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Physicochemical properties of canola oil, olive oil and palm olein blends

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Abstract

Oil blending has been recognized as one of the most potent solution in producing vegetable oils with good storage stabilities and optimum fatty acids compositions. This study was conducted to identify the best oil blends in terms of physicochemical properties between canola, olive and palm olein oil. Canola and olive oils were blended at different ratios of 80:20, 60:40, 50:50, 40:60, and 20:80. Palm olein is stable against rancidity and oxidation thus the above blends were mixed with 20% palm olein. The 80:20 canola: olive blend shows the best properties after being mixed with 20% palm olein compared to other blends. It passed the cold stability test and has significantly the lowest cloud point of 6.0°C ($p<0.05$) which means it can be stored at low temperature (7°C). This blend also has significantly high iodine value of 116.04 $gI_2/100g$ ($p<0.05$), low peroxide content of 17.97 meq O_2/kg and has significantly the lowest free fatty acid value of 0.16% ($p<0.05$). Fatty acid composition has shown that it has high unsaturated oleic acid, C18: 1 (58.83%) and relatively high ratio of linolenic acid (5.24%) - linoleic acid (16.50%) compared to other oil blends. Therefore, the oil blend of 80:20 (canola: olive) with 20% palm olein is recommended for deep-frying and can be kept longer due to its stability.

Introduction

One of the issues surrounding the oils is the stability of the oils themselves. According to a study by Choe *et al*. (2006), this is due to auto-oxidation and photo-oxidation that occurs during processing and storage. The instability of oils can also lead to undesirable taste and flavour of oil, decomposing nutritional quality and also production of toxic compounds. Another problem is the amount of unsaturation in oils. The world has come to realize that high amount of saturated fats in foods are one of the main causes of coronary heart diseases such as atherosclerosis. Ramsden *et al.* (2013) stated that increasing the intake of unsaturated and polyunsaturated fats can help in reducing the risk of coronary heart diseases. Another issue of vegetable oils is the ratio of omega-3 and omega-6 fatty acids. Lands (1992) and Okuyama (2001) also found that the ratio of omega-3 and omega-6 fatty acids ingested by humans is significant in maintaining cardiovascular health. Regardless of those, the ratio of omega-3 and omega-6 have a interactions that closely related in influencing bodies' inflammatory and homeostatic processes. Altering this ratio also can change bodies' metabolic and inflammatory rate (Tribole, 2007). However Mozaffarian *et al.* (2005); Willett (2007); and Griffin (2008) stated that only omega-3 is significant in preventing cardiovascular diseases while omega-6 are not.

Oil with high amount of unsaturated and polyunsaturated fatty acids such as linoleic acid and linolenic acid is more prone towards oxidation and this is where oil blending comes in play. Leonardis and Macciola (2012) showed that thermal stability of virgin olive oil greatly increased when blended with palm oil if the composition of olive oil is around 20% or less. Based on study by Basoglu *et al.* (1996), addition of 20% palm olein with soft oils showed the desired clarity during shelf storage. Blending of oil can also reduce the risk of cloudy and partial crystallization in palm olein (Siddique *et al*., 2010). By blending, the melting point of edible oil can be reduced and the oil quality is preserved. Consumers demands for oils with lower values of viscosity, density and low melting point. By blending, oil with sustainable viscosity can be obtained because it allows the blends to remain free from any added chemicals (Siddique *et al.*, 2010). The antioxidants in oils prevent the oxidative degradability of oils. Chu and Kung, (1998) stated that by blending, the physicochemical properties of oils remain stable without any changes in their chemical composition. The presence of Vitamin E (tocopherol) in palm oil promote the oxidative stability against rancidity reaction compared to other vegetable oils (Tawfik *et al*., 1999).

In this study, olive oil and canola oil have been

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selected as primary samples to be blended with palm olein. Olive oil and canola oil were blended at different ratios and analysed for their cold stability, cloud points, free fatty acid percentages, iodine values, peroxide values and fatty acid compositions. Palm olein was added later and the same analyses were conducted. The objectives of this study were to investigate the physicochemical properties of individual olive oil, canola oil, palm olein and blends of the oils at different ratios.

Materials and Methods

Materials

Two samples which include canola oil (Wintercorn Edible products PTY LTD, Australia) and olive oil (100% purity from Delima Oil Products, Malaysia) were bought from local market. Palm olein sources from palm oil were obtained from Felda Enstek, Nilai.

