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RESEARCH PAPER

Effect of intermittent frying on the stability of vitamins A and D in commercially fortified oils

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تأثير القلي المتقطع على ثبات فيتامين (أ) وفيتامين (د) في الزيوت المدعمة

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Abstract. Fat-soluble vitamins and fatty acids are very sensitive to high temperature and oxidation. In this study, stability of vitamins A and D, and physiochemical changes were investigated in two types of oils, palm olein (PO) and a blend of PO and sunflower oil (OB). The intermittent frying was performed at two different temperatures 160 and 190 °C. Batches of French fries (500 g) were fried in a deep-fat fryer for 5 cycles, a cycle per day. In each cycle, food was fried every 15 min with a total frying time of 5 h per day. Oil samples were taken at the end of each heating cycle to measure vitamins A and D concentration, free fatty acid (FFA), peroxide value (PV) and color. In PO, vitamin A was reduced by 96.7% after 25 h of frying at 160 °C and it was completely depleted after 15 h at 190 °C. In OB, the vitamin was reduced by 72.2% after 25 h of frying at 160 °C; and it was completely depleted at 190 °C at the end of frying cycles. Vitamin D was less stable, its content in PO decreased by 67.0% and 80.0% at 160 °C and 190 °C, respectively, after 5 h of frying. In OB, it was reduced by 50.0% and 67.0% at 160 °C and 190 °C, respectively, after 5 h of frying. It was found that both types of oil and frying temperatures showed significant effect on vitamin A concentration, while they did not show any effect on vitamin D. Red color increased linearly with frying time in both oils, while fried at two frying temperatures. The change in color was significantly associated with the vitamin A depletion. A low, but significant, association was found between color changes and depletion of vitamin D. In conclusion, the stability of these vitamins depended on the types of oil and temperature of frying. These were more stable in OB compared to PO, and similar stability was observed in the cases of FFA and PV.

Keywords: Frying, Vitamin Depletion, Vitamin A, Vitamin D, Retinol, Cholecalciferol, Fat-Soluble vitamins.

المستخلص: تعتبر الفيتامينات الذائبة في الدهون والأحماض الدهنية حساسة جدًا لدرجات الحرارة المرتفعة والأكسدة. في هذه الدراسة، تم قياس ثبات فيتامينات (أ) و (د) والتغيرات الفيزيوكيميائية في نوعين من الزيوت، زيت النخيل وخليط من زيت النخيل وزيت عباد الشمس (يسمى لاحقا بالخليط). تم استخدام الزيوت في القلي المتقطع على درجتين حرارة مختلفتين: ١٦٠ و١٩٠ درجة مئوية. تم قلي دفعات من البطاطس (٥٠٠ جرام) في مقلاة عميقة لمدة إجمالية بخمس دورات، دورة واحدة في اليوم. في كل دورة، تم قلي دفعة من البطاطس كل ١٥ دقيقة حيث كان وقت القلي الكلي ٥ ساعات في اليوم. تم أخذ عينات من الزيت في نهاية كل دورة لقياس تركيز الفيتامينات (أ) و (د)، الأحماض الدهنية الحرة (FFA) ، قيمة البيروكسايد (PV) واللون. وجد أن فيتامين (أ) نقص بنسبة ٩٦,٧٪ بعد ٢٥ ساعة من القلي في زيت النخيل عند ١٦٠ درجة مئوية، ونفد تمامًا بعد ١٥ ساعة عند ١٩٠ درجة مئوية. أما في الخليط، فقد انخفض الفيتامين بنسبة ٧٢,٢٪ بعد ٢٥ ساعة من القلي عند ١٦٠ درجة مئوية. ونفد تمامًا عند ١٩٠ درجة مئوية في نهاية دورات القلي. كان فيتامين (د) أقل ثباتا، حيث انخفض محتواه في زيت النخيل بنسبة ٦٧٪ و٨٠٪ عند ١٦٠ درجة مئوية و١٩٠ درجة مئوية، على التوالي، بعد ٥ ساعات من القلي. أما في الخليط، انخفض بنسبة ٥٠٪ و٦٧٪ عند ١٦٠ درجة مئوية و١٩٠ درجة مئوية، على التوالي، بعد ٥ ساعات من القلي. وجد أن كلا من نوع الزيت ودرجات حرارة القلي لهما تأثير ذو دلالة احصائيةعلى تركيز فيتامين (أ)، بينما لم يكن لهما تأثير على فيتامين (د). زاد اللون الأحمر خطيًا مع وقت القلي في كلا الزيتين، بينما قل عند درجتي حرارة القلي. ارتبط التغيير في اللون بشكل كبير بنضوب فيتامين أ. تم العثور على ارتباط منخفض، ولكن ذو دلالة احصائية، بين تغيرات اللون ونضوب فيتامين د. في الختام، يعتمد استقرار هذه الفيتامينات على أنواع الزيت ودرجة حرارة القلي حيث كانت أكثر استقرارًا في الخليط مقارنة بزيت النخيل حيث لوحظ استقرار مماثلا للأحماض الدهنية الحرة وقيمة البيروكسايد.

