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Physicochemical Properties and Oxidative Stability of Vegetable Oils during Repeated Frying of Potato Chips

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ABSTRACT

Physicochemical Properties and Oxidative Stability of Vegetable Oils during Repeated Frying of Potato Chips

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Deep-fat frying is a widely used cooking method to make fried products with savory flavor and desirable texture. Although frying temperature, frying time, antioxidant content, and fatty acid composition have been reported to be factors that can affect the chemical reactions during frying process, fatty acid composition of a frying oil is the most important variable for its quality. Commercial frying oil

is generally repeatedly used in frying. However, oxidative stability and volatile compounds of repeatedly used frying oils with different fatty acid compositions and antioxidant contents have been little studied. Therefore, it is necessary to study the changes in physicochemical properties, oxidative stability, and volatile compounds of repeatedly used frying oils with different fatty acid compositions. Thus, physicochemical properties and oxidative stability of refined coconut oil (RCO), refined soybean oil (SBO), pure olive oil (POO), and vegetable shortening (VST) during repeated frying of potato chips were determined in this study.

Potato chips were fried in an oil for 4 min at 180±5°C. After the chips were taken out, the oil was heated for 2 min for the next frying. This process was repeated with 80 cycles. The oils were collected at every 20^{th} cycle. Changes in fatty acid composition, total phenolic contents, tocopherols, DPPH radical scavenging activity, color (Hunter *L*, a**, and *b**), peroxide value (PV), acid value (AV), conjugated dienes (CD), total polar compounds (TPC), *p*-anisidine value (*p*-AN), and volatile compounds of the oils were monitored.

Polyunsaturated fatty acids of the tested oils significantly decreased after frying ($P<0.05$). SBO among the tested oils was the highest in tocopherols, followed by POO and VST, while they were not detected in RCO. Tocopherols in SBO, POO and VST, and DPPH radical scavenging activities of POO and VST significantly

decreased after frying (P<0.05). Significantly strong correlations between total tocopherol contents and DPPH radical scavenging activities of POO and VST were observed (P<0.01). *L** values of the oils significantly decreased, and *a** and *b** values significantly increased after frying (P<0.05). AV, CD, TPC, and *p*-AN of the oils significantly increased after frying (P<0.05). RCO, which has a high level of saturated fatty acids, seemed to be the most stable among the tested oils, considering the levels of CD and *p*-AN. Volatile compounds in the oils significantly increased after frying (P<0.05). Compositions and contents of alkanals, 2-alkenals, and 2,4-alkadienals in the oils during frying were affected by their fatty acid compositions.

In conclusion, fatty acid composition and tocopherol content of frying oils may be important factors that significantly affect physicochemical properties, oxidative stability, and levels and compositions of volatile compounds in repeatedly used oils.

Key words: Deep-fat frying; Fatty acid composition; Tocopherol; Physicochemical property; Oxidative stability; Volatile compound

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INTRODUCTION

Deep-fat frying is one of the best cooking techniques to make palatable foods with golden color, savory flavor, and desirable texture through a complete immersion of food materials in a frying oil. During frying, heat is transferred from oil to food materials, and water in fried products evaporates simultaneously with the products absorbing the oil (Nayak et al., 2016). In commercial frying process, frying oils are usually repeatedly used, consequently significantly decreasing quality of fried foods with formation of nonvolatile and volatile degradation products, some of which are potentially harmful to human health (Takeoka et al., 1997).

Frying temperature, frying time, antioxidant contents, and fatty acid composition are important factors that affect chemical reactions (hydrolysis, oxidation, and polymerization) of the oils during frying (Choe and Min, 2007). Especially, oxidative stability of frying oils against the chemical reactions is differently affected by their fatty acid compositions (Karakaya and Şimşek, 2011). A number of previous studies have reported changes in physicochemical properties of different edible oils during frying process or heating. Xu et al. (2015) evaluated oxidative stability of camellia oil, palm oil, and peanut oil during frying at 170°C. Peterson et al. (2013) determined polymerized

triglycerides, total polar compounds (TPC), peroxide value (PV), *p*-anisidine value (*p*-AN), fatty acid composition, and volatile compounds of sunflower oil, high-oleic sunflower oil, rapeseed oil, high-oleic rapeseed oil, and palm olein during heating at 170°C, reporting that quality of the oils could be affected by their fatty acid compositions.

Physical parameters such as color and viscosity, and chemical parameters such as acid value (AV), PV, TPC, and *p*-AN have been generally considered to assess the quality of the oils (Mba et al., 2016). TPC and polymer contents (PC) have been considered to be reasonable to evaluate quality of frying oils in Europe, where they have recommended legal rejection limits of TPC and PC as 24-27% (w/w) and 10-12% (w/w), respectively (Hosseini et al., 2016). On the other hand, in Korea, AV and PV have been used to monitor quality of oils, and legal rejection limits are different by the types of the oils (Food Code, 2016). Formation of volatile compounds, especially aldehydes, in oils during frying could be determined by a headspace-solid phase microextraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS) (Thomsen et al., 2016). Also, degradation rate of antioxidants and antioxidant activity of oils could be analyzed to evaluate their oxidative stability (Karakaya and Şimşek, 2011).

Although frying oils are generally repeatedly used for production of fried products,

oxidative stability and volatile compounds of repeatedly used frying oils with different fatty acid compositions and antioxidant contents have been little studied. Thus, in this study, physicochemical properties and oxidative stability of refined coconut oil (RCO), refined soybean oil (SBO), pure olive oil (POO), and vegetable shortening (VST), which are widely used frying oils and have quite different fatty acid compositions, were determined during repeated frying of potato chips.

MATERIALS AND METHODS

1. Materials

RCO, SBO, POO (a mixture of refined and virgin olive oil), VST (a mixture of palm oil and palm stearin), and fresh potatoes were purchased from local markets in Seoul, Korea. The oils were stored at 4°C until used for frying. Fatty acid compositions of the fresh oils are shown in Table 1. A mixture of 37 fatty acid methyl esters (FAME), α-, γ-, and δ-tocopherols, pentanal, hexanal, octanal, decanal, 2-hexenal, 2-octenal, 2,4-heptadienal, 2,4-decadienal, *p*-anisidine, boron trifluoride (BF_3)-methanol solution, 2,2-diphenyl-1-picrylhydrazyl (DPPH), Folin-Ciocalteau reagent, and gallic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetic acid, acetonitrile, chloroform, ethanol, ether, hexane, isooctane, methanol, phenolphthalein, potassium hydroxide, potassium iodide, 2-propanol, starch, sodium carbonate, sodium hydroxide, and sodium thiosulfate were purchased from Samchun Chemical (Seoul, Korea). All chemicals and solvents were of analytical reagent grades.

