



Oxidative stability of virgin coconut oil compared with RBD palm olein in deep-fat frying of fish crackers

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Abstract

The oxidative stability of virgin coconut oil (VCO) in deep fat frying at $185 \pm 5^\circ\text{C}$ for a total of 30 hours was evaluated and compared with that of similarly-treated RBD palm olein (RBDPO) based on changes in the peroxide value (PV), p-anisidine value (p-AV), total oxidation (TOTOX) value, total polar compound (TPC) content and color. The sample used in the frying study is a favorite Malaysian snack, fish crackers, a dried product comprising mainly of sago starch and comminuted fish. Twenty grams of the crackers were fried for 60-90 seconds in 1.5 kg of oil, 12 batches a day at an interval of 5 minutes, for five consecutive days. On each day of frying, fresh oil was added to replenish the oil used to its original volume before the next frying was carried out. Results show that there was a significant increase ($P < 0.05$) in all the parameters tested with frying time, regardless of the oil use. However, the rate of change differed between the two oils. The highest values for peroxides (meqO_2/kg) were 14.02 (initial value, 1.31) for RBDPO recorded after the third day of frying and a significantly ($P < 0.05$) lower value of 10.07 (initial value, 3.62) for VCO over the same period of time. These represented a 10.7- and 2.8-folds increase in peroxide values, respectively, for VCO and RBDPO. The highest peroxide value for VCO (12.24) was recorded after the fourth day of frying. For p-anisidine result, the value recorded at the end of the frying period was 6.27 for RBDPO and 5.87 for VCO. The rate of increase in total oxidation (TOTOX) value was faster in RBDPO (5.19 units per day) compared to VCO (3.67 units per day) during the five consecutive days of frying. The amount of total polar compounds (TPC) in VCO (15.11%) was significantly lower ($P < 0.05$) than that of RBDPO (19.3%). The color of the oils increased with frying time, and being initially near colorless, the change in red color index for VCO was far greater than for RBDPO. RBDPO did not undergo a significant red color change until the third day of frying.

Key words: Frying stability, virgin coconut oil, RBD palm olein, fish crackers.

Introduction

Coconut (CO) and its extracted oil from copra have served as important foods for thousands of years. Presently, virgin coconut oil (VCO) is gaining wide popularity in the scientific field and among the public. It is believed that VCO is more beneficial than usually obtained copra oil since the mode of extraction retains more biologically active components such as vitamin E and polyphenols ¹. The continued rise in demand for VCO can be attributed not only to its superior flavor, but also to reports of its potential health benefits. Because no chemical or high heat treatment is imposed on the oil, the beneficial minor components in the oil are retained. VCO is reported to lower the lipid levels in serum and tissues, and possesses high potential in protecting low-density lipoproteins against oxidative stress induced by physiological oxidants ¹. Apart from that, the oil is also well known for its high content of medium-chain triacylglycerols, which are used in medical and cosmetic applications. It has a maximum digestibility coefficient which means that it is more rapidly digested than other fat including butter. This is due to its high content of medium chain triacylglycerol (MCT), a mixture of triacylglycerols ranging from caproic to lauric (C_6 - C_{12}) acids ². Since MCT is smaller than long-chain triacylglycerols (LCT), it facilitates the action of pancreatic lipase and is hydrolysed faster and more completely than the latter. Therefore, it can be easily absorbed by the body ^{3,4}. MCT gained a wide acceptance in food formulation, particularly in nutritional management of individuals who are

unable to absorb ordinary dietary fats. The medium-chain triacylglycerols in coconut oil do not raise serum cholesterol or contribute to heart disease like long-chain triacylglycerols in seed oils and are able to decrease total cholesterol, triacylglycerols and phospholipids in serum and tissues as well as increase HDL cholesterol with a corresponding decrease in LDL cholesterol, maybe due to the high polyphenol content ¹.

Studies conducted to determine the effect of VCO in comparison with CO and groundnut (GO) oil on both in *vitro* and in *vivo* lipid peroxidation and the levels of antioxidant enzymes in rats showed that VCO administration increased the antioxidant enzymes and reduced the lipid peroxide content ⁵. VCO polyphenols were also found to be more capable of preventing in *vitro* lipid peroxidation than polyphenols from CO and GO. These results demonstrated that consumption of VCO extracted from fresh coconut meat, with its high content of biologically active components, is superior in antioxidant property to coconut oil extracted by dry processes.

