Effects of Sweet Potato Powder Selected Based on the Polar Paradox Hypothesis on Oil Oxidation in the Preparation of Deep-Fried Croquettes

Jiyea Lee and Jeonghee Surh
Department of Food and Nutrition, Kangwon National University, Gangwon 25949, Korea

ABSTRACT: This study investigated whether sweet potato powder (SPP) and purple SPP (PSPP) could prevent oil oxidation during deep-frying. A volume of soybean oil was repetitively used for deep-frying croquettes coated with either SPP or PSPP. An aliquot of the fried oil was collected (SPP and PSPP oils) before and after each frying to analyze moisture and lipid oxidation products (LOPs). With increasing numbers of frying, the moisture content in oils significantly increased without an appreciable difference between SPP and PSPP oils. The total oxidation values reflecting primary and secondary LOPs also significantly increased. However, the values were higher for PSPP oils despite the much higher antioxidant activity of the polar extracts from PSPP compared to SPP. This was attributed to the presence of transition metals. PSPP oils seemed to have association colloids whose interfaces were occupied more with polar antioxidants, thereby transition metals were easily reduced and their pro-oxidative activity increased. The polar paradox hypothesis stating that polar antioxidants are more effective in preventing lipid oxidation in bulk oil is not always applicable to real foods due to various food matrices.

Keywords: antioxidant activity, deep-frying, polar paradox, sweet potato powder, transition metal

INTRODUCTION

Deep-frying is a widely used cooking practice due to its easy and rapid preparation and the preferable texture properties of the resulting fried foods (Choe and Min, 2007; Zaghi et al., 2019). Generally, it uses vegetable oils as heat transfer media with relatively lower specific heat and higher thermal conductivity than water. During deep-frying, vegetable oils that typically have higher proportions of unsaturated fatty acids are exposed to air at a high temperature of 150°C to 190°C, facilitating the thermal oxidation of the oils (Dobarganes et al., 2000; Choe and Min, 2007). Oils that are thermally oxidized contain polar compounds, such as free fatty acids, monoglycerides (MG), diglycerides (DG), hydroperoxides, and various aldehydes (Choe and Min, 2007). Those polar compounds accumulate in oils with frying repetitions (Jo and Surh, 2020) and migrate into fried foods at the same concentrations as that of the oils during the mass transfer between fried foods and oils (Seppanen and Csallany, 2006; Ma et al., 2021). With the reported in vitro toxicities of polar compounds generated from lipid oxidation and their adverse effects on cardiovascular health, the frequent consumption of fried foods has been a safety concern, especially in combination with the repeated use of frying oils (Zaghi et al., 2019).

As one of the methods to prevent oil oxidation, the utilization of phenolic compounds has attracted food scientists due to the “polar paradox” hypothesis stating that polar antioxidants are more effective than nonpolar ones in retarding the oxidation of bulk oils (Frankel et al., 1994; Shahidi and Zhong, 2011; Zhong and Shahidi, 2012; Laguerre et al., 2017). According to the polar paradox hypothesis, “association colloids”, a type of reverse micelles, are formed in bulk oils due to the trace amounts of water and intrinsic surface-active components, such as MG and DG. Polar antioxidants, including phenolics, can be loaded into the water core of association colloids. Depending on the hydrophobicity of polar antioxidants, they can also act as surface-active materials with their polar groups surrounding the water and their aliphatic or aromatic carbon portions extending into the oil. Polar antioxidants can locate at the oil-water interfaces where lipid oxidation occurs and eventually prevent oil oxidation. In contrast, nonpolar antioxidants would be less effective due to the inability to migrate to the oil-water interface.
where oxidation is prevalent because they are solubilized throughout the oil phase (Laguerre et al., 2015).

Based on the polar paradox hypothesis, it was postulated that “water” as a core material of association colloids and “polar antioxidants” as surfactants could be critical in preventing oil oxidation during deep-frying. Therefore, whether the polar paradox hypothesis could be applied to real cooking practice by deep-frying croquettes coated with two types of sweet potato powder [SPP; regular SPP vs. purple SPP (PSPP)] was investigated. The two powders were selected because they have similar proximate compositions, such as moisture and fat content and different levels of polar antioxidants. Compared to sweet potato, purple sweet potato contains considerably higher amounts of anthocyanins, which are polar antioxidants (Li et al., 2019). Specifically, since the mass transfer between oils and fried foods occurs during deep-frying, this study tested whether moisture could act as a carrier of polar antioxidants from the coatings of fried foods to oils, thereby retarding the thermal oxidation of the oils during deep-frying.