Table 1 Fatty acid composition of fresh oils (unit: relative percent)

	Refined coconut oil	Refined soybean oil	Pure olive oil	Vegetable shortening
Fatty acids				
C8:0	5.6±0.1	ND	ND	ND
C10:0	5.4±0.1	ND	ND	ND
C12:0	47.0±0.5	ND	ND	ND
C14:0	19.8±0.9	ND	ND	1.2±0.02
C16:0	10.6±0.4	11.3±0.1	12.0±0.2	50.1±0.4
C18:0	3.6±0.2	4.7±0.03	3.2±0.03	4.7±0.01
C20:0	ND	0.1±0.2	ND	ND
SFA	92.0±0.3	16.1±0.1	15.2±0.2	56.0±0.4
C16:1	ND	ND	0.3±0.6	ND
C18:1n-9*c*	6.5±0.2	21.5±0.1	72.9±0.6	35.9±0.4
C18:1n-9*t*	ND	1.3±0.01	2.0±0.1	0.2±0.4
MUFA	6.5±0.2	22.9±0.1	75.2±0.1	36.1±0.3
C18:2n-6*c*	1.6±0.1	53.7±0.2	9.4±0.1	7.9±0.1
C18:3n-3*c*	ND	7.3±0.04	0.2±0.4	ND
PUFA	1.6±0.1	61.0±0.2	9.6±0.4	7.9±0.1

ND: not detected

Values are means and standard deviations (n=3).SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; and PUFA: polyunsaturated fatty acids

2. Frying procedure and sampling

To prepare potato chips, fresh potatoes were washed, peeled, and cut into slices of 4 mm thickness using a potato slicer. They were immersed in cold water and then pat dried with paper towels. Each oil (4 L) was placed in an electric fryer with 6 L capacity (Delki, Goyang, Korea) and heated to 180±5°C. The potato chips were fried for 4 min. After the chips were taken out, the oil was heated again for 2 min before the next frying. This process was repeated with 80 cycles. At every 20^{th} cycle, 80 mL of the oil was collected and stored at -20°C until analyzed.

3. Analysis of fatty acid composition

The oils were methylated using BF_3–methanol solution according to AOCS Official Method (2009) Ce 2-66. The fatty acid composition was determined using an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a capillary column (DB-23, 30 m x 0.25 mm x 0.25 μm, J&W Scientific, Folsom, CA, USA) and a flame ionization detector. Oven temperature was programmed as follows: from 50°C to 160°C at 25°C/min, to 220°C at 4°C/min held for 8 min, and to 250°C at 25°C/min held for 5 min. Split ratio was 1:50. Injector and detector temperatures were kept at 220 and 260°C, respectively. Fatty acids were identified with retention times of the standards and expressed

as % (relative area).

4. Analysis of total phenolic contents, tocopherols, and DPPH radical scavenging activity

Total phenolic (TP) contents of the oils were determined according to a Folin-Ciocalteau reagent method by Bail et al. (2008) with some modification. To prepare phenolic extracts, 1 g of each oil and 2 mL hexane were mixed in a test tube, and 2.5 mL methanol:water (90:10) solution was added, followed by vortexing for 1 min and centrifuging at 1350×g for 5 min. The extraction procedure was carried out three times for each oil and all of the three methanolic extracts were combined. The methanol:water (90:10) solution was added to make final volume be 10 mL. Eighty μL of each extract was placed into a test tube along with 200 μL water and 250 μL Folin-Ciocalteau reagent. After 5 min, 500 μL 10% (w/v) sodium carbonate were added, mixed, and held at room temperature for 60 min. Absorbance was measured at 765 nm using an UV-vis spectrometer (Spectramax 190, Molecular Devices, Sunnyvale, CA, USA) against a blank sample. TP content was expressed as gallic acid equivalents (GAE) mg/g oil, using a standard curve generated with a range of 2.5-100 μg gallic acid per 1 mL.

Tocopherols of the oils were analyzed using an HPLC (Ultimate 3000; Thermo

Scientific Dionex, Waltham, MA, USA) equipped with a silica-based column (ZORBAX Eclipse Plus C18, Agilent Technologies, Santa Clara, CA, USA) according to a method by Gliszczyńska-Świgło and Sikorska (2004). Each oil was dissolved in 1 mL 2-propanol, followed by filtering the solution using a 0.2 μm hydrophobic syringe filter (Advantec MFS Inc., Dublin, CA, USA). Mobile phase was methanol and acetonitrile (1:1) at 1.5 mL/min. A fluorescence detector was set at an emission wavelength of 325 nm and an excitation wavelength of 295 nm. Tocopherols were identified by comparing their retention times with those of corresponding standards.

DPPH radical scavenging activities of the oils were determined according to a method by Brand-Williams et al. (1995). Fifty μL of each oil was added with 950 μL 0.2 mM DPPH in methanol. The mixture was vortexed and held at room temperature for 5 min in the dark. Absorbance was measured at 515 nm using the UV-vis spectrometer against a blank sample. DPPH radical scavenging activity (%) was calculated as follows:

DPPH radical scavenging activity (%) = (1 - absorbance of the sample/absorbance of the DPPH solution) x 100.

5. Physicochemical properties

Hunter *L** (lightness: black (0) to white (100)), *a** (greenness (-) to redness (+)), and *b** (blueness (-) to yellowness (+)) values of the oils were measured using a spectrophotometer (CM-5, Konica Minolta Co., Tokyo, Japan). VST was melted at 60°C and the other oils were placed in a water bath at 30°C. Twelve mL of each oil was placed in a glass cuvette (10 mm path length). The cuvette was washed with hexane before the next measurement. AV, PV, and *p*-AN of the oils were determined according to AOCS Official Method (2009) Ca 5a-40, Cd 8-53, and Cd 18-90, respectively. Conjugated dienes (CD) of the oils were determined spectrophotometrically at 234 nm and read against hexane as blank. An extinction coefficient of 29,000 mol/L was used to quantify the concentrations of conjugated dienes (Saguy et al. 1996). TPC of the oils were spectrophotometrically determined at 490 nm using a method based on a correlation between TPC contents and absorbances of the oils proposed by Xu (2000). The equation used for a conversion of the absorbance to TPC (%) was: $y = -2.7865x^2 + 23.782x + 1.039$, where y is TPC (%) of an oil and x is its absorbance.

6. Analysis of volatile compounds

Volatile compounds of the oils were determined using a HS-SPME-GC/MS

method. Fiber type, extraction condition, and operating conditions followed a method by Lee et al. (2007) with a slight modification. One g of each oil was weighed in a headspace vial and placed into a shaking water bath at 65°C for 15 min for equilibrium. Extraction temperature was 65°C because VST melts above 60°C. After that, a fiber coated with divinylbenzene/carboxen/polydimethylsiloxane (50/30 μm film thickness, Supelco, Bellefonte, PA, USA) was inserted into the headspace of the vial and maintained for 60 min at 65°C to extract volatile compounds. The fiber was desorbed for 10 min in injection port of a Shimazdu QP2010 Plus gas chromatography (Shimazdu Co., Kyoto, Japan) equipped with a 0.75 mm ID glass injection liner, a capillary column (DB-5, 30 m x 0.25 mm x 0.25 μm, J&W Scientific, Folsom, CA, USA), and a mass selective detector. Oven temperature was programmed as follows: 40°C held for 2 min, to 160°C at 6°C/min, and to 280°C at 10°C/min held for 2 min. Interface and ion source temperatures were kept at 260°C. Helium was used as carrier gas at 25 cm/s. Injector temperature was kept at 250°C and splitless mode was used for injection. Scan mode was used for data analysis. Mass peaks of volatile compounds were identified by matching with mass spectrum and similarity indices of the National Institute of Standards (NIST) library or retention times of chemical standards spiked with RCO at cycle 0, which was free of these compounds under the same conditions.

7. Statistical analysis

All experiments were carried out in triplicate. The results were expressed as means±standard deviations. Independent t-test, one-way analysis of variance (ANOVA) with Duncan's multiple range test, Pearson correlation test, and principal component analysis (PCA) combined with VARIMAX rotation were performed with SPSS program (version 21.0, SPSS Chicago, IL, USA).