الكلمات المفتاحية: القلي، استنفاد الفيتامينات، فيتامين أ، فيتامين د، ريتينول، كوليكالسيفيرول، الفيتامينات الذائبة في الدهون.

Introduction

Malnutrition due to micronutrients deficiency is a major global concern, which is also affecting Middle East countries. According to World Health Organization (WHO, 2010), deficiencies reported in the Middle East include calcium, iodine, iron, and zinc, folate, vitamin A, and vitamin D. Intervention strategies have been adopted to reduce the deficiencies among populations; including fortification of food with micronutrients (Allen et al., 2006). Vegetable oils have been proposed as a vehicle for fat-soluble vitamins in food fortification strategies. However, fat-soluble vitamins are not stable during processing and their retention is questionable especially at high processing temperatures (Hrncirik, 2010). The exposure of vegetable oils to high frying temperatures in the presence of

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oxygen and moisture (i.e. deep-fat or shallow frying) results in several chemical changes. These changes resulted in the decline of oil quality and acceptability (Al-Khusaibi and Rahman, 2021). The peroxide value (PV) measures the concentration of hydroperoxides formed due to oxidation reactions, while free fatty acids % (FFA) measures the concentration of free fatty acids formed due to hydrolysis of triglycerides. It has been reported that peroxide value increased with the increase in frying time (Park and Kim, 2016; Arsalan et al., 2017). Park and Kim (2016) reported an increase in the PV after 100 frying cycles (10 cycles per day for 10 days). They found that the degree of change in PV was associated with the type of oil (canola oil, soybean oil, lard and palm olein). The highest percentage change was found in lard and the least change was in palm olein. The increase in PV due to thermal oxidation was also reported (Moh et al., 1999; Gotoh and Wada, 2006). FFA was approved as an index of oil degradation by the 28th session of the Codex Committee on Methods of Analysis and Sampling held in Budapest, Hungary in 2005 (Gotoh and Wada, 2006). The FFA concentration increased with the increase on frying cycles (Sohu et al., 2020; Garg et al., 2021). Codex Alimentarius has set a limit for FFA in oils extracted from quick frozen French fried potatoes to be 1.5 % (Codex 2019). Different countries have set different maximum limits of FFA%. In general, it is in the range of 0.5-2.5% depending on each country's legislations (Dobargarnes et al., 1998; Firestone, 1993).

There have been extensive studies on the stability of different vitamins either in food samples or in vegetable oils during frying. Examples are vitamin E (Hou et al., 202; Hu et al., 2020; Adu et al., 2019; Santos et al., 2018b), vitamin C (Islam et al., 2021; Santos et al., 2018a), vitamin K (Omotosho 2015). The vitamins retention in different food samples during differing food preparation methods was reviewed in several review, such as Leskova et al. (2006); and Fillion and Henry (1998). Several studies were conducted to study the stability of vitamin A during different cooking methods, such as boiling and baking and shallow frying (Hrncirik, 2010), storage (Favaro et al., 1991; Silalahi et al., 2017; Ikram et al., 2021), extrusion (Ribeiro et al., 2021; Sharma et al., 2020), heat treatments (namely pasteurization, boiling and sterilization) (Sachdeva et al., 2019), boiling and repeated deep-fat frying (Favaro et al., 1992), heating at 180°C for 5 min with no food samples. Rady et al. (2019) studied the degradation of vitamin C and β-carotene during frying of sweet potato in soybean oil. Their sample preparation included two steps of frying (one cycle), par-frying for 60 s and finish frying for 3 min, both at 180°C. They reported 49% and 70% decreased in vitamin C and β-carotene, respectively. Simonne and Eitenmiller (1998) studied the stability of vitamin A, in the form of retinyl palmitate, during simulated deep-fat frying (using cotton balls) at 185 °C for 30 h of frying. They reported higher stability in palm olein than in soybean or corn oil. Favaro et al. (1991) reported high retention of vitamin A in rice and beans cooked by boiling for 40 min. However, 42% depletion was found in soybean oil subjected to four pan-frying at 115-117 °C. Riaz et al. (2009) reported high losses of vitamin A and D during extrusion.