MATERIALS AND METHODS

Chemicals and food materials
Folin-Ciocalteu reagent, gallic acid monohydrate, 2,2-diphenyl-1-picrylhydrazyl (DPPH), hexane, iso-octane (trimethylpentane), cumene hydroperoxide (80%), ferrous chloride (FeCl2), ammonium thiocyanate, 1-butanol, 1,1,3,3-tetraethoxypropane (TEP), 2-thiobarbituric acid (TBA), and p-anisidine (4-methoxyaniline) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Butylated hydroxytoluene (BHT) and Karl-Fischer (KF) titration reagent (Hydranal®-Composite 2) were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan) and Honeywell International, Inc. (Charlotte, NC, USA), respectively. Na2CO3, potassium chloride (KCl), sodium acetate, HCl, ethanol, chloroform, and methanol of the highest grade were purchased from Showa Chemical Industry Co. (Tokyo, Japan). SPP and PSPP produced from 100% domestic raw materials were purchased from Puresan Agricultural Corporation (Seoul, Korea) and Incha Corporation (Seoul, Korea), respectively.

Proximate composition and color property of SPP and PSPP
The proximate composition, including moisture, crude ash, crude fat, crude protein, and carbohydrate, was determined according to the Association of Official Analytical Chemists-approved standard methods (Helrich, 1990). The color was measured using a CR400 chroma meter (Konica Minolta Sensing, Osaka, Japan) and expressed as lightness (L), redness (a), and yellowness (b).

Determination of transition metals in SPP and PSPP
Transition metals in the powders were determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES, 5110VDV, Agilent Technologies, Inc., Santa Clara, CA, USA) after digesting the powders with 2 mL nitric acid and 7 mL hydrogen peroxide in a microwave digestion system (Ethos Touch Control, Milestone, Inc., Sorisole, Italy). The ICP-OES parameters for the Cu and Fe analysis were as follows: radiofrequency power 1.2 kW, plasma flow 12 L/min, nebulizer gas flow rate 0.7 L/min, auxiliary gas flow rate 1.0 L/min, radial viewing mode, and viewing height 4 mm.

Determination of β-carotene and anthocyanin in SPP and PSPP
β-Carotene was determined following the protocol of Li et al. (2017). The powder (1 g) was dispersed in 15 mL ethanol and extracted twice on a horizontal shaker (BS-21, Jeio Tech Co., Ltd., Gimp, Korea) at 25°C, 150 rpm for 30 min. The extract was centrifuged (5810R, Eppendorf, Hamburg, Germany) at 4°C, 3,091 g for 30 min, and the resulting supernatant was concentrated using a rotary evaporator (CH/R-100, Buchi, Flawil, Switzerland) at 45°C and 200 mbar. After filtering (Syringe Filter Unit, 13HP045AN, Advantec, Tokyo, Japan), the absorbance of the concentrate was measured at 453 nm using a spectrophotometer (EON microplate spectrophotometer, BioTek Instruments, Winooski, VT, USA). The β-carotene concentration was determined using its molar extinction coefficient at 453 nm in ethanol (141,000 L/mol cm).

Anthocyanin was determined according to the pH differential method with a slight modification (Lee et al., 2005). The powder (1 g) was dispersed in 9 mL of 30% ethanol and extracted thrice on a shaker (BS-21, Jeio Tech Co., Ltd.) at 60°C for 3 h. The extract was centrifuged (5810R, Eppendorf) at 4°C, 3,091 g for 20 min, and the supernatant was adjusted to a final volume of 15 mL. The resulting solution was fivefold diluted separately with 0.025 M KCl (pH 1.0) and 0.4 M sodium acetate (pH 4.5), and the absorbance of the diluted portions was measured at 520 and 720 nm (EON microplate spectrophotometer, BioTek Instruments, Winooski, VT, USA). Anthocyanin content was calculated using the following equation:

\[ \text{Anthocyanin content} = A \times MW \times DF \times (1,000/s) \]

and expressed on a cyanidin-3-glucoside (C3G) basis, where

\[ A = (A_{520 \text{ nm}} - A_{700 \text{ nm}})_{pH \ 1.0} - (A_{520 \text{ nm}} - A_{700 \text{ nm}})_{pH \ 4.5} \]