RESULTS AND DISCUSSION

1. Fatty acid composition of the frying oils

Fatty acid compositions of the frying oils used 80 times repeatedly are shown in Table 2. In RCO and VST, palmitic (C16:0) and stearic acids (C18:0) significantly increased after the frying 80 times repeatedly, and only C18:0 in POO significantly increased ($P<0.05$). Only oleic acid (C18:1) in RCO significantly decreased from 6.5% to 4.8% ($P<0.05$). Linoleic acid (C18:2) in the oils except SBO significantly decreased, and linolenic acid (C18:3) in SBO and POO significantly decreased from 7.3% to 7.1% and from 0.2% to 0%, respectively ($P<0.05$). These results similar to a previous study, reporting that fatty acid compositions of camellia oil, palm oil, and peanut oil, in which pre-fried potatoes were repeatedly fried, were rarely changed (Xu et al., 2015). Ratio of C18:2 to C16:0 (C18:2/C16:0) can be an indicator to monitor oxidation level of a frying oil (Aladedunye and Przybylski, 2009). C18:2/C16:0 of RCO, POO, and VST significantly decreased after frying ($P<0.05$). Despite of low proportion of unsaturated fatty acids (UFA) in RCO, C18:2/C16:0 of RCO remarkably decreased from 0.15 to 0.07. On the other hand, the fatty acid composition and C18:2/C16:0 of SBO, which had the highest polyunsaturated fatty acids (PUFA) among the tested oils (Table 1), rarely changed

after frying. Saturated fatty acids (SFA) in RCO, POO, and VST significantly increased, and PUFA in RCO, SBO, POO, and VST significantly decreased after frying ($P<0.05$). These results corresponded with a previous study, reporting that lipid oxidation results in degradation of UFA, consequently increasing SFA (Kamal-Eldin, 2006).

Table 2 Fatty acid composition of frying oils used 80 times repeatedly (unit: %, relative area)

	Refined coconut oil		Refined soybean oil		Pure olive oil		Vegetable shortening	
Cycle	0	80	0	80	0	80	0	80
C16:0	10.6±0.4	11.7±0.1*	11.3±0.1	11.6±0.3	12.0±0.2	12.6±0.3	50.1±0.4	51.2±0.1*
C18:0	3.6±0.2	4.0±0.1*	4.7±0.03	4.9±0.1	3.2±0.03	3.3±0.1*	4.7±0.1	4.8±0.01*
C18:1	6.5±0.2	4.8±0.4*	21.5±0.1	21.7±0.1	72.9±0.6	73.3±1.4	35.9±0.4	35.6±0.3
C18:2	1.6±0.1	0.8±0.1*	53.7±0.2	53.3±0.3	9.4±0.1	8.7±0.2*	7.9±0.1	7.1±0.1*
C18:3	ND	ND	7.3±0.04	7.1±0.2*	0.2±0.4	ND	ND	ND
C18:2/C16:0	0.15±0.01	0.07±0.01*	4.75±0.03	4.6±0.14	0.8±0.01	0.7±0.01*	0.16±0.00	0.14±0.00*
SFA	92.0±0.3	94.4±0.5*	16.1±0.2	16.7±0.3	15.2±0.2	15.9±0.4*	56.0±0.4	57.1±0.1*
MUFA	6.5±0.2	4.8±0.4*	22.9±0.1	23.0±0.2	75.2±0.7	74.9±0.6	36.1±0.3	35.8±0.1
PUFA	1.6±0.8	0.8±0.1*	61.0±0.2	60.3±0.2*	9.6±0.4	8.7±0.2*	7.9±0.1	7.1±0.1*

Values are means and standard deviations (n=3).

Significantly different within the same oil (*P<0.05; t-test).

ND: not detected; SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; and PUFA: polyunsaturated fatty acids

2. Total phenolic contents, tocopherols, and DPPH radical scavenging activities of the frying oils

Changes in TP contents of the repeatedly used frying oils are shown in Table 3. TP contents of all the oils were expected to decrease with frying cycles due to thermal destruction of phenolic compounds. However, TP contents of all the oils were not significantly different after frying ($P<0.05$).

Tocopherols and their antioxidant activity in an oil are significant factors on its oxidative stability besides its fatty acid composition (Xu et al., 2015). Changes in tocopherols in the repeatedly used frying oils are shown in Table 4. Tocopherols were not detected in RCO. Total tocopherol contents of SBO, POO, and VST at cycle 0 were significantly different ($p<0.05$) with 89.9, 14.9, and 8.7 mg/100 g oil, respectively. Tocopherols in the initial SBO were higher than in POO and VST. Tocopherol contents of soybean oil, olive oil, and palm stearin were reported to be 84.60, 17.46, and 3.8 mg/100 g oil, respectively (Gliszczyńska-Świgło and Sikorska, 2004; Speranza et al., 2015), which were similar to our study. During frying, α-, (β+γ)-, and δ-tocopherols of SBO, POO, and VST significantly decreased ($P<0.05$). Total tocopherols of SBO, POO, and VST after the 80 cycle frying decreased from 89.9 to 82.9 mg/100 g oil, from 14.9 to 2.3 mg/100 g oil, and from 8.7 to 0.6 mg/100 g oil, respectively, and their degradation rate (-7.8%) in SBO was remarkably lower than those in POO (-84.8%) and VST (-93.5%).

Measurement of DPPH radical scavenging activity is a typical way for monitoring reducing power of antioxidants in oil (Brand-Williams et al., 1995). Changes in DPPH radical scavenging activities of the repeatedly used frying oils are shown in Table 5. DPPH radical scavenging activities of POO and VST after the 80 cycle frying significantly decreased from 31.3% to 19.3% and from 39.8% to 12.5%, respectively ($P<0.05$). Significantly strong correlations between total tocopherols and DPPH radical scavenging activities of POO ($r^2=0.87$) and VST ($r^2=0.90$) were observed ($P<0.01$).

Table 3 Changes in total phenolic contents of repeatedly used frying oils (unit: GAE mg/g oil)

Cycle	Refined coconut oil	Refined soybean oil	Pure olive oil	Vegetable shortening
0	0.02±0.01[NS]	0.04±0.04[NS]	0.05±0.03[NS]	0.04±0.02[NS]
20	0.04±0.00	0.08±0.08	0.04±0.01	0.03±0.03
40	0.05±0.02	0.02±0.00	0.06±0.02	0.03±0.01
60	0.07±0.02	0.04±0.05	0.05±0.03	0.03±0.01
80	0.08±0.05	0.13±0.13	0.02±0.01	0.03±0.01

NS: not significant

Values are means and standard deviations (n=3).

Table 4 Changes in tocopherols in repeatedly used frying oils (unit: mg/100 g oil)