Several studies have been conducted on the stability of vitamin D during different cooking methods, such as boiling and baking and shallow frying (Hrncirik, 2010), fortification and storage (Silalahi et al., 2017; Moeller et al., 2018), pasteurization/sterilization and storage (Kaushik et al., 2014), drying (Sławińska et al., 2016). In some studies, using frying as a processing method, the concentration in the food was measured instead of oil (Omotosho, 2015; Ložnjak et al., 2018). Zareie et al. (2019) studied the stability of vitamin D3 in fortified canola oil heated in an oven at different temperatures (100 - 180 °C) for several times (5 - 30 min). The retention of the vitamin was temperature and initial concertation dependent. The highest loss was at 180 °C (67% depletion). Loznjak et al. (2018) measured the content of vitamin D_2 and D_3 in sunflower oil after pan-frying for 1 minute at a temperature described as "high level" without measuring the oil temperature. The vitamin retention was 70% and 72% for vitamin D_2 and D_3, respectively. However, there is a lack of literature on its stability during deep-fat frying. The available literature discusses the stability of vitamin D during shallow frying (Jakobsen and Knuthsen, 2014; Hrncirik, 2010), which is expected to have less detrimental effect compared to deep-fat frying. For example, the concentration of polymerized triglycerides in oil used for shallow frying was less than 1.3%, which was negligible and it did not show excessive use of the oil as in the deep-fat frying (Jakobsen and Knuthsen, 2014). Adu et al. (2019) showed that changes in vitamins levels of vegetable oils was greatly influenced by the nature of food being fried.

Most of the studies that investigates the stability of vitamins A and vitamin D included the retention of vitamins at storage conditions and cooking, e.g. pan-frying. In addition, studies that investigated the retention at high frying temperatures did not mimic the industrial repeated frying cycles. Both factors (i.e. high temperature and repeated frying cycles) could result in higher rate of oil oxidation, which can negatively affect the stability of vitamins. The aim of this study was to determine the effect of intermittent frying on the stability of vitamins A and D in two vegetable oils, and to correlate the depletion of the vitamins with the physico-chemical parameters related to the quality.

Materials and Methods

Samples

Refined bleached and deodorized palm olein (PO) and a blend of the palm olein and sunflower oil in a ratio of 40:60 (OB) were provided by Areej Vegetable oil and

Derivatives Company (SAOC). Both oils were fortified by the manufacturer with vitamins A and D3. Par-fried French fries were purchased from the local market (McCain Alimentaire S.A., Harnes, France). The French fries were stored at -18 °C until used for frying.

Frying

Intermittent frying was done by frying a batch of 500g of French fries every 15 min interval for 5 h daily for 5 days (i.e. 0, 5, 15, 20, 25 h). The sample took 7 min to get fried and 8 min were idle time until the next batch of frying. The frying was done in a 12 L deep fryer (Frymaster, model No. H117-2BLCSC, U.S.A) at two temperatures (i.e. 160 and 190 °C). At the end of each 5 h of frying cycle, oil samples were collected in amber bottles and kept at -18 °C until further analysis.