Oxidative stability is one of the most important indicators for maintaining the quality of edible oils. To date, many studies have been conducted to evaluate the oxidative stability of various refined seed oils and hydrogenated oils ^{6,7}. In the search for suitable frying oils, many vegetable oils have been subjected to hydrogenation to increase their stability. Hydrogenation adds cost to production of oil and also causes transformation of *cis*- to *trans*-unsaturated fatty acid. This brings about undesirable

nutritional effects by generation of excessive amounts of *trans*-fats^{8,9}. There are limited studies on tropical oils, with the exception of palm olein and *Moringa* oil¹⁰. VCO, which is in the category of tropical oils, has the potential for use in deep-fat frying due to its low level of unsaturation and unique composition. Thus, the aim of this study was to evaluate the oxidative stability during deep-fat frying of virgin coconut oil and to compare it with RBD palm olein, which is widely used as a standard frying oil. The food material used in the study was fish crackers, locally known as 'keropok ikan'. It is made from comminuted fish muscle, sago starch, salt and sugar.

Material and Methods

Materials: RBD palm olein used in the frying experiment was obtained from a local retail store in Serdang area while virgin coconut oil was donated by the Halal Product Research Institute, University Putra Malaysia. The fish crackers used in frying were purchased from a local retail outlet. Chemicals and solvents used were either of analytical or HPLC grade purchased from BDH Laboratories (Poole, England) and Merck (Darmstadt, Germany).

Frying of fish crackers: The intermittent frying of fish crackers was carried out in a 2 L Philips fryer Model HD 6121 (Philips Malaysia Sdn. Bhd, Penang, Malaysia), which initially contained 1.5 kg of oil (either VCO or RBDPO). On the first day of frying, the oil was conditioned by heating to 185±5°C and held for 30 min¹¹, and the fish crackers were fried until bubbling of the oil ceased (estimated time of 60-90 s). Twelve batches of 20 g fish crackers were fried at 5 min intervals. At the end of the 12th frying, the fryer was switched off and the oil covered and allowed to cool down overnight. Used oil sample (70 g) was collected at the end of each day and kept in amber bottles at -20°C for further analyses. Each day, fresh oil was added to replenish the oil to its initial level in the fryer^{11,12}. Frying was carried out for five consecutive days.

Oil analyses: The AOCS standard methods¹³ were used to determine the peroxide value (PV) (Method Cd 8-53), while the PORIM test methods¹⁴ were used to determine the *p*-anisidine value (*p*-AV) (Method p2.4) and specific extinction, E_{1%¹cm} at 233 and 269 nm (Method p2.15).

Total polar compounds (TPC) were determined using the standardized IUPAC¹⁵ method 2.507 (mini-column method). Frozen oil samples of 10 g were warmed in an oven to about 60°C and homogenized. Sep-Pak Vac 6cc (C18-1g) cartridge filled with silica (80 µm particle size and 125 Å pore size, Waters corp. Milford, MA USA) was used as a mini-column for the separation of the polar and non-polar compounds. One gram of the sample was weighed to the nearest 0.001g into a 10 ml volumetric flask and dissolved first in about 8 ml of a mixture of light petroleum ether and diethyl ether at a ratio of 90:10 (v/v Solvent 1) and made up to the volume with the same solvent mixture. The cartridge was first conditioned by wetting it with diethyl ether followed by equilibration using light petroleum ether. Five ml of the prepared sample was introduced into the cartridge at a flow rate of approximately 2 ml/min using a dropping funnel. Non-polar compounds were eluted with 60 ml of Solvent 1 into a previously weighed 250 ml round bottom flask to obtain Fraction 1. Substances adhering to the outlet of the cartridge were also washed with the same solvent mixture into the flask. The polar fraction was removed from the

cartridge by eluting with 50 ml of diethyl ether (Solvent 2) to obtain Fraction 2 in a separate, previously weighed flask. The solvents were evaporated from both flasks under vacuum in a rotary evaporator at 60°C. The flasks were then dried under vacuum for 1 h and weighed. Fractions 1 and 2 represented the non-polar (unaltered triacylglycerols) and the polar components (altered triacylglycerols due to frying and natural accompanying polar compounds), respectively.