	Cycle	α-Tocopherol	(β+γ)-Tocopherol	δ-Tocopherol	Total
Refined coconut oil	0	ND	ND	ND	ND
	20	ND	ND	ND	ND
	40	ND	ND	ND	ND
	60	ND	ND	ND	ND
	80	ND	ND	ND	ND
Refined soybean oil	0	9.6 ± 0.3^{a}	57.3 ± 0.4^{a}	23.0 ± 0.3^{a}	89.9 ± 0.9^{a}
	20	9.5 ± 0.2^{ab}	56.1 ± 0.8^{a}	22.7 ± 0.3^{a}	88.3 ± 1.3^{a}
	40	9.1 ± 0.3^{b}	53.1 ± 1.3^{b}	22.0 ± 0.3^{b}	84.2 ± 1.6^{b}
	60	9.4 ± 0.4^{ab}	53.1 ± 0.6^{b}	22.0 ± 0.2^{b}	84.5 ± 1.1^{b}
	80	9.2 ± 0.1^{b}	51.7 ± 0.5^{b}	22.1 ± 0.2^{b}	82.9 ± 0.4^{b}
Pure olive oil	0	14.0 ± 0.2^{a}	0.8 ± 0.0^{a}	0.06 ± 0.00^{a}	14.9 ± 0.2^{a}
	20	10.4 ± 1.1^{b}	0.6 ± 0.1^{b}	0.05 ± 0.01^{a}	11.0 ± 1.2^{b}
	40	7.6 ± 1.0^{c}	0.4 ± 0.04^{c}	0.04 ± 0.01^{b}	8.0 ± 1.0^{c}
	60	4.6 ± 1.0^{d}	0.2 ± 0.03^{d}	0.04 ± 0.01^{bc}	4.9 ± 1.0^{d}
	80	2.1 ± 0.7^{e}	0.1 ± 0.01^{e}	0.03 ± 0.01^{c}	2.3 ± 0.7^{e}
Vegetable shortening	0	6.9 ± 0.2^{a}	1.1 ± 0.3^{a}	0.7 ± 0.1^{a}	8.7 ± 0.1^{a}
	20	3.2 ± 0.6^{b}	0.6 ± 0.1^{b}	0.5 ± 0.1^{b}	4.3 ± 0.8^{b}
	40	1.0 ± 0.8^{c}	0.3 ± 0.04^{c}	0.3 ± 0.1^{c}	1.6 ± 0.9^{c}
	60	0.3 ± 0.03^{c}	0.1 ± 0.03^{d}	0.2 ± 0.04^{cd}	0.6 ± 0.1^{d}
	80	0.4 ± 0.1^{c}	0.02 ± 0.01^{d}	0.2 ± 0.03^{d}	0.6 ± 0.1^{d}

ND: not detected

Values are means and standard deviations (n=3).

[a-e]Values with different superscripts represent significant differences within the same columns in each oil ($P<0.05$; one-way ANOVA and Duncan's multiple range test).

Table 5 Changes in DPPH radical scavenging activity of repeatedly used frying oils (unit: %)

Cycle	Refined coconut oil	Refined soybean oil	Pure olive oil	Vegetable shortening
0	20.3±1.8^{NS}	86.5±4.1^{NS}	31.3±2.9^{a}	39.8±9.5^{a}
20	15.9±3.7	85.8±2.9	26.7±4.4^{ab}	23.6±1.8^{b}
40	15.5±2.8	85.9±3.9	23.2±3.9^{bc}	19.4±4.5^{bc}
60	16.0±2.3	82.3±7.1	22.1±3.2^{bc}	15.1±3.2^{bc}
80	16.4±2.6	78.8±8.5	19.3±2.9^{c}	12.5±2.3^{c}

NS: not significant

Values are means and standard deviations (n=3).

$^{a-c}$Values with different superscripts represent significant differences within the same columns ($P<0.05$; one-way ANOVA and Duncan′s multiple range test).

3. Physicochemical properties of the frying oils

Color is a useful parameter often used in food industry for prompt monitoring of oil quality. Color of an oil during frying may be changed by brown pigments eluted from fried foods to the oil and degradation products derived from fatty acids in the oil during hydrolysis, oxidation, and polymerization (Nayak et al., 2016). Changes in *L*, a*,* and *b** values of the repeatedly used frying oils are shown in Table 6. In general, *L** values of the oils decreased, and *a** and *b** values increased during frying. These results similar to a previous study, reporting that *L** value of virgin coconut oil decreased, and *a** and *b** values increased during 8 h of frying (Srivastava et al., 2015). However, *b** value of POO at cycle 0 was higher than at cycle 80, probably because the initial POO contained a high amount of chlorophylls and carotenoids, which in turn might be rapidly degraded during frying (Abenoza et al., 2015). It was found that carotenoid content and *b** value of an olive oil had a significant correlation: the more the carotenoid content, the higher the *b** value (Minguez-Mosquera et al., 1991), suggesting that the initial POO in this study might contain a certain level of carotenoids considering the initial POO had relatively high *b** value, although their level was not measured in this study. However, *b** value of POO decreased just until cycle 20 of the frying in this study.

AV is a quality parameter to determine free fatty acids in an oil (Nayak et al.,

2016). AV of RCO, POO, and VST steadily increased (Fig. 1a) ($P<0.05$). On the other hand, AV of SBO slightly increased during frying. At cycle 80, AV of POO was 0.55, the highest among the oils. However, POO did not exceed legal rejection limits (less than 3.0) regulated by the Food Code (2016) in Korea.

PV is a typical quality parameter for measuring hydroperoxides in oil. PV of RCO and SBO significantly increased during the repeated frying ($P<0.05$) (Fig. 1b). PV of SBO marginally increased after the frying. PV of POO and VST not significantly increased. These results corresponded with previous studies, reporting that PV of frying oil may not increase constantly during frying because hydroperoxides are very unstable under frying temperature (Nayak et al., 2016; Guillén and Uriarte, 2012). However, PV of RCO remarkably increased during frying; this result is different from the other oils.

When oxidation of PUFA in an oil during frying process, double bond positions of PUFA are shifted, and as a result, conjugated double bonds are formed. Thus, measuring CD can be a reliable indicator on oxidation products of the oil during frying (Farhoosh et al., 2012). CD of all the oils significantly increased during the repeated frying ($P<0.05$) (Fig. 1c). CD of POO increased from 4.9 to 14.3 mmol/L, the highest increment rate among the oils. CD of SBO increased from 10.5 to 21.8 mmol/L, the highest among the oils. On the other hand, CD of RCO marginally increased with the lowest levels. These results suggest that RCO, which had the

lowest level of PUFA, may have lower oxidation products with conjugated double bonds than the other oils.

TPC of all the oils significantly increased during the repeated frying ($P<0.05$) (Fig. 1d). TPC of SBO showed the highest increment rate and levels. After frying, TPC of all the oils did not exceed the legal rejection limits after the 80 cycle frying.

p-AN is a quality parameter to determine contents of aldehydes such as 2-alkenals and 2,4-alkadienals in frying oil (Xu et al. 2015). *p*-AN of all the oils significantly increased during frying ($P<0.05$) (Fig. 1e). After frying, *p*-AN of SBO increased from 3.0 to 47.7, the highest increment rate and levels. On the other hand, *p*-AN of RCO marginally increased with the lowest levels.

RCO seemed to be the most stable among the oils during frying considering CD and *p*-AN of RCO, which were significantly lower than those of the other oils. On the other hand, although oxidation of SBO, which had the highest level of tocopherols (Table 4), might be suppressed by tocopherols in the oil during frying (Choe and Min, 2007), CD and *p*-AN of SBO had the highest among the oils. Nayak et al. (2015) reported that C18:3 showed the highest oxidation rates, followed by C18:2 and C18:1 among C18:0, C18:1, C18:2, and C18:3. RCO had the highest level of SFA, while SBO had the highest level of PUFA among the tested oils (Table 1). Thus, these results imply that the more UFA in the oil, the more oxidation and degradation products are formed during frying.

