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Stability of blended palm oils during potato frying

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Abstract

The aim of this study was to determine hydrolytic stability [acid value (AV)] and oxidative stability [peroxide value (PV) and conjugated dienes (CD)] of selected blended oils during potato frying. The blended oils were prepared by blending palm oil with corn oil (POCO), sesame oil (POSO) and rice bran oil (PORBO). Blended vegetable oils were prepared in a ratio of 1 to 1 (v/v) and tested for 0, 10 and 20 times after frying potato. AV and PV were determined by titration method, while CD was determined using the spectrophotometric method. Increasing frequency of oil frying contributed to increased level of AV in all blended oils. PVs were increased in all samples, with most noticeable increment observed in POSO, followed by PORBO and POCO. CD levels of the blended oils were also increased after 20 times of potato frying compared with the unused oil and after 10 times of frying. POCO was the most stable oil in terms of hydrolytic and oxidative stabilities. It is most suitable for deep-fat frying of potato chips and industrial application.

Introduction

Fat is one of the essential nutrients in both human and animal diets. Nutritionally, fat is a concentrated source of energy, where 1 g of fat gives 9 kcal. Fat is composed of one unit of glycerol and three units of fatty acids, and it embraces a broad variety of chemical substances. It also includes mono- and diglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols and other substances. Fats are carriers for vitamins A, D, E and K, and it provides essential fatty acids for human growth and regulation of body system. Fats also enhance sensory quality of foods we eat by providing a smooth texture and imparting flavour, thus contribute to satiety.

Malaysian Dietary Guidelines recommend a desirable fat intake ranging between 20% and 30% of energy (NCCFM, 2005). Intake of a high percentage of saturated fatty acid (SFA) is however not recommended. Similarly, high intake of polyunsaturated fatty acid (PUFA) may also increase susceptibility of fat to oxidation (Hu *et al*., 1997). In Malaysia, vegetable oils are the main source of dietary fat, contributing to as much as 18% of total calories from fat intake among Malaysian (NCCFN, 2005). Palm oil (PO) is the major fat used in Malaysian diet. Nowadays, PO is one of the popular and increasingly used food ingredients and by the food industries worldwide. Food processing industries have higher preference for PO due to the level of saturated fat that offers stability and higher resistant to oxidation when heating at high temperature. Most of the vegetable oils contain a high level of PUFA which are more vulnerable to oxidative changes. The oxidative changes of PUFA produce various oxidation products including trans fatty acid (TFA). TFA possess undesirable metabolic side effects such as alteration of cellular metabolism and cell function (O'Holohan, 1997).

Although PO is the best oil with wide versatility and stability in various food applications, blended oil may produce a better oxidative stability and has lower level of saturated fat than PO. Recently, we reported the fatty acid balance and vitamin E content of three blended vegetable oils, namely POCO, POSO and PORBO prepared by mixing 50:50 (w/w) PO with corn oil (CO), sesame oil (SO) and rice bran oil (RBO), respectively (Azrina *et al*., 2009). Previous studies also reported the importance of blended vegetable oils for improving blood lipid

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levels of individuals (Sundram *et al.*, 1996; St-Onge *et al.*, 2003). Therefore, in this study, we aimed to evaluate stability of three blended oils (POCO, POSO, PORBO) following potato frying of up to 20 times. Determination of quality index and stability of blended oils are important since most Malaysians consumed fried food products daily and overuse of oil in cooking.

Materials and Methods

Chemicals and reagents

Ethanol (analytical grade) and chloroform (analytical grade) were purchased from HmbG Chemicals (Hamburg, Germany) and Fisher Scientific (Selangor, Malaysia), respectively. Phenolphthalein, potassium iodide and sodium thiosulfate were obtained from VWR Chemicals (England, UK), and fatty acid methyl ester (FAME) standard was purchased from AccuStandard (CT, USA). All the other chemicals and solvents of analytical grade were supplied by Merck (Selangor, Malaysia).

Materials

White potatoes were purchased from wet market in Sri Kembangan, Selangor, Malaysia. Oil samples of low saturated fat (CO, SO and RBO) and PO were purchased from a local supermarket in Malaysia. All oil samples were commercially packed in 1.5 L plastic bottle.

Sample preparation

The steps for preparation of blended oil mixtures were based on our preliminary study as described by Azrina *et al.* (2009). Potato frying method was adapted from a previous study (Lalas *et al.*, 2006) with some modifications. The potatoes were peeled and washed before used, sliced into discs of 0.5 cm thickness and 2.5 cm in diameter, using a mechanical slicer. A tray of 100 g potatoes was deep fried using each type of the blended oils (50 g) in a deep-fryer (Elba, Malaysia). Potato frying was carried out when the oil temperature reaching 175°C and oil temperature was maintained at 175 ± 5°C. After each time of deep-fat frying, the oil was removed from the fryer and stored at 4°C. Additional oil was not added during the frying process.