MW is the molecular weight of C3G (442.9 g/mol), DF is the dilution factor, and \( \epsilon \) is the molar extinction coefficient of C3G (26,900 L/mol cm).
Total reducing capacity (TRC) and DPPH radical scavenging activity of SPP and PSPP depending on extraction solvents

The antioxidant activity of SPP and PSPP was evaluated for three different solvent extracts at a wide range of polarity, with a consideration of the polarity index (PI) of the solvents, water (PI=9.0), ethanol (PI=5.1), and n-hexane (PI=0; Snyder, 1974). The powder (1 g) was dispersed separately in 9 mL water, ethanol, and hexane and extracted twice on a shaker (BS-21, Jeio Tech Co., Ltd.) at 25°C, 150 rpm for 4 h. The following centrifugation and filtration processes were the same as the preparation step for anthocyanin determination.

TRC was determined according to the Folin-Ciocalteu reagent method (Singleton et al., 1999). Each extract (1 mL) was added with 10% Folin-Ciocalteu reagent (1 mL) and mixed thoroughly for 5 min. After adding 10% Na2CO3 (1 mL), the mixture was allowed to react at room temperature in the dark for 1 h. Its absorbance was measured at 700 nm (EON microplate spectrophotometer, BioTek Instruments). TRC was expressed as gallic acid equivalents (GAEs). The DPPH radical scavenging activity based on both hydrogen atom transfer and single electron transfer was determined as follows (Brand-Williams et al., 1995; Liang and Kitts, 2014): each extract (100 μL) was mixed with 0.2 mM DPPH (1 mL) in ethanol, and the absorbance of the mixture was monitored at 525 nm with an interval of 5 min for 24 h (EON microplate spectrophotometer, BioTek Instruments). Distilled water and 0.2 mM gallic acid were used as a blank and positive control of the method, respectively. The DPPH radical scavenging activity was calculated as the percent inhibition of the sample relative to that of a blank.

Croquette preparation and frying oil sample collection

The croquette was prepared according to the recipe of Jo and Surh (2020). Potatoes were steamed for 1 h, cooled at room temperature, peeled off, and mashed. Mashed potatoes (30 g) were rolled in a spherical shape and coated with 4 g beaten egg and 1.5 g SPP or PSPP. Before deep-frying, an aliquot of new soybean oil was sampled (“Before”). Soybean oil (2.5 L) was preheated in a deep fryer (Kitchen-Art, Incheon, Korea) at 180°C, and five croquettes were deep-fried in hot oil for 1 min. After moving the fried croquettes out and cooling the oil for 1 h, 40 mL of the fried oil were collected as a sample (“Day 1, after frying”). For reuse, the remaining oil was stored for 24 h in a deep fryer covered with a stainless-steel lid and wrapped thoroughly with aluminum foil. When the oil had cooled down, and the croquettes residue had settled, 40 mL of the oils were collected after filtering with a filter paper [ECO430(43C), Winners, Seoul, Korea; “Day 2, after filtering”]. The fried oil in a fryer was reused on the 3rd and 10th days without adding new soybean oil, with the same sample preparation process. The frequency and timing of frying oil reuse mimicked the typical deep-fat frying conditions conducted in actual cooking. That is, 40 mL of the oils were collected before deep-frying croquettes each day as samples that correspond to “Day 3, before frying” and “Day 10, before frying” oils. The other oil samples were also collected following the above protocol. All oil samples were measured for color immediately after collecting them. The oils were refrigerated at 4°C until analysis. Each sample was added with 0.1 g BHT to prevent further oxidation and sealed in an amber glass vial with a Teflon-lined cap.

Color measurement

The color of the frying oils was measured using a Lovibond colorimeter (Lovibond PFX880/L, The Tintometer Ltd., Amesbury, UK). Forty milliliters of the oil were taken in a 5.25-inch glass cell (13.8×1.9×3.9 cm3) and measured for its lightness (L), redness (a), and yellowness (b).

Determination of moisture

The moisture in the frying oils was quantified by a KF titration (Ruiz, 2004) method using a KF potentiometric titrator (702 SM Titrino, Metrohm, Flawill, Switzerland). One gram of oil dissolved in 50 mL methanol/isopropyl alcohol (2:1, v/v) was titrated with a KF titration reagent (Hydranal Composite 2, Honeywell International, Inc.). Moisture content was automatically calculated by a titrator based on volumetric analysis.