Mass fraction of polar compounds or total polar compounds (TPC) is given by $TPC (\%) = (W_p/W_s) \times 100$, where W_p is the weight in grams of the polar fraction 2 and W_s is the weight in grams of the test portion added to the column¹⁵.

Color was determined using the method described in PORIM test methods¹⁴. Frozen oil samples were melted by placing them at 60°C in an oven until completely melted. The liquid samples were then placed in a 1-inch cell and the color was determined at 30°C by achieving the best possible match with the standard color slides of red and yellow indices using a Lovibond tintometer Model E (Salisbury, England).

All values presented are means of triplicate determination with standard deviations. Statistical analyses were carried out using Student's *t*-test, using SPSS Version II software and ANOVA using SAS¹⁶ system Version 8e. Significant differences between values at $P < 0.05$ levels were separated using Duncan's multiple range test.

Results and Discussion

Initial quality of fresh oils: The characteristics of fresh refined, bleached, deodorized palm olein (RBDPO) and virgin coconut oil (VCO) are shown in Table 1. RBDPO has peroxide value, *p*-anisidine value and total polar compounds when compared with the VCO. The higher values in VCO may be because it had not been subjected to any refining process. The RBDPO was higher in red and yellow units which may be attributed to its β-carotene content¹⁷. The Lovibond red unit for RBDPO should not exceed 1.2±0.6¹⁸. The near-zero red and yellow units for VCO indicates its visually colorless state. The total polar compounds of both oils fell within the range proposed by Moreira *et al.*¹⁹ indicating they have not gone through extensive oxidation during storage and are suitable for use in the frying experiment.

Quality changes in oil during frying

Peroxide value (PV): PV is a measure of the amount of peroxides formed in fats and oils through autoxidation and oxidation processes²⁰. Generally, it is a measure of the degree of initial oxidation of fats and oils. Changes in the peroxide values of RBDPO and VCO during frying are shown in Fig. 1. There was a marked increase in the PV for RBDPO on the first day of frying and these continued to rise until the third day of frying, after which it fell slightly in the last two days of frying. The PV for VCO increased until the fourth day and decreased slightly on the fifth day. The

Table 1. Initial quality of fresh RBD palm olein and virgin coconut oil.

Characteristic	RBD palm olein	Virgin coconut oil
PV (meqO ₂ /kg)	1.31 ± 0.06	3.62 ± 0.10
<i>p</i> -AV	0.24 ± 0.01	0.48 ± 0.02
TOTOX (2PV + <i>p</i> -AV)	2.86 ± 0.13	7.72 ± 0.15
TPC (%)	2.05 ± 0.08	2.29 ± 0.11
Lovibond Color	0.8R + 5.0Y	0.1R + 0.2Y

rate of formation and breakdown of peroxides was significantly ($P < 0.05$) higher in RBDPO. This is shown by its slope during the first three days of frying, with a rate of $2.85 \text{ meqO}_2/\text{kg}/\text{day}$ compared to $1.45 \text{ meqO}_2/\text{kg}/\text{day}$ for VCO. This indicates VCO to be slightly more resistant to oxidation which may be attributed to its lower level of unsaturated fatty acids.

The results also indicate that time of frying had a significant ($P < 0.05$) effect on the PV of all samples which increased with frying time up to a certain peak value after which it began to decrease¹⁰. The maximum level for peroxide value for RBDPO was reached on the third day of frying ($14.02 \text{ meqO}_2/\text{kg}$) whereas for VCO it was recorded on the fourth day of frying ($12.24 \text{ meqO}_2/\text{kg}$).

***p*-Anisidine value (*p*-AV):** Compared to PV, the *p*-AV method is a more reliable and meaningful test because it measures the secondary oxidation products, which are more stable during the heating process²¹. The *p*-anisidine reagent reacts with the non-volatile portion of fatty acids left behind when hydroperoxides break down to aldehydes. This test has an enhanced sensitivity for unsaturated aldehydes, especially 2,4-dienals, but does not measure the ketonic secondary products of oxidation.

Changes in the *p*-AV during the 5 consecutive frying days are shown in Fig. 2. The *p*-AV method determines the amount of α and β -alkenals content and all those compounds able to react with *p*-anisidine reagent produced in the oil as a result of oxidation¹⁴.