Determination of acid value

Acid value (AV) of oil sample was determined based on titration method described by Nielsen (1994) with some modifications. Briefly, 7.0 g of heated oil sample was weighed into a 250 ml Erlenmeyer flask and 75 ml of ethanol was then added to the mixture. The mixture was preheated to 60-65ºC before addition of 1 ml of phenolphthalein indicator. The flask was swirled for 30 sec and 0.25 N sodium hydroxide (NaOH) solution was added to complete titration.

Determination of peroxide value

Peroxide value (PV) was determined based on titration method (Nielsen, 1994) with slight modification. Briefly, 10.0 g of heated oil sample was used for titration with 50 ml of acetic acid-chloroform (3:2, v/v) added to the oil sample. The mixture was then added with 1 ml of saturated potassium iodide solution and finally added with 100 ml of distilled water before titration.

Determination of conjugated dienes

Determination of conjugated dienes (CD) was done based on the colourimetric method described by Kähkönen *et al.* (2001) with slight modification. Briefly, 0.03 g of heated oil sample was weighed and dissolved in 2,2,4-trimethylpentane (isooctane) and bring to 10 mL volume. The absorbance was measured with a Secomam UV-Vis spectrophotometer (Cedex, France) set at 234 nm using a quartz cuvette. Isooctane was also used as a solvent blank.

Statistical analysis

All data were presented as mean ± standard deviation. Statistical significant differences for the oil samples between different frying frequency were determined based on one-way analysis of variance (ANOVA). The significant value was set at $p<0.05$.

Results and Discussion

Effect of frying on fatty acid composition

Based on our previous study (Azrina *et al.*, 2009), the result shows that unheated blended oils supplied about 8.4-9.9% SFA, 11.1-12.9% MUFA and 7.5-9.9% PUFA for our daily nutrient intake. Compared to the unheated oils, 10 times of potato frying had percentages of SFA and MUFA increased from 29-35% to 29-37% and from 38-44% to 38-45%, respectively. However, the percentages of PUFA reduced from 22-32% to 19-31% during 10 times of potato frying. The most reduction of PUFA and increment of SFA, as well as MUFA were observed in the heated PORBO (Azrina *et al.*, 2009).

Blending of palm oil and other unsaturated vegetable oils (CO, SO and RBO) resulted in great changes of fatty acids composition. Palm oil blended with unsaturated vegetable oils has a lower level of SFA and a higher level of MUFA as well as PUFA

Table 1. Acid values of blended oils at different frying frequency

Sample*	Frying frequency	Free fatty acids (%)
PO	0	0.18 ± 0.0^{a}
	10	0.27 ± 0.1^{a}
	20	0.27 ± 0.1^{a}
POCO	0	0.30 ± 0.1^{a,b}
	10	0.40 ± 0.0^{b}
	20	0.20 ± 0.0^{a}
POSO	0	0.20 ± 0.0^{a}
	10	0.40 ± 0.0^{b}
	20	0.80 ± 0.0^{c}
PORBO	0	1.60 ± 0.0^{a}
	10	1.80 ± 0.0^{b}
	20	2.00 ± 0.1^{c}

*All data are presented as mean ± standard deviation. Different superscript lower case letters show a significant difference between the frying frequency. PO: palm oil; POCO: blended palm oil-corn oil; POSO: blended palm oil-sesame oil; PORBO: blended palm oil-rice bran oil.

Table 2. Peroxide values of blended oils at different frying frequency

Sample*	Frying frequency	Peroxide value (mEq/kg)
PO	0	2.50 ± 0.0^{a}
	10	8.74 ± 1.8^{b}
	20	11.24 ± 1.8^{c}
POCO	0	16.24 ± 1.8^{a}
	10	16.25 ± 1.8^{a}
	20	17.49 ± 3.5^{a}
POSO	0	5.00 ± 3.5^{a}
	10	27.47 ± 3.5^{b}
	20	28.74 ± 1.8^{b}
PORBO	0	6.24 ± 1.76^{a}
	10	7.31 ± 3.44^{a}
	20	7.50 ± 0.0^{a}

*All data are presented as mean ± standard deviation. Different superscript lower case letters show a significant difference between the frying frequency. PO: palm oil; POCO: blended palm oil-corn oil; POSO: blended palm oil-sesame oil; PORBO: blended palm oil-rice bran oil.

compared with the unblended PO (Noor Lida *et al*., 2002). The beneficial effect of blended PO is greater, especially the desirable effect on plasma lipids. Palmitic acid is a saturated fatty acid, but its presence in PO has no plasma cholesterol-raising effect (Sundram *et al*., 1994).