Free fatty acid and Peroxide Value Analysis

Free fatty acids (FFA) were measured by titration to the American Oil Chemists' Society (AOCS) Official Method Ca 5a-40. Recommended oil sample size according to the method was mixed with hot neutralized 95% ethyl alcohol and phenolphthalein indicator, and the mixture was titrated with NaOH of recommended strength. The FFA % was calculated according to the following equation:

$$FFA \text{ as oleic acid, } \% = \frac{\text{ml of NaOH} \times N \times 28.2}{weight\ of\ sample} \quad \text{Equation (1)}$$

Peroxide value (PV) were measured according to AOCS official methods Cd 8b-90. Recommend sample size was mixed with 50 ml of 3:2 acetic acid-isooctane solution. After adding 0.5 ml of KI solution and allowing the mixture to stand for 1 minute, it was titrated with 0.1N sodium thiosulfate. Titration was carried out until the disappearance of yellow color. Then 0.5 ml of starch indicator solution was added. Titration was carried out until the disappearance of blue color. A blank determination was conducted with reagents without sample. PV value was measure by the following equation:

$$\text{Peroxide value (milliequivalents peroxide/1000 g sample)} = \frac{(S - B) \times N \times 1000}{\text{weight of sample}} \quad \text{Equation (2)}$$

where, S is the volume of sodium thiosulfate from sample titration (mL); S is the volume of sodium thiosulfate from titration of blank; and N is the normality of sodium thiosulfate solution. All measurements were in triplicate and the mean value ± standard deviations are reported.

Vitamin A and D Analysis

Vitamin A was measured according to AOAC official method 2001.13 using High Performance Liquid Chromatography (HPLC, Agilent technologies, Germany) with ZORBAX E Clipse Plus C18 column. Two grams of sample were weighed in erlenmeyer flask, added 50 mg of pyrogallic acid and added 40 ml of ethanol. Then 20 ml of 50 % KOH were added and saponified for 45 min. After saponification, 10 ml of acetic acid were added and the sample was kept at room temperature. This was made up to 100 ml with diluent tetrahydrofuran (Ethanol, 50:50) and then 20 ul was injected in HPLC. The mobile Phase used was acetonitrile:water (70:30). The results were expressed as µg/g using the following formula:

$$\text{vitamin A, µg/g (as retinol)} = \frac{RF \times PkHT \times 100}{W} \quad \text{Equation (3)}$$

where RF is the response factor for vitamin A; PkHT is the total test sample peak height or area of all trans and 13-cis retinol; and W is the weight of test portion (g). Vitamin D was analyzed following the AOCS official method 2002.05 HPLC (Agilent technologies, Germany) with LiChrosorb 5 RP18 column. The normal phase was ZORBAX RX-SIL (4.6x250 mm, 5 micron) from REST-EK, USA. Sample was prepared by mixing 2 gm of sample, 500 mg of ascorbic acid, 50 ml of 95% ethanol and 2 ml vitamin D2 as internal standard. The mixture was saponified for 30 min with 50% KOH. After saponification, 50 ml of distilled water was added through the condenser, solution was transferred to separating funnel and 100 ml of 40% ethanol was added. The vitamin was extracted by the addition of 75 ml of hexane. After phase separation, layer of hexane was removed and collected into a 250 ml separatory funnel. This was done twice and the separated layers were combined. The combined phase was washed once with 50 ml of 1M KOH, twice with 50 ml of 40% ethanol and with water for 4 times, consecutively. A pinch of Butyl Hydroxy Toluene (BHT) and 15 ml ethanol were added and the hexane was evaporated at 45 °C. After evaporation, 2 ml of mixture of cyclohexane and n-heptane were added. The extract was injected in HPLC with normal phase and vitamin D2 and D3 was collected. The collected sample was dried and then 0.5 ml of acetonitrile-methanol (80:20) was added and the solution was injected in HPLC in reverse phase. Vitamin D3 content was calculated using the following equation:

$$\text{Vitamin D3, µg/100g} = \frac{AD_3 \times mD_2 \times 100}{AD_2 \times ms \times F} \quad \text{Equation (4)}$$

where AD_3 is the peak area for vitamin D3; AD_2 is the peak area for vitamin D2; mD_2 is the weight of vitamin D2 added to the test portion (µg); ms is the weight of test portion (g); and F is the response factor (D_3/D_2) at 265 nm.

Color Analysis

The color of oils was measured using a Lovibond Tintometer, UK (Seial No: 16352 and 12435) with a 5¼" cell. The measurement was done as per the manufacture instructions. The cell was filled with oil sample and placed in the meter. The lamp was switched on and the viewing tube was focused until a sharp image of the aperture was observed. A set of standard color filter was adjusted to match the sample color. When both sample and standard color matched, the value of red color was noted.

