P < 0.05) better oxidative stability than in the transesterified blend. However, the sensory panel could not differentiate the intensity of rancid off-flavour between the two, as indicated by the statistical analyses which were not significantly different (P > 0.05). The lack of correlation between the TBA value and sensory evaluation score has been noted in other studies (Che Man & Tan, 1999; Krevchenia & Fennema, 1988). The banana chips fried in CS, which contained the highest level of polyunsaturated FA, were more susceptible to oxidation during storage, had the biggest change in TBA value and were most rancid.

This study, shows that the transesterified PS/PKO blend was significantly more susceptible to lipid oxidation during frying than the control blend. However, since the transesterified blend has some nutritional advantages over the hydrogenated ones, it is still a viable process. The antioxidant activity of the transesterified blends can be improved by adding some optimum concentration of antioxidants to the blends after the transesterification process. It might be difficult to compare the oxidative stability of CS with the transesterified and control blends since they did not contain similar FA profiles. Nevertheless, the results from CS provided a reference for comparing the oxidative deterioration in the blends.

#### Acknowledgements

The authors would like to thank the Malaysian government for awarding the IRPA fund to Prof. Dr. Hasanah M. Ghazali that made this study possible.

<sup>&</sup>lt;sup>b</sup> Values within each column with different letters (a, b or c) are significantly (P < 0.05) different.

#### References

- Aitzetmuller, K. (1996). Oxidative stability of interesterified blends. Journal of the American Oil Chemist's Society, 73, 539.
- AOCS. (1989). In: D. Firestone, Official methods and recommended practices of the American Oil Chemist's Society. (4th ed.). Champaign: American Oil Chemist's Society Press.
- Applewhite, T. H. (1981). Nutritional effects of hydrogenated soya oil. Journal of the American Oil Chemist's Society, 58, 260–269.
- Augustin, M. A., Asap, T., & Heng, L. K. (1987). Relationships between measurements of fat deterioration during heating and frying in RBD olein. *Journal of the American Oil Chemist's Society*, 64, 1670–1675.
- Augustin, M. A., Heng, L. K., & Idris, N. A. (1988). Evaluation of potato crisps fried in market samples of palm olein, corn oil and soya oil. *Pertanika*, 11, 399–406.
- Augustin, M. A., Lee, K. H., & Yau, K. T. (1987). Comparison of the frying performance of market samples of palm olein, corn oil and soya oil in Malaysia. *Pertanika*, 10, 265–303.
- Billek, G., Guhr, G., & Waibel, J. (1978). Quality assessment of used frying fats. *Journal of the American Oil Chemist's Society*, 55, 726–733.
- Blumenthal, M. M. (1996). Frying technology. In Y. H. Hui, *Bailey's industrial oil and fat products* (Vol. 3, 5th ed., pp. 429–482). USA: John Wiley.
- Che Man, Y. B., & Tan, C. P. (1999). Effects of natural and synthetic antioxidants on changes in refined, bleached, and deodorised palm olein during deep-fat frying of potato chips. *Journal of the American Oil Chemist's Society*, 76, 331–339.
- Chong, C. L. (1994). Chemical and physical properties of palm oil and palm kernel oil. In Technical Committee of 1994 Palm Oil Familiarisation Program, Selected readings on palm oil and its uses (pp. 60–77). Kuala Lumpur, Malaysia: PORIM, Ministry of Primary Industry.
- Crosby, T. G. (1993). Pourable shortening containing lauric fat and method for preparing same. US Patent 5 268 191.
- Cuesta, C., Sanchez-Muniz, F. J., & Hernandez, I. (1991). Evaluation of nonpolar methyl esters by column and gas chromatography for the assessment of used frying olive oils. *Journal of the American Oil Chemist's Society*, 68, 443.
- Du Plessis, L. M., & van Niekerk, P. J. (1981). Evaluation of peanut and cottonseed oils for deep frying. *Journal of the American Oil Chemist's Society*, 58, 575–578.
- Fritsch, C. W. (1981). Measurements of frying fat deterioration: a brief review. *Journal of the American Oil Chemist's Society*, 58, 241–272.
- Ghazali, H. M., Maisarah, A., Yusof, S., & Yusoff, M. S. A. M. (1995). Triglycerides profiles and melting properties of lipase-catalysed transesterified palm stearin and coconut oil. *Asia Pac. J. of Mol. Bio. and Biotechnol.*, 3, 280–289.
- Gray, J. I. (1978). Measurement of lipid oxidation: a review. Journal of the American Oil Chemist's Society, 55, 539–546.
- Idris, N. A., Abdullah, A., & Halim, A. H. (1992). Evaluation of palm oil quality: correlating sensory with chemical analyses. *Journal of the American Oil Chemist's Society*, 69, 272–275.
- Jackson, J. C., Bourne, M. C., & Barnard, J. (1996). Optimisation of blanching for crispiness of banana chips using response surface methodology. *Journal of Food Science*, 61, 165–166.
- Ke, P. J., Cervantes, E., & Robles-Martinez, C. (1984). Determination of thiobarbituric acid reactive substances (TBARS) in fish tissue by an improved distillation-spectrophotometric method. *Journal of the Science of Food and Agriculture*, 35, 1248–1254.
- Krevchenia, M., & Fennema, O. R. (1988). Effects of cryoprotectants on frozen burbot fillets and a comparison with whitefish fillets. *Journal of Food Science*, *53*, 1104–1108.
- Lai, O. M., Ghazali, H. M., & Chong, C. L. (1998a). Effect of enzymatic transesterification on the melting points of palm stearin-sunflower oil mixtures. *Journal of the American Oil Chemist's Society*, 75, 881–885.
- Lai, O. M., Ghazali, H. M., & Chong, C. L. (1998b). Physical properties of *Pseudomonas* and *Rhizomucor miehei* lipase-catalysed