Preparation of oil blends

Both canola oil and olive oil were blended at different ratios: 80:20, 60:40, 50:50, 40:60, and 20:80 (A, B, C, D and E) by heating at 40°C using magnetic stirrer (Siddique *et al*., 2010). The blended oils were analyzed for physicochemical characteristics using the method as described. After that, 20% palm olein was added to the above blended oils and further analyse.

Cloud point

Approximately, 20-25 g of all the blended oil were heated to 130°C and cooled in cold water bath and stirred. After the sample has reached a temperature of 10°C above the cloud point, stirring was done steadily and rapidly in circular motion to prevent supercooling and solidification of fat crystals on the side or the bottom of the bottle. At this point, the bottle was observed regularly for the presence of cloudiness (the thermometer was no longer visible) (AOCS Official Method Cc 6-25).

Cold stability

Approximately 20-25 g of all the blended oil were filtered and transferred to a clean, dry bottle. The bottle was fully filled with the sample and closed with cork stopper. The bottle was then immersed in ice bath at 7°C. After 5.5 hours, the sample was observed for its clarity. The oil clear appearance of oils indicate that the oil is stable at low temperature storage (AOCS Official Method Cc 11-53).

Iodine value

Approximately, 0.130 g of all the blended oil were weighed into 500 ml conical flask with glass stopper. A blank flask which contains no oil was prepared. About 15 ml of cyclohexane and acetic acid solution were mixed in a 1:1 ratio, and then added into the sample flask and blank flask. Then, 25 ml of Wij's solution was added to both flasks and they were closed with glass stopper and properly shaken. The flasks were left in the dark for 1 hour. After that, 20 ml of potassium iodide and 150 ml of distilled water were added to release the iodine from non-reacted iodine monochloride. Finally, the mixtures were all titrated with sodium thiosulphate solution until yellow colour nearly disappeared before 1-2 ml of starch solution was added as indicator and titration continued. This process ended when blue colour of starch solution totally disappeared (AOCS method Cd 1d-92, 1993b).

Peroxide value

Approximately 5 g of all the blended oil were weighed and put into 250 ml conical flask. A blank flask which has no oil was prepared. The flasks were added with 30 ml of mix solvent acetic acid-chloroform was added and left for a minute while swirling the flasks occasionally. Then, 30ml of distilled water was added. The mixture was then titrated with 0.1N of sodium thiosulphate until brown colour is obtained and 0.5ml of 1% starch solution was added and titration continued until the blue/grey colour vanished. The mixture must be vigorously shaken during titration to ensure all the iodine is liberated from the chloroform layer (AOCS method Cd 8-53, 1993c).

Free fatty acids

Approximately 28.2 g of all the blended oil were weighed and added into 250 ml conical flask. Then, the sample was dissolved with 50 ml 99% isopropanol and mixed completely. Finally, the mixture was titrated with 0.1N sodium hydroxide solution. Phenolphtalein was used as indicator. The last drop is achieved when the colour of indicator changed to pink for at least 30 seconds (AOCS method Ca 5a-40, 1993)

Fatty acid content

Approximately 100 mg of all the blended oil were weighed and put into universal bottle. Then 5 ml of hexane and 250 µl of sodium methoxide solution was added and capped tightly. The mixture was vortexed for 1 min, paused every 10 s to allow the mixture of oil to collapse. Next, 5 ml of saturated sodium

chloride was added into the bottle cap and shaken vigorously for 15 s and left the bottle for 10 minutes. Finally, the hexane (top layer) was transferred into a vial containing sodium sulfate. About 0.5 µl of fatty acid methyl esters (FAMEs) was injected into gas chromatography (Hewlett Packard 6890, GC model G1530A) equipped with flame ionization detector (Hewlett Packard 6890, GC model G1530A) and fitted with a BPX70 capillary column (30 mm × 0.32 mm × 0.25 µm) to obtain individual peaks of FAMEs. The injector and detector temperatures were 250°C. The column temperature was held at 115oC and increased to 180°C, held for 10 minutes. It continued rising to 240°C and held for 10 minutes. The increasing rate is 8°C/min. The carrier used was nitrogen set at flow rate 16 ml/min (Nielsen, 2010).

Statistical analysis

All analysis were done in triplicate (n=3) and the data were statistically analyzed by one-way analysis of variance (ANOVA) procedure, using Minitab software. Significant differences ($p<0.05$) between means were determined.