Statistical Analysis

Analysis of variance (ANOVA) was used to compare between means of different independent variables followed by Least Significant Difference (LSD) using SPSS (IBM SPSS Statistics 2020). A significance probability value of 0.05 was used.

Results and Discussion

Changes in Free Fatty Acids and Peroxide Value

The changes in the free fatty acids (FFA) of palm olein (PO) and oil blend (OB) are shown in Figure 1. This figure clearly shows linear increase ($r^2 > 0.99$) in the concentration of FFA with the oil usage time. This increase was higher in the PO as compared to the OB at both frying temperatures (i.e., 160°C and 190 °C). The increase in FFA was well documented during deep fat frying (Warner, 2004; Tyagi and Vasishtha, 1996). From the change in the FFA, it appeared that OB degraded at lower rate as compared to PO, which indicated better stability at the frying temperatures (i.e. 160°C and 190°C). The change in FFA content during frying process could depend on many factors including frying temperature, number of frying cycles, the food being fried, and replenishment of oil during frying (Karimi et al., 2017). Arsalan et al. (2017) showed different FFA in different oil blends exposed to the same frying conditions (170°C, 10 h of frying with 30 min interval). At the end of the frying process, the values of FFA ranged from 0.84 to 1.13. The

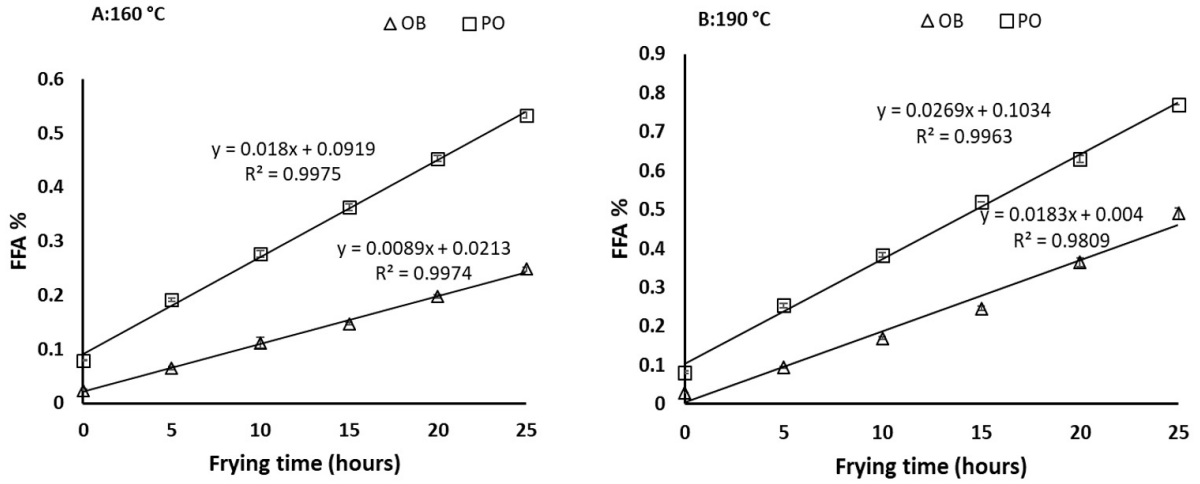

Figure 1. The change in Free Fatty acids (FFA) in palm olein (PO) and oil blend (OB) at A: 160 °C and B: 190 °C