Table 6 Changes in *L**, *a**, and *b** values of repeatedly used frying oils

	Cycle	*L**	*a**	*b**
Refined coconut oil	0	99.6±0.1^{a}	-1.1±0.0^{c}	4.4±0.02^{e}
	20	97.7±0.1^{b}	-0.9±0.1^{bc}	7.3±0.5^{d}
	40	96.1±0.4^{c}	-0.7±0.2^{ab}	8.9±0.3^{c}
	60	94.4±0.1^{d}	-0.5±0.2^{a}	10.7±0.4^{b}
	80	92.5±0.1^{e}	-0.4±0.2^{a}	12.6±0.8^{a}
Refined soybean oil	0	99.0±0.1^{a}	-2.8±0.2^{b}	9.8±1.0^{e}
	20	97.6±0.4^{a}	-2.8±0.1^{b}	12.2±0.7^{d}
	40	95.9±0.7^{b}	-3.0±0.1^{b}	15.8±0.9^{c}
	60	93.5±1.0^{c}	-2.8±0.3^{ab}	20.1±1.6^{b}
	80	90.9±1.5^{d}	-2.2±0.5^{a}	23.9±1.7^{a}
Pure olive oil	0	95.2±0.05^{a}	-4.1±0.0^{d}	27.0±0.1^{a}
	20	95.0±0.3^{a}	-3.8±0.1^{cd}	18.3±0.2^{d}
	40	93.5±0.4^{b}	-3.5±0.2^{bc}	19.9±0.6^{d}
	60	91.8±1.0^{c}	-3.1±0.4^{ab}	22.9±1.3^{c}
	80	90.5±1.2^{c}	-2.9±0.5^{a}	25.1±1.6^{b}
Vegetable shortening	0	97.6±0.1^{a}	-4.4±0.1^{c}	17.0±0.5^{d}
	20	94.4±0.4^{b}	-4.2±0.1^{c}	22.5±0.2^{c}
	40	92.6±0.6^{c}	-3.9±0.2^{b}	25.9±1.2^{b}
	60	91.4±0.7^{d}	-3.6±0.2^{a}	27.4±1.5^{ab}
	80	90.6±0.4^{d}	-3.4±0.2^{a}	28.2±1.4^{a}

Values are means and standard deviations (n=3).

$^{a-e}$Values with different superscripts represent significant differences within the same columns in each oil ($P<0.05$; one-way ANOVA and Duncan′s multiple range test).

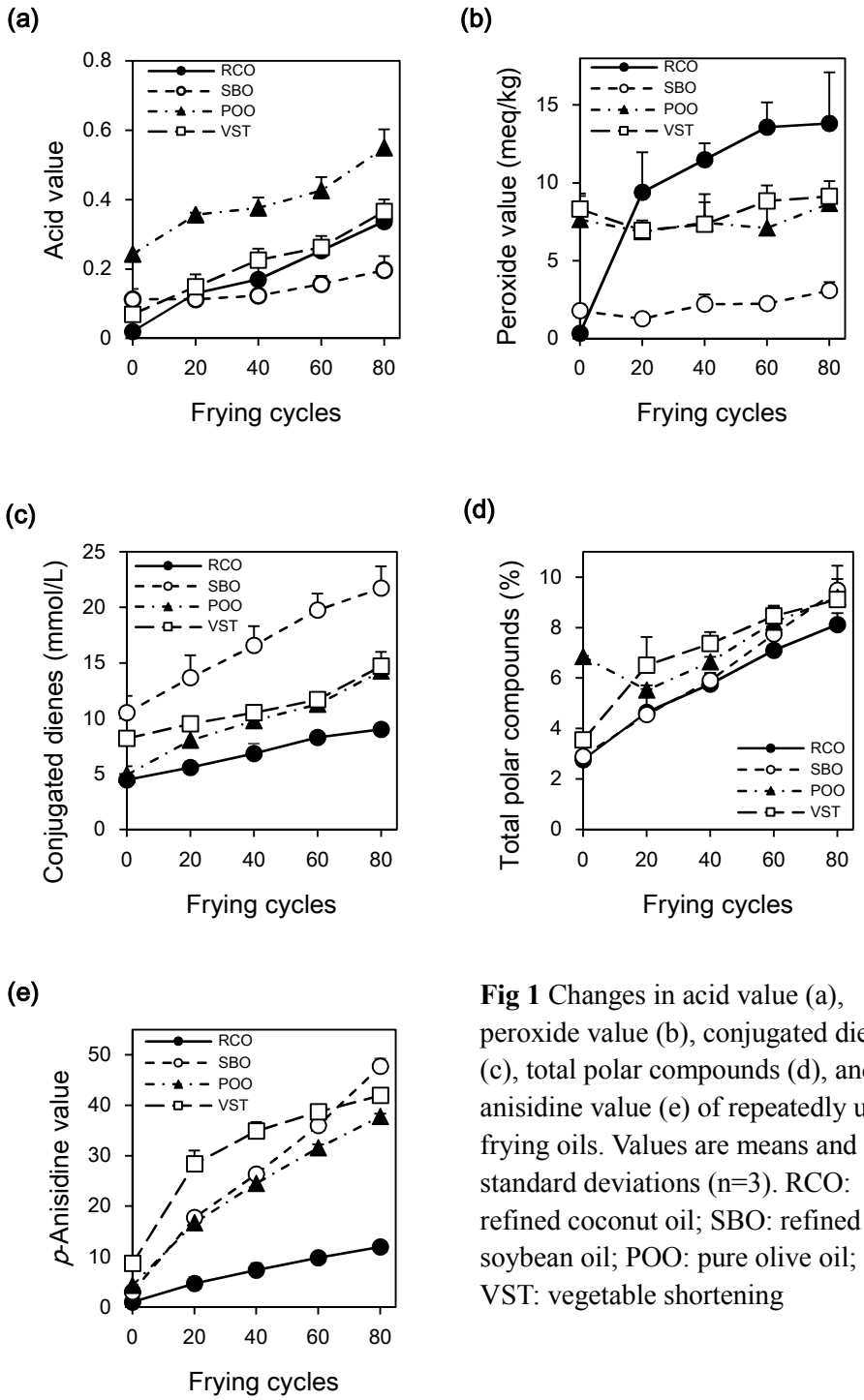

Fig 1 Changes in acid value (a), peroxide value (b), conjugated dienes (c), total polar compounds (d), and *p*-anisidine value (e) of repeatedly used frying oils. Values are means and standard deviations (n=3). RCO: refined coconut oil; SBO: refined soybean oil; POO: pure olive oil; and VST: vegetable shortening

4. Volatile compounds in the frying oils

After frying, numerous volatile compounds were generated (Fig. 2). Six alkanals (pentanal, hexanal, heptanal, octanal, nonanal, and decanal), eight 2-alkenals (2-propenal, 2-butenal, 2-pentenal, 2-hexenal, 2-heptenal, 2-octenal, 2-nonenal, and 2-decenal), and three 2,4-alkadienals (2,4-heptadienal, 2,4-nonadienal, and 2,4-decadienal) were identified by matching with mass spectra and similarity indices of the National Institute of Standards (NIST) library and retention times of compound standards (Table 7).

Changes in total volatile compounds, alkanals, 2-alkenals, and 2,4-alkadienals in the repeatedly used frying oils are shown in Fig. 3. Total volatile compounds in all the oils significantly increased until cycle 20, and then showed little changed until the end of frying ($P<0.05$). Changes in alkanals, 2-alkenals, and 2,4-alkadienals showed the same tendency as in the total volatile compounds. These results were similar to a previous study, reporting that changes in volatile compounds in oils did not show a linear increase during heating at 170°C (Petersen et al., 2013). These results imply that although volatile compounds derived from oxidation of fatty acids in an oil are constantly generated during frying, contents of volatile compounds in the oil could be changed depending on thermal degradation and emission of the volatile compounds into the atmosphere and reactions with food materials (Choe and Min, 2007; Guillén and Uriarte, 2012). After

frying, RCO, POO, and VST had the largest alkanals, while SBO had the largest 2,4-alkadienals.