Results and Discussion

Cold test

From Table 1, palm olein, 40:60 canola: olive with 20% palm olein (DP) and 20:80 canola: olive with 20% palm olein (EP) samples were failed to pass this test compared to other samples. According to Sarin *et al.* (2009) oil becomes cloudy due to the fact that oil has saturated fatty acids. Since saturated fatty acids have high melting point which promotes clouding faster than unsaturated fatty acids and that is why palm olein, DP and EP turned cloudy after 5.5 hours. The presence of water vapour inside oil samples can also make the oils cloudy rapidly. The result in this study was similar with Wai Lin and Wee Lam (1996) which stated that the lower the iodine value of palm olein, the less its resistance towards cold test.Based on their study, palm olein with IV of 60 failed the cold stability test after 3 hours. Similar with this study, the IV of palm olein is 58.01 resulted in a failed cold test as well. They also stated that when IV values decrease, the more lower resistant of oils toward cold test.

Cloud points

Cloud point is a point where oil starts to turn cloudy and no longer completely soluble in order to determine its physical resistance towards lower temperature. Figure 1 and Figure 2 show the value of cloud point before addition of palm olein and after addition of palm olein. Results shown that canola oil has the lowest cloud point temperature, which was around -3°C while palm olein has the highest cloud point temperature with 10.7°C compared to other samples. Whereas after addition of palm olein, the lowest cloud point was AP and the highest was EP. This analysis is important in order to identify the minimum temperature of storage for oil.

High cloud point in palm olein and EP mainly due to the high content of saturated fatty acids in an oil sample because unsaturated fatty acids have lower melting points compared to saturated fatty

Table 1. Cold test results of canola, olive, palm olein and their blends

Oil Samples	Cold Test
Canola	Passed
Olive	Passed
Palm Olein	Failed
A (80:20 canola:olive)	Passed
B (60:40 canola:olive)	Passed
C (50:50 canola:olive)	Passed
D (40:60 canola:olive)	Passed
E (20:80 canola olive)	Passed
AP (A + palm olein)	Passed
BP (B + palm olein)	Passed
CP (C + palm olein)	Passed
DP (D + palm olein)	Failed
EP (E + palm olein)	Failed

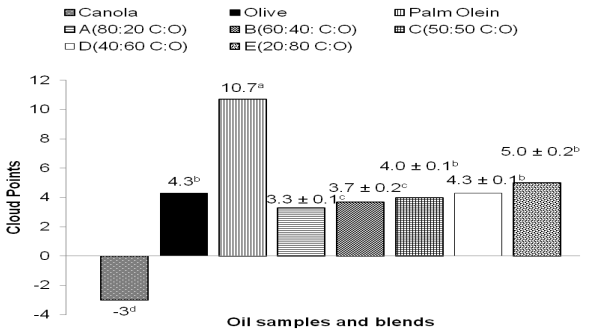

Figure 1. Cloud points of oil samples and blends before addition of palm olein

*All values are shown as mean±standard deviations (n = 3)
*Small letters a, b, c, d indicate significant different ($p<0.05$) between blended oils

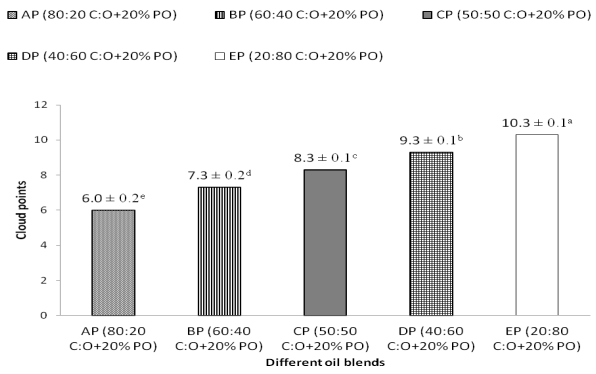

Figure 2. Cloud points of different oil blends after addition of palm olein

*All values are shown as mean±standard deviations (n = 3)
*Small letters a, b, c, d, e indicate significant different ($p<0.05$) between blended oils