Determination of conjugated diene (CD) and conjugated triene (CT)

The frying oil (0.03 g) was dissolved in 10 mL isooctane and filled up to 25 mL with additional isooctane. The absorbance of the solution was measured at 233 and 268 nm for CD and CT, respectively, using a spectrophotometer (UV-1650, Shimadzu, Kyoto, Japan). The CD and CT values were expressed as the extension value (E) using the following equation: \( E = A / (C_l \times l) \), where A is the absorbance at either 233 or 268 nm, \( C_l \) is the concentration of the sample solution (g/100 mL), and \( l \) (cm) is the pathlength of the cuvette (Pegg, 2004).

Determination of the peroxide value (PV)

The PV of the frying oils was determined according to the ferric thiocyanate method, which is based on the ability of peroxides to oxidize ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}; Chapman and Mackay, 1949). The FeCl2 solution was prepared by adding 0.0328 M BaCl2 solution slowly with stirring to 0.036 M FeSO4·7H2O solution and precipitating excess BaSO4 with 10 N HCl (1 mL). The frying oil (0.01 g) was dissolved in 3 mL methanol/butanol (2:1, v/v). The sample solution was sequentially added with
Table 2. Transition metals, β-carotene, anthocyanin, and total reducing capacity of SPP and PSPP, as influencing factors on oil oxidation

| Variable                  | SPP        | PSPP       |
|---------------------------|------------|------------|
| Transition metal (mg/kg)  | 5.9±2.2    | 7.2±1.9    |
| Cu                        | 85.6±35.5  | 75.5±32.0  |
| Fe                        | 4.1±0.0*** | 4.7±0.1*** |
| Crude protein             | 6.1±4.4    | 198.3±11.5 |
| Carbohydrates             | 83.1       | 82.8       |
| Color property            |            |            |
| Lightness (L)             | 81.2±0.06  | 56.10±0.01*** |
| Redness (a)               | 1.33±0.00  | 15.79±0.00*** |
| Yellowness (b)            | 13.77±0.01 | 0.51±0.01*** |

Data are presented as mean±SD (n=3). Significant differences between samples by t-test (***P<0.001).

Statistical analysis
All experiments were performed in triplicate, and the results were expressed as the mean±standard deviation of the measurements. Analysis of variance and Duncan’s multiple range test were conducted using IBM SPSS Statistics (version 24.0, IBM Corp., Armonk, NY, USA). P<0.05 was considered significant.

RESULTS AND DISCUSSION

Comparison of physicochemical properties between SPP and PSPP
The proximate composition, color property, and antioxidant activities of SPP and PSPP are shown in Table 1 and 2. The moisture and crude fat contents were not significantly different between the two powders, suggesting that there might be no appreciable difference in the levels of association colloids formed in the frying oil when the powders were used as coating ingredients for deep-frying.
Crude ash was statistically higher in PSPP than in SPP (P<0.001; Table 1), whereas there was no significant difference in the content of transition metals (i.e., Cu and Fe; Table 2), indicating that the levels of pro-oxidative metals that are loaded into the water core of association colloids might be similar when the metals in the powders were effluxed to frying oils. Compared to SPP, PSPP was significantly lower in lightness and yellowness and higher in redness (P<0.001; Table 1), presumably due to the appreciably higher amounts of anthocyanin and relatively lower amounts of β-carotene (P<0.001; Table 2). The β-carotene (a lipophilic compound) content was determined as 1.11 and 0.54 μg/g in SPP and PSPP, respectively, approximately twice higher for SPP. However, yellowness was 27 times higher for SPP than for PSPP, indicating that the strong redness caused by the higher amounts of anthocyanin of PSPP might have masked its yellowness by carotenoid pigments. Indeed, the anthocyanin (a hydrophilic compound) content in PSPP was 198.3 μg/g as C3G equivalents, which was 33 times higher than SPP (P<0.001; Table 1), resulting in an appreciably higher TRC of polar extracts from PSPP. In detail, the TRC of the water and ethanol extract from PSPP was 3,151 and 809 μg/g as GAEs, respectively, approximately twice as much as SPP. In contrast, there was no significant difference in the TRC of the nonpolar hexane extract (Table 2). Similarly, the DPPH radical scavenging activity was also higher in PSPP and polar extracts than in their counterparts (Fig. 1). Considering the polar paradox hypothesis stating that polar antioxidants are more active in bulk oil than nonpolar antioxidants due to their better affinity to the interface of association colloids (Laguerre et al., 2011; Shahidi and Zhong, 2011), PSPP was expected to be more effective in retarding oil oxidation during deep-fat frying.