Levels of pentanal, nonanal, decanal, 2-nonenal, 2-decenal, 2,4-heptadienal, and 2,4-nonadienal were significantly different among the tested oils after the 80 times repeated frying ($P<0.05$) (Fig. 4). Pentanal, nonanal, and 2-decenal have been known as off-flavor compounds in thermally oxidized oils: the more these compounds, the more off-flavor causing deterioration of oil quality is induced (Choe and Min, 2007; Pokorny, 1989). Pentanal, nonanal, and decanal were more in the repeatedly used RCO, POO, and VST than in the SBO. Especially, nonanal was predominantly detected in the RCO, POO, and VST. 2-Nonenal and 2-decenal were more in the POO and VST than in RCO and SBO. 2,4-Nonadienal was more in the RCO and VST than in the SBO and POO. On the other hand, 2,4-heptadienal was more in the SBO than in the RCO, POO, and VST. These results were similar to previous studies: Guillén and Uriarte (2012) reported that predominant volatile compounds of extra virgin olive oil and sunflower oil were nonanal and 2-decenal, and that of virgin linseed oil was 2,4-heptadienal after heating at 180°C. Wang et al. (2016) reported that generated volatile compounds, especially aldehydes, of soybean oil, corn oil, and canola oil during heating at 185°C were clustered by proportions of fatty acids (C18:1, C18:2, and C18:3) of the frying oils and there were

three clusters of aldehydes: 2-decenal and 2-undecenal (cluster 1 derived from C18:1), pentanal, hexanal, 2-octenal, and 2,4-decadienal (cluster 2 derived from C18:2), and 2-propenal, 2-hetepanl, and 2,4-heptadienal (cluster 3 derived from C18:3).

PCA for the volatile compounds of the repeatedly used frying oils are shown in Fig. 5. Component 1 was characterized by pentanal, heptanal, octanal, nonanal, decanal, 2-hexenal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2,4-nonadienal, and 2,4-decadienal. PCA scores of RCO, POO, and VST moved into positive scores of component 1 with an increase of frying cycle. Component 2 was characterized by 2-propenal, 2-butenal, 2-pentenal, and 2,4-heptadienal. PCA scores of SBO moved into positive scores of component 2 with an increase of frying cycle. Especially, 2-propenal, 2-butenal, and 2-pentenal, which were detected only from SBO during frying, contributed to statistical classification between SBO and the other oils. SBO had 7.3% C18:3, higher than the other oils. In accordance with C18:3 in SBO significantly decreasing after frying (Table 1), 2-propenal derived from C18:3 significantly increased during frying ($P<0.05$). 2-Propenal has been considered to be a possible carcinogen and can be generated during frying and transferred to fried products (Abraham et al., 2011). This result agrees with a previous study, reporting that the more proportions of PUFA in an oil, the more 2-propenal increased during heating at 180°C (Guillén and Uriarte, 2012; Wang et al.,

2016).

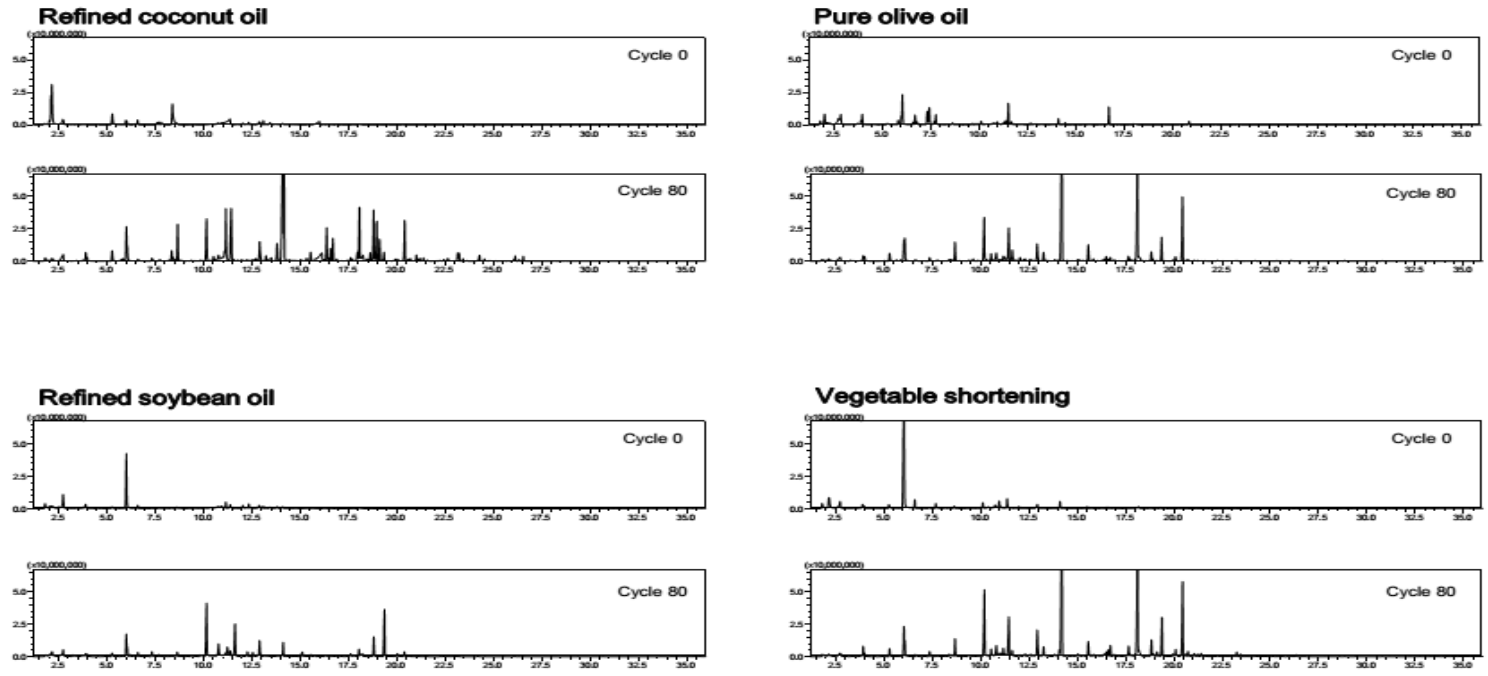

Fig 2 GC/MS chromatograms of frying oils used 80 times repeatedly

Table 7 Molecular weights and base peaks of detected alkanals, 2-alkenals, and 2,4-alkadienals in repeatedly used frying oils

	Molecular weights	Base peaks
Pentanal [1)]	86	44
Hexanal	100	44
Heptanal [2)]	114	43
Octanal	128	43
Nonanal	142	57
Decanal	156	43
2-Propenal	56	56
2-Butenal	70	41
2-Pentenal	84	55
2-Hexenal	98	41
2-Heptenal	112	41
2-Octenal	126	41
2-Nonenal	140	41
2-Decenal	154	44
2,4-Heptadienal	110	81
2,4-Nonadienal	138	81
2,4-Decadienal	152	81

1) The compounds written in bold face were identified by matching with mass spectra and similarity indices of the NIST library and retention times of compound standards.

2) The compounds written in non-bold face were identified by matching with mass spectra and similarity indices of the NIST library.