During frying, the *p*-AV for RBDPO and VCO increased significantly ($P < 0.05$) with the frying time. RBDPO was more susceptible to oxidation than the VCO, as indicated by their higher *p*-AV. The highest value recorded at the end of the frying period were 6.27 for RBDPO and 5.87 for VCO. The difference in *p*-AV between the two oils was not statistically significant ($P < 0.05$). This may be due to the small amounts of linoleic acid present in the oils. Chu *et al.*²² found that high amounts of linoleic acid can cause a bigger change in *p*-AV throughout the frying period. The rate of increase in the *p*-AV was faster in RBDPO. This is also noticeable during the first three days of frying, which is $1.31/\text{day}$ and $0.77/\text{day}$, respectively.

Good frying oil should have *p*-AV of less than ten⁹. In this case the values of 6.27 for RBDPO and 5.87 for VCO are still within acceptable limits even after the frying period. Thus, it can be concluded that the oils have not undergone extensive degradation, despite being used in frying for five days.

Total oxidation value (TOTOX): $\text{TOTOX} = 2\text{PV} + p\text{-AV}$ ²³. The total oxidation values (TOTOX) of RBDPO and VCO are shown in Fig. 3. The values increased significantly ($P < 0.05$) with frying time in both oils. TOTOX value is the representative index of oxidative deterioration, since it takes into account both the peroxides and aldehydes²⁴.

Hydroperoxides are unstable especially at high temperatures encountered in deep-fat frying; therefore, they decompose to give secondary oxidation products that are *p*-anisidine-reactive. An increase by one PV unit corresponds to an increase of about two *p*-AV units. Patterson²⁵ has rationalized this by pointing out that peroxides have two oxygen molecules whilst aldehydes have only one. The TOTOX value increased faster in RBDPO than VCO during the five consecutive days of frying, with a rate of 5.19 units per day compared to VCO, at 3.67 units per day. The results

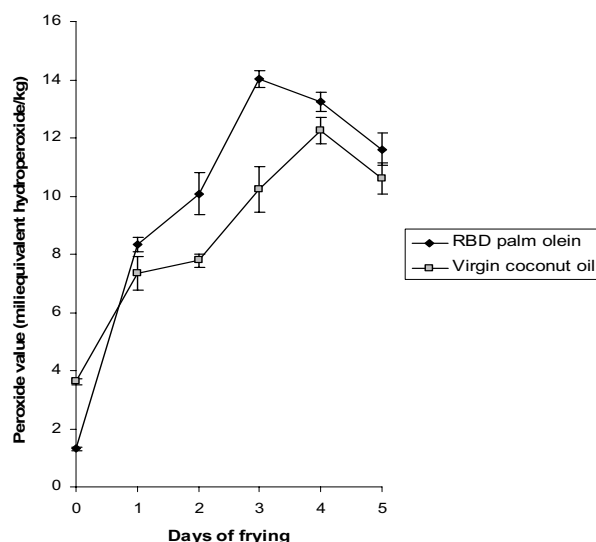


Figure 1. Changes in peroxide value during frying of fish crackers.

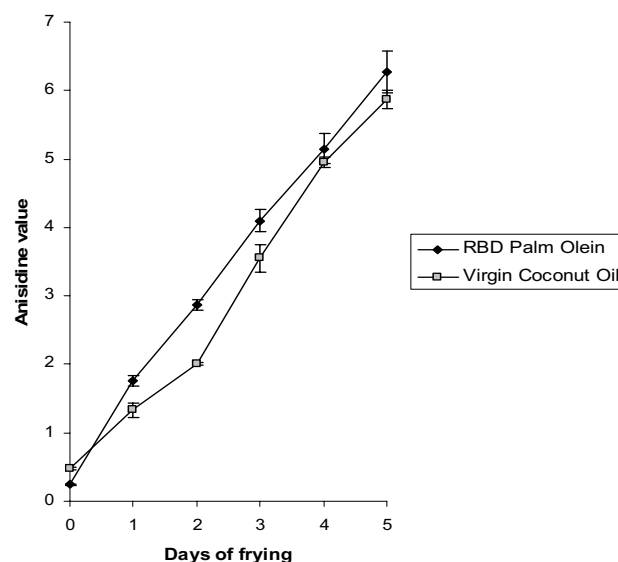


Figure 2. Changes in *p*-anisidine value during frying of fish crackers.