CO was selected in this study since it is fairly stable towards oxidation. It also contains trace amount of 18: 3 fatty acid that oxidises twice faster as 18: 2 fatty acid, and 20 times more rapid than 18: 1 fatty acid (Ching, 2000). Although SO contains low level of tocopherol, it has high amount of other phenols that seem to be unique to it which also contributed to its stability towards oxidation (Shahidi *et al*., 1997). RBO, on the other hands, was selected due to its potential advantage over the other edible oils with similar fatty acids composition as it contains high levels of tocopherols, tocotrienol as well as γ-oryzanol besides its cholesterol lowering potential (Berger *et al*., 2003). Therefore, this study achieved its goal for searching of a compositionally modified vegetable oil from natural resources by blending an unsaturated oil with a heat-stable palm oil.

Resistance of oils and fats to oxidation is depending on factors such as degree of unsaturation, presence of antioxidants or pro-oxidants and prior abuse (Coppin and Pike, 2001). Antioxidants can delay or inhibit lipid peroxidation by inhibiting the initiation or propagation of oxidative chain reaction (Javanmardi *et al*., 2003). Thus antioxidants in the oil samples may concurrently retard formation of oxidation product. Changes in chemical indicators (AV, PV and CD) of blended oil samples at 0, 10 and 20 times of potato frying are summarised in Tables 1-3. All values obtained were compared with the values for PO.

Acid value

As shown in Table 1, non-heated PORBO had the highest AV (1.6%), followed by POCO (0.3%) and POSO (0.2%). These values were higher than the level determined for PO (0.18%). The percentages of AV determined for all blended oils before heat treatment were within the acceptable range since AV level for frying oils should be less than 2% (Lalas *et al*., 2006) or not greater than 2.5 mg/g oil (Osawa *et al*., 2007). The high AV in blended oils could be due to the fact that unsaturated fat has higher oxidation rate than saturated fat during heat treatment (Warner and Mounts, 1993). Nevertheless, the values were not significantly different from our preliminary data (data not shown) of the same blended oils. Theoretically, AV is known to be high when the free fatty acid (FFA) content is high. FFA content differs from AV, which could be due to the fact that acid phosphates as well as amino acids contribute to the acid level (Wrostald *et al*., 2000). However, AV in oil sample is more attributable only to free fatty acids.

Comparing between different frying times, only AV level of PO showed no significant difference

Table 3. Conjugated dienes of blended oils at different frying frequency

Sample*	Frying frequency	Conjugated dienes (A_{234nm})
PO	0	5.36 ± 0.1[a]
	10	5.40 ± 0.0[a]
	20	5.21 ± 0.3[a]
POCO	0	4.97 ± 0.9[a]
	10	4.74 ± 0.4[a]
	20	5.02 ± 0.0[a]
POSO	0	4.41 ± 0.0[a]
	10	6.24 ± 0.0[b]
	20	6.38 ± 0.5[b]
PORBO	0	4.34 ± 0.0[a]
	10	5.54 ± 0.1[b]
	20	5.54 ± 0.7[b]

*All data are presented as mean ± standard deviation. Values of conjugated dienes were expressed as absorbance values taken at 234 nm. Different superscript lower case letters show a significant difference between the frying frequency. PO: palm oil; POCO: blended palm oil-corn oil; POSO: blended palm oil-sesame oil; PORBO: blended palm oil-rice bran oil.

between non-heated and heated PO. AV level determined for the oil samples that heated for 10 and 20 times were increased from 0.4% to 0.8% and from 1.8% to 2.0% respectively for POSO and PRBO. However, AV level for POCO was reduced from 0.4% to 0.2%. No change of AV level was found for palm oil between 10 and 20 times of potato frying. The results showed a two-time reduction in AV level for POCO after 20 times of potato frying compared with the other blended oils, which could be due to degradation of long-chain FFA occurred in POCO as CO has higher percentage of PUFA (60.9%) than the other high PUFA oil samples (44-53%) (Azrina *et al*., 2009). Therefore, a higher degradation rate of AV from CO is expected. As foreseen, heating released more fatty acids from the glycerol backbone, which contributed to the increased percentage of AV in POSO and PORBO. In contrast, palm oil that contains a high saturated remained as the most stable oil in term of decomposition of the fat at a slower rate.

In this study, blended oil samples were used in frying potato slices that containing high moisture content. Moisture and potential catalytic agents in the potato slices are the factors that increased lipase activity (Barnes and Galliard, 1982), thus increased the level of AV in the oil samples. Besides, the formation of free acids, monoglycerides, diglycerides and glycerol would speed up degradation of the remaining triacylglycerides by allowing a greater emulsification of water from food into the oil (Sangdehi, 2005). The increment of AV of all oil samples after 10 times potato frying was mainly due to the water molecule in potato slices, which further accelerate acid hydrolysis of the blended oils. Besides, continuous heating of oil at 180°C during potato frying promotes chemical changes in the oil, in term of rapid deterioration (Irwandi *et al*., 2005). Moreover, the loss of acidity in the oil samples could be due to the volatilization of the free fatty acids, since the oils were left overnight at 4°C before next frying process.