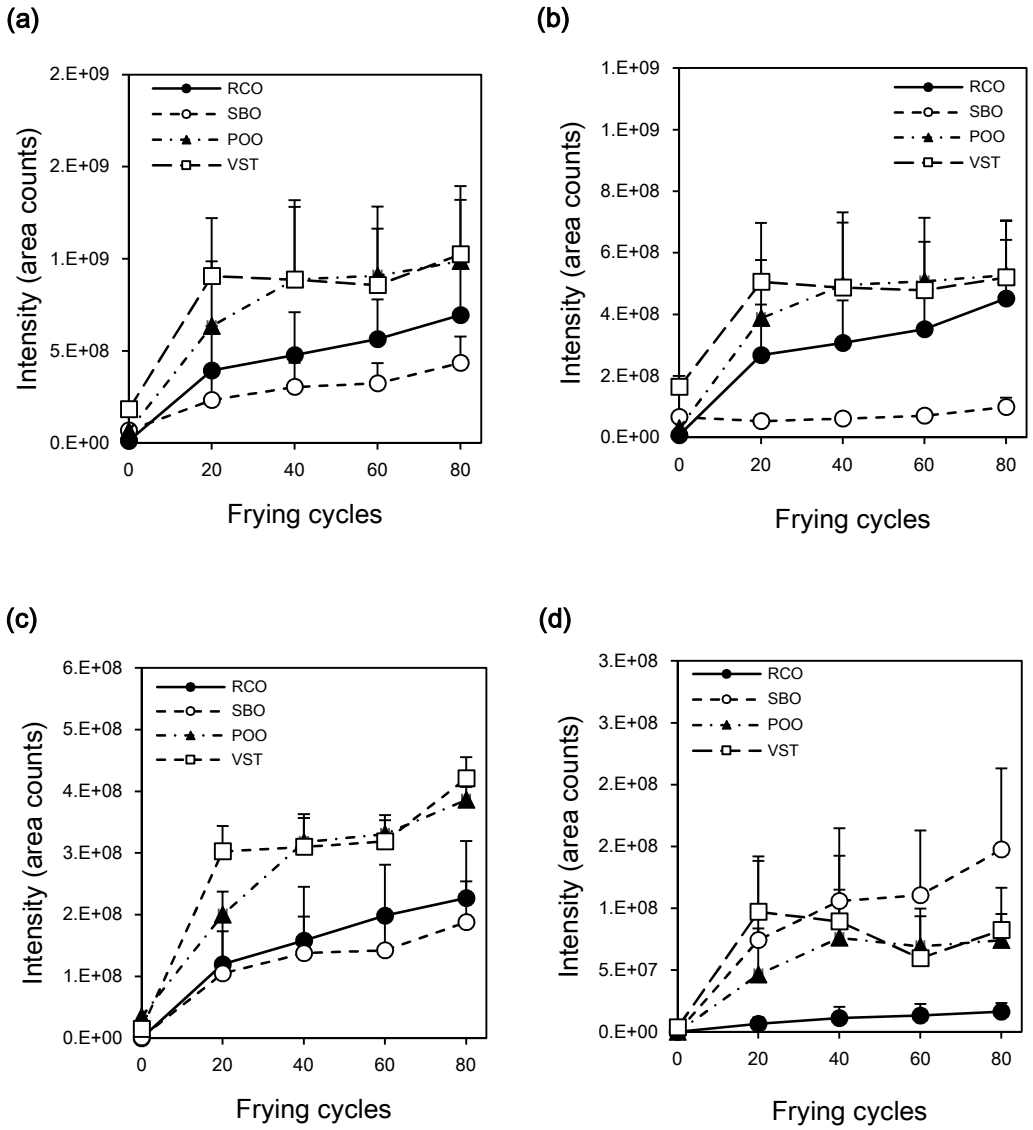

Fig 3 Changes in total volatile compounds (a), alkanals (b), 2-alkenals (c), and 2,4-alkadienals (d) in repeatedly used frying oils. Values are means and standard deviations (n=3). RCO: refined coconut oil; SBO: refined soybean oil; POO: pure olive oil; and VST: vegetable shortening

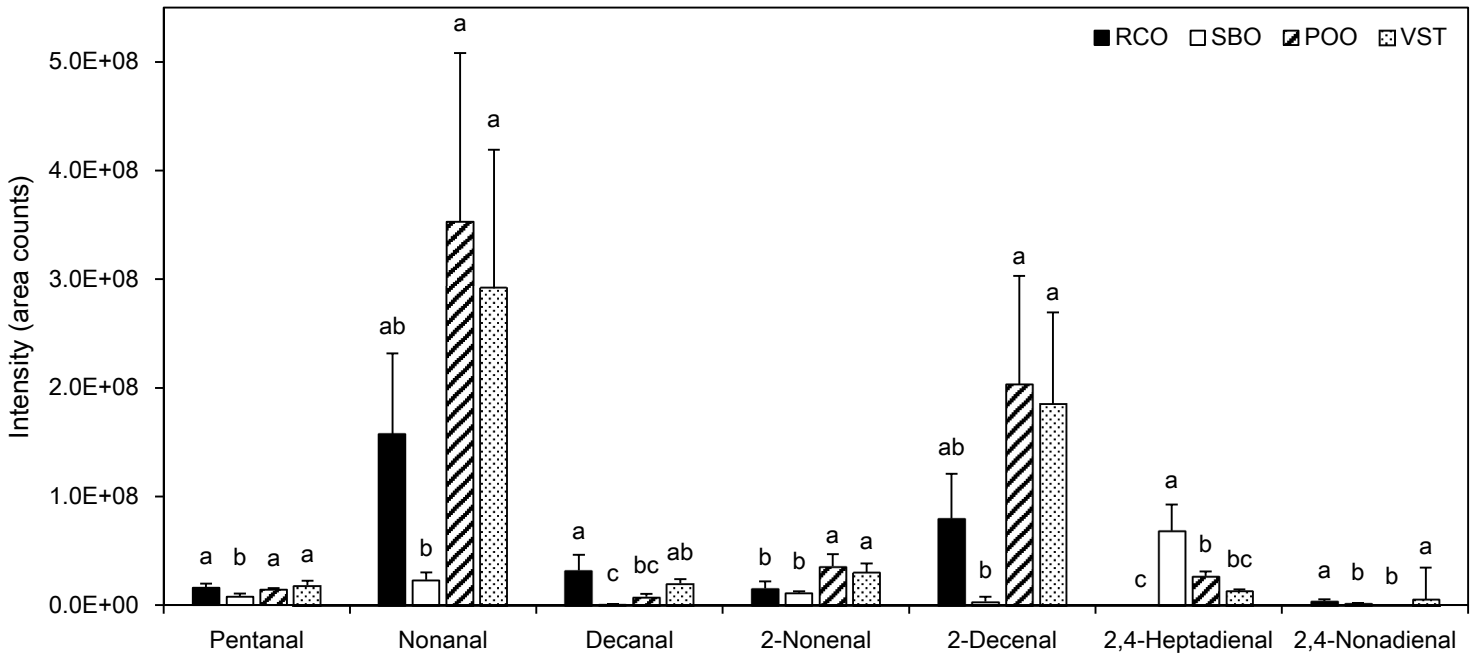

Fig 4 Volatile compounds in repeatedly used frying oils at cycle 80. Values are means and standard deviations (n=3). [a-c]Values with different superscripts represent significant differences within the same compounds ($P<0.05$; one-way ANOVA and Duncan's multiple range test). RCO: refined coconut oil; SBO: refined soybean oil; POO: pure olive oil; and VST: vegetable shortening