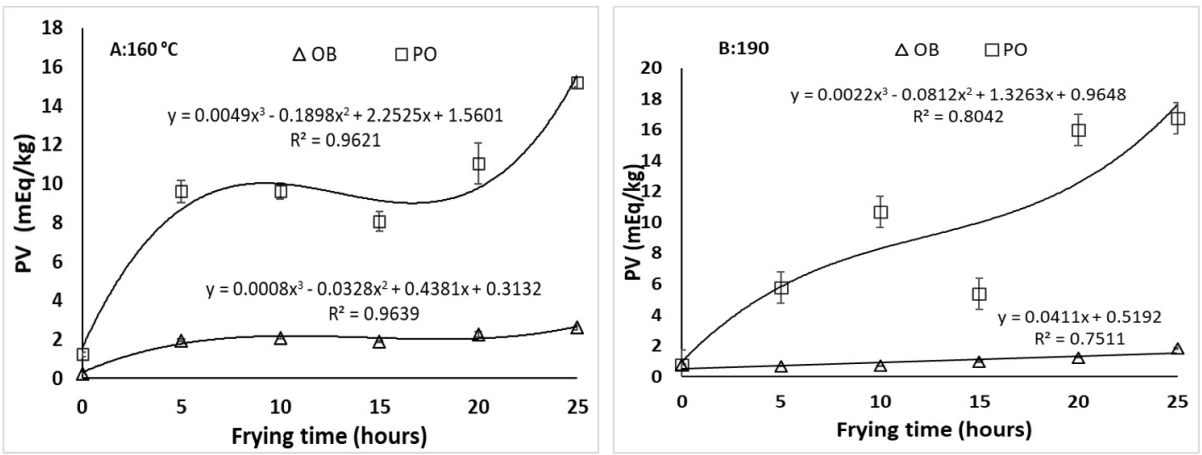

Figure 2. The change in peroxide value (PV) in palm olein (PO) and oil blend (OB) at A: 160 °C and B: 190 °C

Table 1. Change in vitamin A concentration (µg/g) in palm olein and oil blend used for frying at 160 °C and 190 ° C

Frying time (h)/Temperature	Palm Olein		Oil Blend	
	160 °C	190 °C	160 °C	190 °C
0	11.05 ± 0.04[a]	11.03 ± 0.01[a]	13.07 ± 0.09[a]	10.01 ± 0.07[a]
5	5.06 ± 0.04[b]	1.05 ± 0.01[b]	9.15 ± 0.05[b]	4.6 ± 0.24[b]
10	1.69 ± 0.05[c]	0.32 ± 0.02[c]	6.9 ± 0.09[c]	2.43 ± 0.35[c]
15	0.86 ± 0.02[d]	ND	5.83 ± 0.11[d]	1.31 ± 0.17[d]
20	0.42 ± 0.00[e]	ND	4.59 ± 0.06[e]	0.68 ± 0.03[e]
25	0.36 ± 0.00[e]	ND	3.63 ± 0.06[f]	ND

Values are expressed as mean ± SD of triplicate readings
Values with different superscript letters in a column are significantly different at $p = 0.05$

Table 2. The effect of oil type, temperature, and their interaction on vitamin A depletion.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
oil	115.55	1	115.55	8.296	0.005
Temperature	120.93	1	120.93	8.682	0.004
oil*Temperature	36.28	1	36.28	2.605	0.111

difference in the FFA formation due to the type of oils was also reported by Azimah et al. (2017). Karimi et al. (2017) reported different values in the oil discarded by restaurants and street vendors in Kenya. The final FFA content ranged from 0.68 to 3.95. The maximum accepted level of FFA varied from one country to another and ranged from 0.5 to 2.5% (Dobargarnes et al., 1998; Firestone, 1993).

Peroxide value (PV)increased significantly as a function of frying temperature, frying time and types of oil. OB had lower changes in PV during frying, which was in accordance to the FFA results. Baltacıoğlu et al. (2017) reported that change in PV during frying is significantly influenced by oil type and frying temperature. With the variation of frying parameters such as the number of frying cycles and frying temperature, PV values in the range 9.65 - 20 (Baltacıoğlu et al., 2017; Marinova et al., 2012). Paunović et al. (2020) reported 75 and 78% increase in peroxide value in sunflower oil and palm olein, respectively.

Degradation of vitamin A

The initial vitamin A content was around 11 µg/g in PO and 13 µg/g in OB. Table 1 shows the change in the concentration of vitamin A in PO and OB at 160 and 190 °C frying temperatures. After 25 h of frying cycles at 160 °C, content of the vitamin in PO decreased to 0.36 µg/g, which represented 97% reduction of the initial content. At 190 °C, the vitamin was completely destroyed after 15 h, which can be attributed to the higher temperature of frying. Simonne and Eitenmiller (1998) reported higher retention of vitamin A in palm olein followed by corn oil and least in soybean oil exposed to simulated frying at 185°C for 30 min. Omotosho (2015) reported that vitamin A was greatly reduced in cocoyam fried in

Table 3. Change in vitamin D concentration (µg/g) in palm olein and oil blend used for frying at 160 °C and 190 ° C.