Changes in the moisture content and color of frying oil
The moisture content of the oil (Table 3) was 200 ppm before deep-frying. With an increasing number of frying repetitions, the moisture content of the frying oils increased significantly (P<0.001) to 293 to 610 ppm for SPP and 380 to 637 ppm for PSPP presumably due to the transfer of water from the croquettes to the frying oils. For most of the oils collected, there was no significant difference in the moisture contents between the two oil groups, which could be attributed to the similar water content of the two powders (Table 1). According to Laguerre et al. (2011), the increased moisture would form association colloids in oils, allowing polar substances to place within the colloids and amphiphilic substances to
concentrate at the interfaces. Commercial vegetable oils have not only nonpolar triglycerides but also amphiphilic components, such as MG, DG, phospholipids, and fatty acids (Laguerre et al., 2011). In addition, water-soluble substances, such as metals and polar antioxidants, in foods could migrate into the oils along with water during deep-frying (Rosseli, 1998). Therefore, the observed changes in the moisture content of the oils will be discussed later in oil oxidation, as the physicochemical status of the various substances in oils is affected once the association colloids are formed (Laguerre et al., 2011; Laguerre et al., 2015).

The color properties of the oil are shown in Table 4. With an increasing number of frying, the lightness of the oils decreased ($P<0.001$), with the increases in the yellowness and the weak fluctuations in the redness ($P<0.001$). It could be attributed to the formation of dark brown polymers mediated by lipid peroxyl radicals generated at high temperatures (Koh et al., 2015), the release of pigments from the croquettes into frying oils (Jo and Surh, 2020; Lee and Surh, 2021), and/or the thermal degradation of anthocyanins and subsequent formation of polymeric color products (Jiang et al., 2019). For most of the oils collected, the redness of the oils was negative, even for the oils in contact with PSPP, which appeared to be independent of the anthocyanin content. The yellowness of PSPP oils was relatively higher than that of SPP oils (Table 4) despite the much lower yellowness of PSPP powder (Table 1). The phenomenon could be attributed to the characteristic response of anthocyanins to heat (i.e., thermal degradation of anthocyanins and formation of a polymeric color; Patras et al., 2010; Jiang et al., 2019). Anthocyanins in PSPP were degraded and polymerized during deep-frying and thereby lost their

### Table 4. Color properties of the oil used for deep-frying croquettes coated with either SPP or PSPP

| Oil sample       | Lightness (L) | Redness (a) | Yellowness (b) |
|------------------|---------------|-------------|----------------|
|                  | SPP           | PSPP        | Significance   | SPP           | PSPP        | Significance   | SPP           | PSPP        | Significance   |
| Before           | 94.7±0.0d     | 94.7±0.0d   | −10.3±0.0i     | −10.3±0.0i    | 43.2±0.0i    | 43.2±0.0i    |
| Day 1, after frying | 81.0±0.1i   | 89.0±0.3h   | −9.9±0.1f      | −10.6±0.3d    | 53.0±0.0g    | 60.2±0.1d    |
| Day 2, after filtering | 99.0±0.1b  | 96.6±0.1b   | −12.3±0.0d     | −11.9±0.1h    | 61.2±1.0i    | 63.2±1.0i    |
| Day 3, before frying  | 97.8±0.0b   | 98.1±0.1b   | NS             | −12.5±0.2e    | 65.1±0.1f    | 65.0±0.1f    |
| Day 3, after frying  | 106.2±0.4i  | 103.0±0.3i  | NS             | −14.2±0.1d    | 74.4±1.4i    | 71.3±0.2f    |
| Day 4, after filtering | 90.0±0.1i   | 92.9±0.4i   | NS             | −10.5±0.1c    | 67.0±1.0i    | 67.3±1.0i    |
| Day 10, before frying | 93.4±0.1e  | 89.5±0.6e   | NS             | −11.6±0.1d    | 69.7±1.0b    | 66.7±0.5d    |
| Day 10, after frying  | 86.8±0.1h   | 89.3±0.6e   | NS             | −10.5±0.1c    | 63.6±0.2a    | 71.7±0.5f    |
| Day 11, after filtering | 89.8±0.1g  | 86.8±2.4f   | NS             | −10.2±0.0b    | 65.1±0.1i    | 68.5±0.1b    |

Data are mean±SD (n=3).
Different letters (a-h) within the same column are significantly different at the specified $P$-value.
Significant differences by Duncan’s multiple range test at *$P<0.05$, **$P<0.01$, and ***$P<0.001$.
SPP, sweet potato powder; PSPP, purple sweet potato powder; NS, not significant.