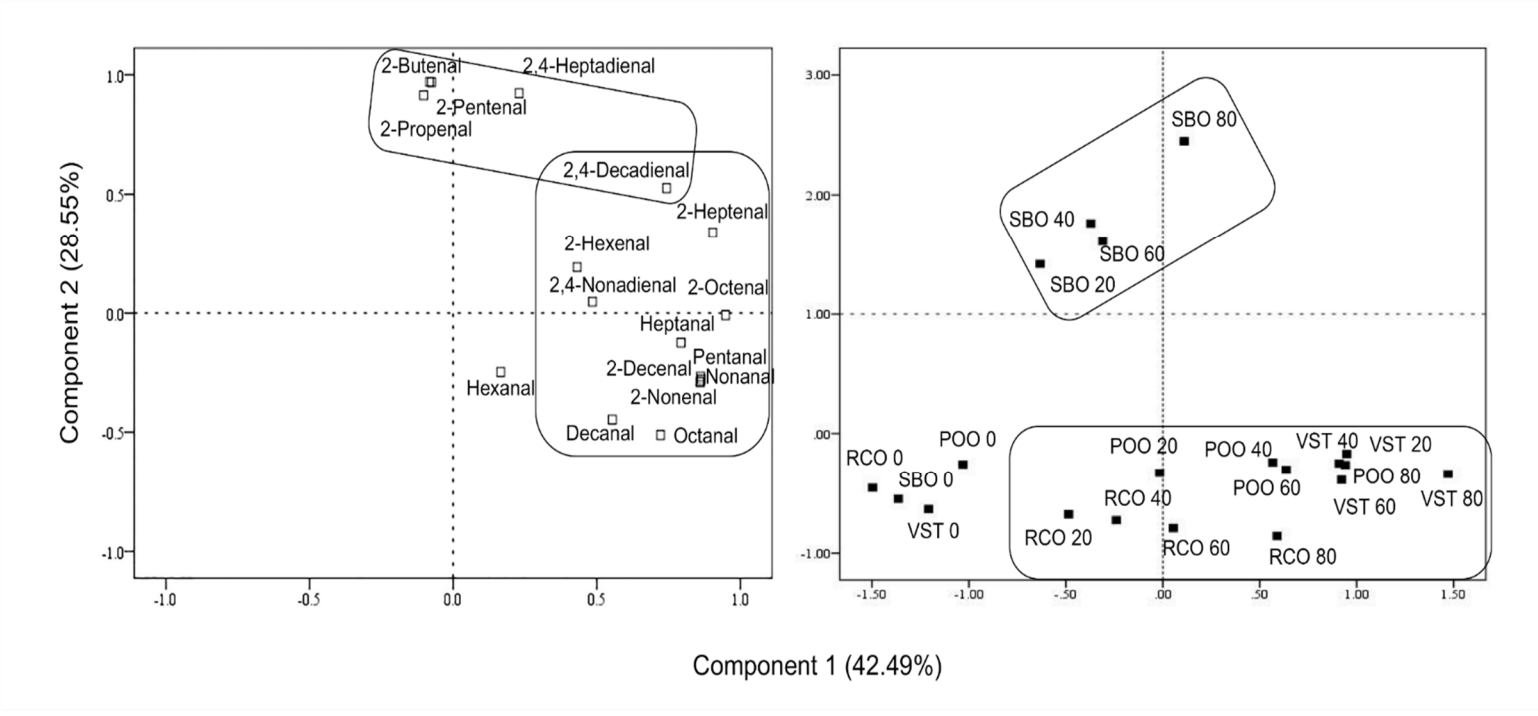

Fig. 5 PCA for volatile compounds in repeatedly used frying oils. RCO: refined coconut oil; SBO: refined soybean oil; POO: pure olive oil; and VST: vegetable shortening. Numbers after the oils are frying cycles

CONCLUSION

In this study, four frying oils with different fatty acid compositions and tocopherol contents were studied to determine physicochemical properties and oxidative stability of the oils repeatedly used for frying of potato chips. Although fatty acid compositions of the frying oils are slightly changed during the repeated frying, PUFA in all the oils significantly decreased after frying and SFA in RCO, POO, and VST significantly increased ($P<0.05$). *L** values of all the oils significantly decreased, and *a** and *b** values significantly increased ($P<0.05$). AV, CD, TPC, and *p*-AN of all the oils significantly increased ($P<0.05$). RCO, which had a high level of SFA, seemed to be the most stable among the tested oils, considering levels of CD and *p*-AN. Compositions and contents of alkanals, 2-alkenals, and 2,4-alkadienals in the oils were affected by their fatty acid compositions.

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국문초록

감자 칩을 반복하여 튀긴 기름의 이화학 특성 및 산화 안정성

유기선

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식품영양학과

튀김(deep-fat frying)은 식재료를 가열한 튀김유에 완전히 담가 고소한 풍미와 이상적인 식감(texture)을 가진 식품으로 가공하는 조리법 중 하나이다. 현재까지 튀김 과정에서 발생하는 화학 반응에 미치는 인자로 튀김 온도, 튀김 시간, 항산화제 함량, 지방산 조성 등이 보고되었다. 상업적으로 튀김유는 튀김 조리에 반복하여 사용되고 있음에도 불구하고 현재까지 보고된 선행연구들은 단순히 기름을 가열할 때 발생하는 이화학 특성에 대한

보고가 대부분이었다. 그러므로 반복 사용한 기름의 이화학 특성 및 산화 안정성 변화와 휘발성 물질 분석에 대한 연구가 필요하다.

본 연구에서는 상업적으로 많이 이용되고 지방산 조성이 다른 정제 코코넛유(refined coconut oil), 정제 대두유(refined soybean oil), 퓨어 올리브유(pure olive oil), 쇼트닝(vegetable shortening)을 튀김유로 선정하였다. 각각의 튀김유 4 L를 튀김기에 넣고 온도가 180±5℃가 되도록 가열한 후, 감자 칩을 4분간 튀겨내고 다시 2분간 예비 가열하여 다시 180±5℃가 되도록 하였다. 이 과정은 총 80번 반복하였고, 20번째마다 기름을 채취하여 분석에 사용하였다. 감자 칩을 반복하여 튀긴 기름의 이화학 특성 및 산화 안정성 변화를 비교하기 위해 지방산 조성, 총 폴리페놀 함량, 토코페롤, DPPH 라디칼 소거능, 색도, 산가, 과산화물가, 공액이중결합법, 총극성 물질, 아니시딘가, 휘발성 물질을 측정하였다.

튀김 후 모든 기름의 다가 불포화 지방산은 유의적으로 감소하였다($P<0.05$). 튀김 후 모든 기름의 총 폴리페놀 함량은 유의적인 차이가 없었다($P<0.05$). 튀김 전 정제 대두유, 퓨어 올리브유, 쇼트닝의 총 토코페롤 함량은 각각 89.9, 14.9, 8.7 mg/100 g oil이었으며, 튀김 횟수에

따라 유의적으로 감소하였다(P<0.05). 퓨어 올리브유와 쇼트닝의 DPPH 라디칼 소거능은 튀김 횟수에 따라 유의적으로 감소하였다(P<0.05). 튀김 횟수에 따른 퓨어 올리브유와 쇼트닝의 총 토코페롤 함량 변화와 DPPH 라디칼 소거능 변화 사이에 유의적인 상관관계가 있었다(P<0.01). 모든 기름의 *L** 값은 튀김 횟수에 따라 유의적으로 감소하였고, *a**와 *b** 값은 유의적으로 증가하였다(P<0.05). 모든 기름의 산가, 공액이중결합물, 총극성 물질, 아니시딘가는 튀김 횟수에 따라 유의적으로 증가하였다(P<0.05). 공액이중결합물과 아니시딘가를 기준으로 판단하였을 때, 정제 코코넛유가 산화 안정성이 가장 높았다. 튀김 후 모든 기름의 휘발성 물질은 유의적으로 증가하였다(P<0.05). 기름의 지방산 조성에 따라 기름의 주요 휘발성 물질인 alkanal류, 2-alkeanal류, 2,4-alkadienal류의 조성 및 함량이 변화하였다.

결론적으로 지방산 조성과 토코페롤 함량은 반복 사용한 기름의 이화학 특성 및 산화 안정성과 기름에 함유된 주요 휘발성 물질의 함량 및 조성에 상당한 영향을 미치는 중요한 인자가 될 수 있으며, 이에 따라 튀김유와 튀긴 식품의 품질이 달라질 수 있다.

주요어: 튀김; 지방산 조성; 토코페롤; 이화학 특성; 산화 안정성, 휘발성 물질

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