- transesterified blends of palm stearin:palm kernel olein. *Journal of the American Oil Chemist's Society*, 75, 953–959.
- Martin, J. C., Lavillonniere, F., Nour, M., & Sebedio, J. L. (1998).
  Effect of fatty acid positional distribution and triacylglycerol composition on lipid by-products formation during heat treatment III: cyclic fatty acid monomer study. *Journal of the American Oil Chemist's Society*, 75, 1691–1697.
- Melton, S. L., Jafar, S., Sykes, D., & Trigiano, M. K. (1994). Review of stability measurements for frying oils and fried food flavour. *Journal of the American Oil Chemist's Society*, 71, 1301–1308.
- Neff, W. E., & List, G. R. (1999). Oxidative stability of natural and randomised high-palmitic and high-stearic-acids oils from genetically modified soybean varieties. *Journal of the American Oil Chemist's Society*, 76, 825–831.
- Orthoefer, F. T., Gurkin, S., & Liu, K. (1996). Dynamics of frying. In E. G. Perkin, & M. D. Erickson, *Deep frying* (pp. 223–244). Champaign, Illinois: AOCS Press.
- Pearson, A. M., Gray, J. I., Wolzak, A. M., & Horenstein, N. A. (1983). Safety implications of oxidised lipids in muscle foods. *Food Technology*, 37, 121–127.
- Peled, M., Gutfinger, T., & Letan, A. (1975). Effect of water and BHT on stability of cottonseed oil during frying. *Journal of the Science of Food and Agriculture*, 26, 1655–1666.
- Perkin, E. G. (1967). Formation of non-volatile decomposition products in heated fats and oils. *Food Technology*, 21, 125–130.
- Peryam, D. R., & Pilgrim, F. J. (1957). Hedonic scale method of measuring food preferences. Food Technology, 11, 9–11.
- PORIM. (1995). In W. L. Siew, *PORIM test methods* (pp. 72–75, 40–42, 33–36, 37–39, 64–65, 92–101). Kuala Lumpur, Malaysia: Palm Oil Research Institute of Malaysia, Ministry of Primary Industries.
- Raoux, R, Morin, O., & Mordret, F. (1996). Sensory assessment of stored french fries and crisps fried in sunflower and high oleic sunflower oils. *Grasas y Aceites*, 47, 63–74.
- Ray, S., & Bhattachryya, D. K. (1996). Comparative nutritional quality of palm stearin-liquid oil blends and hydrogenated fat (vanaspati). *Journal of the American Oil Chemist's Society*, 73, 617–622.
- Rosu, R., Uozaki, Y., Iwasaki, Y., & Yamane, T. (1997). Repeated use of immobilised lipase monoacylglyceriol production by solidphase glycerolysis of olive oil. *Journal of the American Oil Chemist's Society*, 74, 445–450.
- SAS (1989). Statistical analysis system user's guide: statistics. Cary: SAS Institute Inc.
- Stevenson, S. G., Vaisey-Genser, M., & Eakin, N. A. M. (1984).
  Quality control in the use of deep frying oils. *Journal of the American Oil Chemist's Society*, 61, 1102–1108.
- Smith, L. M., Clifford, A. J., Hamblin, C. L., & Creveling, R. K. (1986). Changes in physical and chemical properties of shortenings used for commercial deep-fat frying. *Journal of the American Oil Chemist's Society*, 63, 1017–1023.
- Tangel, F. P., Leeder, J. G., & Chang, S. S. (1977). Deep fat frying characteristics of butteroil. *Journal of Food Science*, 42, 1110–1113.
- Tyagi, V. K., & Vasishtha, A. K. (1996). Changes in the characteristics and composition of oils during deep-fat frying. *Journal of the American Oil Chemist's Society*, 73, 499–506.
- Warner, K, Orr, P., Parrott, L., & Glynn, M. (1994). Effects of frying oil composition on potato chip stability. *Journal of the American Oil Chemist's Society*, 71, 1117–1121.
- Willett, W. C., Stampfer, M. J., Manson, J. E., Colditz, G. A., Speizer, F. E., Rosner, B. A., Simpson, L. A., & Hennenkens, C. H. (1993). Intake of *trans* fatty acids and risk of coronary heart disease among women. *The Lancet*, 341, 581–585.
- White, P. J. (1991). Methods for measuring changes in deep-fat frying. Food Technology, 45, 75–80.
- Wu, P. F., & Nawar, W. W. (1983). A technique for monitoring the quality of used frying oils. *Journal of the American Oil Chemist's Society*, 63, 1363–1367.

- Zainal, Z., & Yusoff, M. S. A. (1999). Enzymatic interesterification of palm stearin and palm kernel olein. *Journal of the American Oil Chemist's Society*, 76, 1003–1008.
- Zock, P. L., & Katan, M. B. (1992). Hydrogenation alternatives: effects of *trans* fatty acids and stearic acid versus linoleic acid on serum lipids and lipoproteins in human. *Journal of Lipid Research*, *33*, 399–410.