Frying time (h)/Temperature	Palm Olein		Oil Blend	
	160 °C	190 °C	160 °C	190 °C
0	0.054 ± 0.001[a]	0.054 ± 0.006[a]	0.063 ± 0.002[a]	0.057 ± 0.001[a]
5	0.024 ± 0.002[b]	0.006 ± 0.001[b]	0.030 ± 0.002[b]	0.018 ± 0.001[b]
10	0.011 ± 0.001[c]	ND	ND	ND
15	0.004 ± 0.001[d]	ND	ND	ND
20	ND	ND	ND	ND
25	ND	ND	ND	ND

Values are expressed as mean ± SD of triplicate readings
Values with different superscript letters in a column are significantly different at $p = 0.05$

Table 4. The effect of oil type, temperature, and their interaction on vitamin D depletion.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
oil	.012	1	.012	3.595	0.064
Temperature	.010	1	.010	2.846	0.098
oil*Temperature	.012	1	.012	3.611	0.063

canola oil (0.034 µg/g) and was completely lost when the product was fired in soya or vegetable oils. Silalahi et al. (2017) reported 49% reduction of vitamin A concentration when fortified PO was heated at 180 °C for 5 min. Fat-soluble vitamins are sensitive to heat and oxidation, therefore these can be partially or completely lost during food processing. The vitamins depletion was influenced by several factors, such as high cooking temperature, exposure time, and presence of oxygen (Hrncirik, 2010; Silalahi et al., 2017). Extreme of these factors are present in the deep-fat intermittent frying.

Table 5. Correlation between red color of oils and vitamins A and D content

Vitamin	Pearson correlation	*p*-value
A	- 0.814	< 0.001
D	- 0.250	0.034

The rate of depletion of vitamin A in OB was lower than that in PO. After 25 h of frying cycles at 160 °C, content of the vitamin decreased from 13 µg/g to 4 µg/g representing 72% decline. The effect of high temperature of frying (i.e. 190 °C) was evident and complete depletion of the vitamin was detected after 25 h of frying cycles. Similar to the free fatty acids and peroxide values, it can be seen that PO had higher increase in FFA and PV. This may explain the higher rate of vitamin depletion in the oil. Pignitter et al. (2016) compared the stability of vitamin A in soybean oil and palm oil and they found better stability in the palm oil. This was attributed to the superior oxidative stability of palm oil compared to soybean oil, which was also supported in this work as evidenced in the changes of FFA and PV. A two-way ANOVA examined the effect of frying temperature and oil type on vitamin A depletion (Table 2). Vitamin A depletion was significantly influenced by oil type (p = 0.005) frying temperature (p = 0.004).

Degradation of Vitamin D

Table 3 shows the concentration of vitamin D during the 25 h frying cycles in both oils. The Vitamin D content of PO decreased by 67% after 5 h of frying at 160°C and 80% at 190 °C. After 20 h of frying cycles, vitamin D content was completely depleted. At 160 °C, vitamin D was more stable in PO than the OB. While 100% depletion was found after 10 h of frying in the blend, around 80% decrease was detected in the PO. In both oils, vitamin was completely lost after 5 h of frying at 190 °C. Compared to vitamin A depletion, vitamin D was less stable and 100% depletion was detected after 10 h of frying cycles.

It must be noted that studies on the vitamin D retention in food staff during cooking are limited; especially during frying. Hrncirik (2010) reported 40% decrease in vitamin D content after shallow frying in fortified liquid margarine at 180 °C. On the other hand, 70% retention of the vitamin was reported in sunflower oil followed by pan-frying at "high-level temperature" as described by