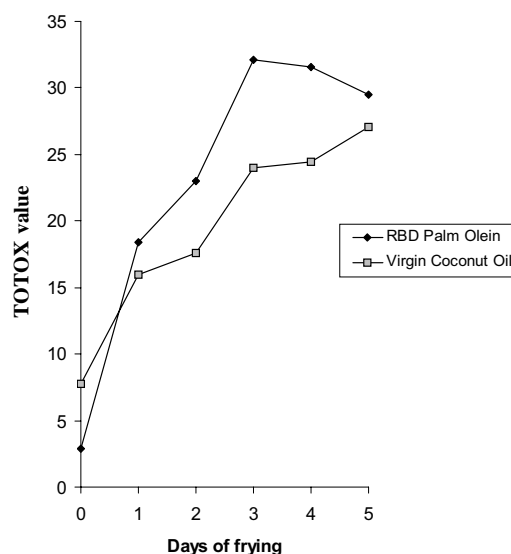


Figure 3. Changes in TOTOX value during frying of fish crackers.

indicated that VCO possesses a greater oxidative stability against deterioration during frying compared to RBDPO. This is because auto-oxidation occurs via self-propagating free radical mechanism between unsaturated fatty acids with O_2 , and RBDPO has a higher degree of unsaturation (53%)²⁶ compared to VCO which has only 10% unsaturated fatty acids. Higher rate of oxidation in frying oil is associated with the presence of easily oxidizable unsaturated fatty acids such as linoleic and linolenic acids^{19,24}. Therefore, the lower the amount of unsaturated fatty acids in the triacylglycerol composition of an oil, the more resistant it is to oxidation. *p*-AV is often used in the industry in conjunction with PV to calculate this so-called total oxidation or TOTOX.

Total polar compounds (TPC): Changes in the total polar compounds (TPC) in both oils during five days of frying are shown in Fig. 4. The polar materials in frying oil contain compounds that linearly relate to the quality of the oil usage over time^{27,28}, TPC appears as the most reliable indicator of fat and oil deterioration. Accumulation of polar compounds is indicative of both hydrolysis and oxidation and the amount of polar materials increased steadily with time of frying^{20,29,30}.

The TPC in all samples increased significantly ($p < 0.05$) over the five consecutive frying days, and the correlation between frying time and TPC is significantly ($p < 0.05$) high ($r = 0.989$). The amounts of TPC after the frying period in RBDPO and VCO were 19.3 and 15.11%, respectively, with the rate of polar compounds formation faster in RBDPO. The lower TPC in virgin coconut oil once again revealed that it was more stable against oxidation than RBDPO. Bogim *et al.*³¹ have also shown that polar compounds in frying oil increased significantly with prolonged heating time. Warner and Gupta³² reported increases in polar compound levels in low- and ultra-low-linolenic soybean oil and cottonseed oil samples (4.0, 4.1 and 12.1%), respectively, after 5 h, and after 25 h frying the levels were increased to 8.5 and 9% for the soybean oil samples and 17% for cottonseed oil.

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 situations³³. Handel and Gurrieri³⁴ found that the rate of increase in TPC correlated to the degree of

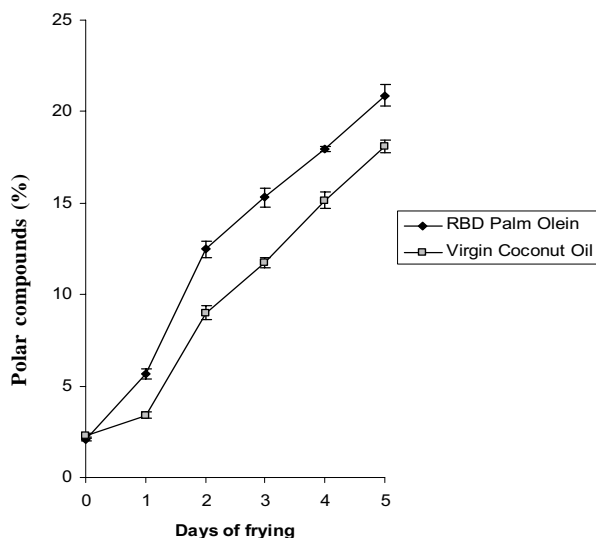


Figure 4. Changes in total polar compounds in oil during frying of fish crackers.

unsaturation since polar compounds were indication of oxidative decomposition. As oxidation occurs mainly at the reactive double bonds of unsaturated fatty acids in the triacylglycerol structure, therefore, the extent of alteration in the triacylglycerol structure of VCO is lower.