### Table 5. Conjugated diene, conjugated triene, and peroxide value as indexes of primary oxidation products in the oil used for deep-frying croquettes coated with either SPP or PSPP with frying repetition

| Oil sample       | Conjugated diene (E) | Conjugated triene (E) | Peroxide value (mEq/kg) |
|------------------|----------------------|-----------------------|-------------------------|
|                  | SPP                  | PSPP                  | Significance            | SPP                  | PSPP      | Significance            |
| Before           | 3.1±0.1d             | 3.1±0.1e             | NS                      | 1.1±0.0f             | 1.1±0.0e             | 0.73±0.04e          | 0.73±0.04f         |
| Day 1, after frying | 3.4±0.1e             | 3.4±0.1d             | NS                      | 1.2±0.1b             | 1.2±0.1e             | 0.99±0.04d          | 0.99±0.02d         |
| Day 2, after filtering | 3.3±0.1e             | 3.6±0.1c             | NS                      | 1.2±0.0a             | 1.3±0.0e             | 1.05±0.07d          | 1.19±0.06d         |
| Day 3, before frying  | 3.3±0.1c             | 3.5±0.1c             | NS                      | 1.1±0.1a             | 1.2±0.0e             | 1.04±0.02d          | 1.37±0.09d         |
| Day 3, after frying  | 3.5±0.3c             | 3.7±0.3c             | NS                      | 1.2±0.1b             | 1.3±0.1c             | 1.48±0.16d          | 1.21±0.04c         |
| Day 4, after filtering | 3.4±0.3c             | 3.3±0.4e             | NS                      | 1.2±0.1b             | 1.1±0.1c             | 1.63±0.16d          | 1.31±0.08c         |
| Day 10, before frying | 3.6±0.1c             | 3.8±0.2d             | NS                      | 1.2±0.0b             | 1.3±0.1b             | 1.59±0.18b          | 1.22±0.05c         |
| Day 10, after frying  | 3.8±0.4b             | 4.5±0.1b             | NS                      | 1.3±0.1b             | 1.5±0.0c             | 1.28±0.06b          | 1.47±0.07c         |
| Day 11, after filtering | 4.1±0.4b             | 4.4±0.2d             | NS                      | 1.4±0.1e             | 1.5±0.1c             | 1.35±0.01c          | 1.21±0.04c         |

Data are mean±SD (n=3).
Different letters (a-f) within the same column are significantly different at the specified $P$-value.
Significant differences by Duncan’s multiple range test at *$P<0.05$, **$P<0.01$, and ***$P<0.001$.
SPP, sweet potato powder; PSPP, purple sweet potato powder; NS, not significant.
Table 6. $p$-Anisidine value as an index of the secondary lipid oxidation products, and total oxidation value of the oil used for deep-frying croquettes coated with either SPP or PSPP

| Oil sample     | $p$-Anisidine value | Total oxidation |
|---------------|---------------------|-----------------|
|               | SPP        | PSPP   | Significance | SPP        | PSPP   | Significance |
| Before        | $-0.02\pm0.03^d$ | $-0.02\pm0.03^d$ | NS | $1.4\pm0.1^i$ | $1.4\pm0.1^i$ | NS |
| Day 1, after frying | $5.35\pm0.14^e$ | $5.45\pm0.25^e$ | NS | $7.3\pm0.1^e$ | $7.4\pm0.3^e$ | NS |
| Day 2, after filtering | $6.47\pm0.11^{a,c}$ | $6.47\pm0.43^{a,c}$ | NS | $8.6\pm0.2^d$ | $8.9\pm0.5^d$ | NS |
| Day 3, before frying | $5.46\pm0.04^e$ | $5.92\pm0.20^e$ | ** | $7.5\pm0.0^e$ | $8.6\pm0.2^d$ | ** |
| Day 3, after frying | $7.61\pm0.09^c$ | $7.16\pm0.49^d$ | NS | $10.6\pm0.3^c$ | $9.6\pm0.4^d$ | NS |
| Day 4, after filtering | $13.75\pm0.43^a$ | $15.47\pm0.90^a$ | NS | $17.1\pm0.0^c$ | $18.1\pm0.9^a$ | NS |
| Day 10, before frying | $5.23\pm0.26^a$ | $7.74\pm0.23^c$ | *** | $8.4\pm0.6^e$ | $10.2\pm0.3^c$ | *** |
| Day 10, after frying | $13.27\pm0.09^b$ | $15.08\pm0.83^a$ | ** | $15.8\pm0.1^b$ | $18.0\pm0.7^a$ | ** |
| Day 11, after filtering | $13.13\pm0.47^b$ | $13.96\pm1.06^b$ | NS | $15.8\pm0.5^b$ | $16.4\pm1.1^b$ | NS |