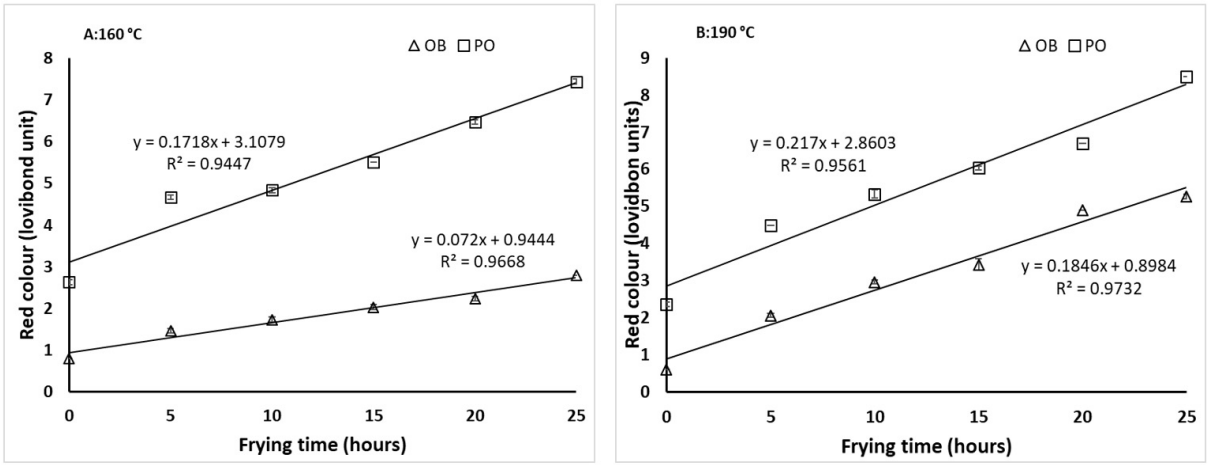

Figure 3. The change in red color in palm olein (PO) and oil blend (OB) at A: 160 °C and B: 190 °C

the authors without measuring the exact value (Ložnjak and Jakobsen, 2018). Mattila et al. (1999) reported high vitamin D_3 retention in baked fish (78-100%) and vitamin D retention in pan-fried mushrooms (80-100%). The effect of cooking parameters on vitamin D retention was influenced by the heating conditions and the type of food being cooked (Jakobsen & Knuthsen, 2014; Ložnjak, & Jakobsen, 2018). Table 4 shows the effect of oil type and frying on vitamin D depletion. Oil type and frying temperature did not show any significant effect on vitamin D depletion. It must be noted that this might be due to the limited number of data resulting from the fast depletion of the vitamin.

Color Analysis

Red color has been always reported as an indicator of the degradation of frying oils (Jurid et al., 2020; Fauziah et al., 2000). The red color was initially high in fresh palm olein (≈ 2.6 units) compared to the blended oil (≈ 0.8 units). PO has been reported to have higher values than other oils and the values reported in this study are in agreement with literature (Fauziah et al., 2000; Low et al., 1998; Tarmizi et. al., 2016). After the 5 days frying cycles, the red color changed by 182% in plam olein and by 250% in the oil blend at frying temperature of 160 °C. Although the change in color in palm olein has been reported to be relatively faster than sunflower oil (Razali et al., 1999), this may not be true in the case of blended oil. It can be noticed that the change was observed higher in the OB compared to the PO (Figure 3). Pearson's correlation was calculated to measure the association between vitamin content and red color change (Table 5). A strong negative association ($r = -0.814$, $p < 0.001$) can be noticed between Vitamin A content and red color. Low association ($r = 0.250$, $p = 0.034$) was found between vitamin D content and red color (-0.250).

Conclusion

The intermittent frying used in this study caused linear increase in the free fatty acids content (FFA) and peroxide value, which showed the deterioration of oil by frying protocol. The depletion of vitamin A was time, temperature and oil type dependent. Vitamin A showed higher stability compared to vitamin D, which depleted completely after 15 h of frying time in PO at 160 °C. The red color of oils was negatively associated with vitamin A concentration, while the association with vitamin D concertation was not significant. The strategies of oil fortifications as an intervention method need to be reassessed in order to make sure that the goals of intervention could be achieved. Based on the maximum limit of FFA, frying in the oil blend at 160 °C resulted in the least depletion of vitamin A. On the other hand, frying in palm olein at 160 resulted in the least depletion of vitamin D. Kinetics of vitamins A and D depletion needs to be studied for the possible predicting of depletion of vitamins as a function of time, temperature and oil type.

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