The limit of the beginning of frying fat abuse is about 24% TPC, whereas the absolute limit is 27% polar materials, beyond which the frying oil should be discarded³⁵. In both RBDPO and VCO, the values did not reach this limit even after five days of frying, indicating the oils were relatively stable against oxidation.

Changes in color: Changes in red and yellow units of RBDPO and VCO before and after frying with the fish crackers are shown in Figs 5 and 6, respectively. The initial red and yellow values for RBDPO and VCO were $0.8R + 5.0Y$ and $0.1R + 0.2Y$, respectively. For both oils, the yellow units increased significantly with time during the frying operations, while the red units did not significantly increase in RBDPO (Fig. 5). The correlation between color readings and frying time were found to be significantly ($p < 0.05$) high (r values for RBDPO and VCO for yellow unit were 0.917 and 0.986, respectively, and for red units 0.878 and 0.966, respectively) and is consistent with the findings of Abdulkarim *et al.*¹⁰ who reported an increase in the color of RBDPO, soybean, canola and *Moringa oleifera* oils with frying time during the frying

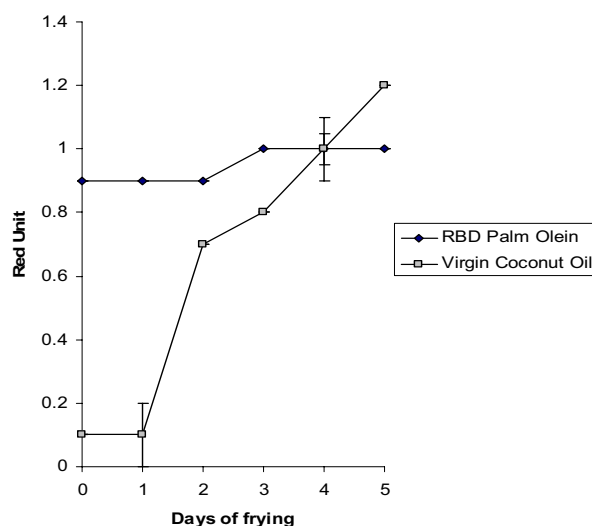


Figure 5. Changes in oil color (red unit) during frying of fish crackers.

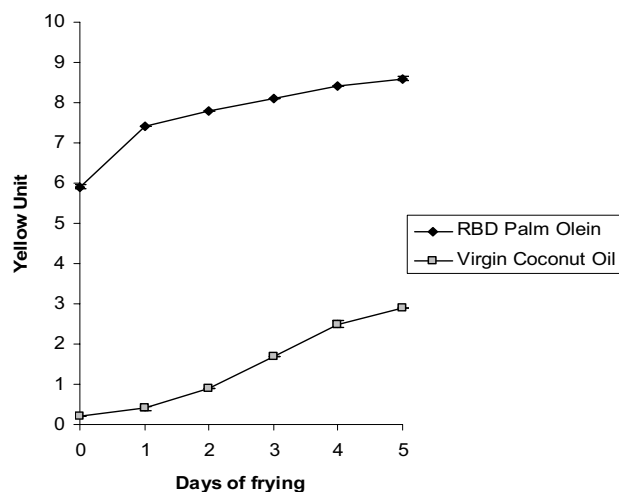


Figure 6. Changes in oil color (yellow unit) during frying of fish crackers.

of potato chips. Being colorless, the large increase in the formation of colored compounds in VCO is, therefore, more obvious compared to RBDPO. The color of the oils increased, probably for two reasons: oxidative deterioration that occurred in the frying oils and color contributed by the food being fried (fish cracker). Contribution from the food being fried toward the redness of VCO was such that at the end of the frying study, the color was greater than that of RBDPO (Fig. 5). The development of yellow color of the two oils may be due to reasons other than oxidation. Food can introduce various components to the oil, such as carbohydrates, proteins, sulfur compounds and trace metals. These compounds react with the oil and its breakdown products resulting in color formation³⁶.

Conclusions

Virgin coconut oil is very stable against oxidative deterioration. Its frying stability is certainly greater than that of RBD palm olein, when fish cracker was used as the food sample. The relative high frying stability will make it attractive to the frying industry especially when targeting foods meant for management of individuals who are unable to absorb ordinary dietary fats due to the high MCT content of virgin coconut.

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