Peroxide value

Levels of PV of the oil samples are shown in Table 2. Result showed that highest level of PV was observed for unheated POCO (16.24 mEq/kg oil), followed by unheated PORBO (6.24 mEq/kg oil), POSO (5.00 mEq/kg oil) and PO (2.5 mEq/kg oil). In this study, levels of PV obtained for the unheated oil samples were below the acceptable level (10 mEq/kg oil) recommended by Codex Standards (1999), except for POCO (16.24 mEq/kg oil). Comparing with the unheated oil, 10 times potato frying contributed to significant increased in the levels of PV for PO (8.74 mEq/kg oil) and POSO (27.47 mEq/kg oil) at $p<0.05$. After 20 times of deep-fat potato frying, PV value for PO was significantly higher than the 10 times potato frying at $p<0.05$, but not for the other blended oil samples. The PV levels for POCO and PORBO were also not affected by the increased frequency of heating.

Unheated blended oil with higher amount of PUFA has lower stability in the presence of light, air and metal (Sherwani *et al*., 2002). The main cause of peroxide formation in oil sample is lipid peroxidation. As POCO contained the highest PUFA level compared with other blended oils, the high PV level for the unheated POCO could be due to external factors prior to the procurement of oils (PO and CO). Generally, oil sample with higher PUFA is more sensitive to auto-oxidation (Frankel and Huang, 1994). Besides that, factors such as old stock, contaminated with metal during processing or poor packaging might increase the PV level of CO before blending.

Increased levels of PV in the heated oil samples could be due to many unknown factors. Smoke point of the blended oils could be one of the factors for the high PV. RBO and PO have higher smoke points compared with CO and SO (Wikipedia, 2016). During the high temperature heating, higher oxidation products will be generated in the oil sample with a lower smoke point. Therefore, heated POSO has higher level of PV than non-heated PV. Another possible reason for the increased PV of heated POSO is destruction of tocotrienol in the oil. Although POSO had the highest level of total tocotrienol compared to the other blended oil (Azrina *et al*., 2009), destruction of this antioxidant accelerates peroxide formation in the heated oil.

Conjugated dienes

Formation of peroxide alone in the heated oil cannot conclude the oxidative stability of the oil sample. Conjugated dienes formation in the heated oil gives a clearer picture of stability of heated oil. The levels of CD in oil samples are shown in Table 3. The results were presented as absorbance values measured at 234 nm. Level of CD in unheated PO (5.36) was the highest, followed by unheated POCO (4.97), POSO (4.41) and PORBO (4.34). After deep-fat potato frying for 10 times, all the oil samples had increased levels of CD (≥5.40), except for POCO (4.74). This finding hints that blending of PO with corn oil is favourable since heating POCO for 10th time showed a higher stability than palm oil, which had a decreased CD level.

After 20 times potato frying, all blended oil samples showed an increment in CD level, except PORBO (Table 3). However, CD level for PO was somehow reduced during the 20th time potato frying. The CD levels were also not significantly differed between non-heated and heated of PO and POCO, except POSO and PORBO. Moreover, no significant differences were found for CD levels of POSO and PORBO heated between 10 and 20 times potato frying.

The high saturated fat content of PO makes it a highly stable oil. If PO is to be reused for many times, blending of PO with CO is advisable because the results showed a reduction in CD level for the blended oil. For higher frequency of reusing frying oil, blending of PO with other PUFA-rich oils is not recommended. Our findings support the fact that CD levels for the reused POSO and PORBO were significantly higher than the non-heated oils. Therefore, POCO is the most suitable blended frying oil that can be reused for up to 20 times potato frying.

Increase frequency of potato frying using the reused blended oils enhances oxidation process of fat, especially the highly unsaturated blended oil. Although POCO has higher PUFA than the other blended oil samples, a possible explanation for the low CD level in POCO after being heated for 10 and 20 times could be related to the higher α-tocopherol content in CO compared to SO and RBO (Azrina *et al*., 2009). A mixture of a high PUFA oil and PO may yield a higher short-term stability than the other blended oils especially when the blended oil is not overheated or reused frequently.

Conclusion

This study suggested that blending of partially saturated PO with unsaturated vegetable oil such as CO is somehow beneficial to human health, where the blended oils maintained a low PV after frying potato for 20 times compared to PO, as well as increase resistance towards oxidation and hydrolysis. Among all blended oils tested, POCO is the most heat-stable blended oil. It also contains a balanced fatty acids composition that can improve health. Therefore, POCO is recommended for deep-fat frying in food industries and household cooking.

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