Table 2. Iodine values, peroxide values and FFA values of oil samples

Oil Samples	Iodine Value (gI_2/100g)	Peroxide Value ($meqO_2$/kg)	FFA Value (%)
Canola	114.47 ± 1.423[a]	5.73 ± 0.949[e]	0.16 ± 0.011[e]
Olive	94.01 ± 1.289[c]	10.62 ± 1.176[d]	0.42 ± 0.008[a]
Palm Olein	58.01 ± 0.204[e]	28.02 ± 0.082[a]	0.11 ± 0.011[e]
A	110.50 ± 2.321[b]	6.64 ± 1.140[e]	0.15 ± 0.005[e]
B	108.96 ± 4.091[b]	9.61 ± 0.573[d]	0.22 ± 0.009[d]
C	104.86 ± 6.773[b]	9.64 ± 0.583[d]	0.26 ± 0.009[c]
D	99.23 ± 3.227[c]	9.97 ± 0.010[d]	0.28 ± 0.004[c]
E	92.86 ± 6.987[c]	9.16 ± 1.038[d]	0.33 ± 0.001[b]
AP	116.04 ± 0.176[a]	17.97± 0.054[c]	0.16 ± 0.015[e]
BP	120.41 ± 0.497[a]	29.91± 0.027[a]	0.2 ± 0.015[d]
CP	107.24 ± 0.181[b]	23.89± 0.062[b]	0.25±0.005[c]
DP	88.50 ± 0.056[d]	17.85± 0.10[c]	0.291±0.010[b]
EP	83.14 ± 0.101[d]	11.37 ± 0.049[d]	0.37±0.005[a]

*All values are shown as mean±standard deviations (n = 3)
*Small letters a, b, c, d, e indicate significant different ($p<0.05$) between blended oils

acids (Sarin *et al.*, 2009). The value of cloud points of canola oil and palm olein is different when compared to cloud points' results from study by Moser (2011). In his study, the cloud points of canola oil and palm olein were -1.3°C and 14.3°C resepectively compared to -3°C and 10.7°C in this study. He stated that long storage of these oils did not have significant impact on the cloud point as well. The results of this study were different from his study may be due to the different origin and processing of raw samples.

Iodine values (IV)

From Table 2, the IV value of palm olein was initially low (58.01 g I_2/100g), but after it was added to the blended canola and olive oils at different ratios, the values of IV for the blended oils increased.The highest IV value is BP with 120.41 g I_2/100g and the lowest is EP with 83.14 g I_2/100g. The increment of IVs is due to the fact that after the oils are blended together, their degree of unsaturation changed leading to changed IVs (Siddique *et al.*, 2010). When oil with high content of linoleic acid is blended with palm olein, the linoleic acid tends to migrate into the oil blends (Abdulkarim *et al.*, 2010). Since canola oil is high in linoleic acid, the IVs of oil blends also increased as amount of canola oil increased. BP has the highest IV value followed by AP, CP, DP and EP. The addition of canola oils and olive oils which are high in unsaturated fatty acids explains why the IV value of the palm olein increased.

Iodine values of canola oil (114.47 g I_2/100g) in this study are also different to those of Siddique *et al.* (2010), which garnered IV of 226 g I_2/100g canola oil. However, it is stated in that study that these values are also in defiance to the theory that IVs should be lower when oils are exposed to light and air. Iodine values (IV) of palm olein (58.01 g I_2/100g) is closely the same with a study by Long *et al*. (2005) which has IV of 58.3 g I_2/100g of olive oil in this study, which was 94 g I_2/100g, was not the same as in other study by Abdel Razek *et al*. (2011), which has IV value of 83 g I^2/100g possibly because of differences in cultivar and purities of olive oil sources.

Peroxide values (PV)

Peroxide value is a common method used to measure lipid oxidation, and is suitable for measuring peroxide formation in the early stages of oxidation (Nawar, 1996). Unsaturated fatty acids presence will easily react with oxygen to form peroxides (Marina *et al*., 2009). Based on Table 2, both BP and CP have the two highest values with 29.909 $meqO_2$/kg and 23.888 $meqO_2$/kg respectively. While the lowest PV was EP with 11.367 $meqO_2$/kg.

In this study, oil blends with higher canola oil have higher PV than blends with less canola oil since oil with high linolenic acid should have high PV (Abdulkarim *et al*., 2007). The PV value from the blends were increased after addition of 20% of palm olein. The higher amount of olive in blends, the lower value of PV obtained. This indicated the natural antioxidants in both palm olein and olive oil lowered the oxidation process compared to other samples. Siddique *et al.* (2010) indicated that the peroxide value of oils also will definitely increase after exposure to light and air at room temperature. The traces amounts of heavy metals can also positively affect enhancement of PV.

Free fatty acid values (FFA)

The amount of free fatty acid is estimated by determining the quantity of alkali that must be added to the fat to render it quite neutral. Hydrolytic rancidity occur when glycerol further convert into

Table 3. Fatty acid compositions of oil samples

Myristic acid (C14:0)	Palmitic acid (C16:0)	Palmitoleic acid (C16:1)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Arachidic acid (C20:0)	Behenic acid (C22:0)
0.82	52.09	3.37	0.06	35.42	0.63	6.61	0.74	0.09
0.84	17.19	0.82	0.50	58.83	16.59	5.25	0.58	0.09
0.34	16.85	0.76	0.42	58.07	16.93	5.45	0.99	0.08
0.55	16.29	1.07	0.62	58.03	17.73	4.88	0.63	0.10
0.24	16.93	0.64	0.40	59.11	17.07	4.82	0.50	0.13
0.27	16.91	0.61	0.39	60.14	17.24	4.22	0.10	0.10

fatty acid (Freeman, 2005). Table 2 shows results of the amount of FFA value increases as the amount of olive oil in blended oil samples increase. AP with the lowest amount of olive oil has the lowest FFA value (0.16%) among the blended oil samples while EP with highest amount of olive oil has the highest FFA value (0.37%).

FFA value of olive oil is quite high (0.42%) but it is in the range of FFA values of olive oil studied in previous study (Frega *et al*., 1999). FFA values of this study (after addition of 20% palm olein) were consistent with previous study (Mai, 2012) where 80:20 canola: olive has the lowest FFA value (0.15%) and 20:80 canola: olive has the highest FFA values (0.32%). High FFA values of olive oil contribute to increased FFA values of oil blends as proved by a study conducted by Leonardis and Macciola (2012), increasing amount of olive oil in oil blends will result in increasing amount of FFA value. The presence of olive oil in the blends contribute in keeping the values of all oil blends at low value due to due to the refining process it undergone (Abdulkarim *et al*., 2010). Olive oils are distinct from other vegetable oils because they may be consumed without extensive refining.

Fatty acid compositions

Fatty acid composition analysis conducted using gas chromatography (GC) detected 10 different types of fatty acids in the blended oils. However only a few fatty acids play important roles in contributing to production of healthier oils. They are the monounsaturated oleic acid, linoleic acid and linolenic acid. GC analysis result has shown that EP has the highest oleic acid percentage at 60.14% followed by DP (59.11), AP (58.8324), BP (58.07), and CP (58.03). In terms of linoleic acid, CP has the highest with 17.73% while AP has the lowest with 16.60%. BP has the highest percentage of linolenic acid with 5.45% while EP has the lowest with 4.22%. The results of fatty acid compositions are shown in Table 3.

Fatty acid compositions of palm olein from this study were not consistent with study conducted before (Dauqan *et al*., 2011). This can be caused by several reasons such as different types of oil samples used in analyses, storage time and exposure to air. There were changes in the amount of saturated fatty acid, palmitic acid of palm olein after it was blended with different ratios of canola-olive. The most prominent fatty acids in PO were palmitic (52.09%) and oleic (35.42%) acid, while all the blends have abundance of oleic (58.02% - 60.14%) and linoleic (16.59% - 17.73%) acids. Blending of PO with blends of canola and olive oil caused the content of palmitic acid to decrease and linoleic acid to increase in the blends. The FA composition thus was changed by blending. Blending of PO in proportions of AP to EP resulted in the reduction of palmitic acid content from 17.19 to 16.90% respectively. Linoleic acid content increased from 16.59% to 17.23. But there was no significant change in the oleic acid content. It is also noticed that the proportion of polyunsaturated/mono-unsaturated fatty acid ratios were significantly ($p<0.05$) decreased and hence, increased the oxidative stability of the blends. Based on research done by Abdulkarim *et al.* (2010), they stated that when different ratios of soybean oil were blended with palm olein, the content of palmitic acid were decrease and linoleic acid were increase in the blends.

Conclusion

This study showed that canola: olive blend at ratio of 80:20 had the best physicochemical properties after

addition of 20% palm olein, compared to other ratios of oil blends. Fatty acids compositions also showed that 80:20 canola: olive with 20% palm olein also had high amount of unsaturated oleic acid (58.83%). Presence of linolenic acid (omega-3) and linoleic acid (omega-6) in the blend were relatively equivalent with 5.25% and 16.59% respectively. It can be concluded that blending of palm olein with 80:20 canola: olive ratio did improve the physicochemical properties of the oil. Addition of 80:20 canola: olive with 20% palm olein may possess good storage stability and may be suitably for processing such as frying.

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