Data are mean±SD (n=3).
Different letters (a-f) within the same column are significantly different at the specified $P$-value.
Significant differences by Duncan’s multiple range test at *$P<0.05$, **$P<0.01$, and ***$P<0.001$.
SPP, sweet potato powder; PSPP, purple sweet potato powder; NS, not significant.

redness and gained brownness instead, leading to a lower lightness of the oils. Results showed a mass transfer from the croquettes to the frying oils during deep-frying.

Primary and secondary lipid oxidation products (LOPs) in frying oils depending on coating powders and frying repetition

CD and CT, the early primary LOPs, significantly increased ($P<0.01$) for both SPP and PSPP oils as the frying repetition increased (Table 5). However, there was not much of a difference between the two oil groups in the levels of CD and CT at the same processing condition. The CD values were higher than those of CT, presumably due to the appreciably higher proportions of linoleic acid than linolenic acid in soybean oil (Surh and Kwon, 2002). PV, an indicator of the second step of the primary LOP, was 0.73 mEq/kg before frying (Table 5). As the frying repetition increased from the first frying on day 1 to the third frying on day 10, the PV of SPP oils increased to 1.48 mEq/kg and decreased to 1.28 mEq/kg ($P<0.001$), whereas the values of PSPP oils kept significantly increasing to 1.47 mEq/kg ($P<0.001$). The different responses to the heating could be attributed to the difference between the formation rate of hydroperoxides and their decomposition rate (McClements and Decker, 2007). As for SPP oils, the decomposition rate of hydroperoxides surpassed their formation rate at the third frying, indicating that the formation of secondary LOP might have been facilitated since then. Indeed, $p$-AV that reflected the secondary LOP significantly increased ($P<0.001$) from 7.61 at the second frying (day 3) to 13.27 at the third frying (day 10; Table 6). For PSPP oils, the formation rate of hydroperoxides appeared faster than their decomposition rate (Table 5). Nevertheless, the change in the $p$-AV of PSPP oils was similar to SPP oils. The TOTOX value that encompassed both primary and secondary lipid oxidation significantly increased ($P<0.001$) with an increasing number of frying repetitions for both SPP and PSPP oils (Table 6). Since the antioxidant activity of polar extracts was higher in PSPP powder than in SPP powder (Table 2), and the content of water that could form association colloids in oils was similar between the two oil groups (Table 3), PSPP oils were expected to be less susceptible to thermal oxidation based on the polar paradox hypothesis. Unexpectedly, the TOTOX values of PSPP oils were higher than those of SPP oils (Table 6).

There are a couple of possible reasons for the observations. First, this could be attributed to the low thermal stability of anthocyanins, which are major antioxidants in polar extracts from PSPP (Patras et al., 2010; Jiang et al., 2019). Most anthocyanins might have been decomposed

![Fig. 2. Expected location and physical status of water, polar antioxidants, transition metals, and hydroperoxides in oil during deep-frying croquettes either coated with sweet potato powder (SPP) (A) or purple SPP (PSPP) (B).](image-url)
Table 7. Pearson correlation coefficients among the levels of lipid oxidation products and moisture in the frying oils

|                | Redness | Yellowness | Moisture | CD   | CT   | PV   | p-AV  | TOTOX |
|----------------|---------|------------|----------|------|------|------|-------|-------|
| Lightness      | -0.882*** | 0.207      | 0.118    | -0.300* | -0.274* | 0.043 | -0.314* | -0.287* |
| Redness        | -0.341*   | -0.166    | 0.334*    | 0.296* | -0.145   | 0.255 | -0.145   | 0.221   |
| Yellowness     | 0.779***  | 0.515***   | 0.501***    | 0.836*** | 0.679*** | 0.718*** |
| Moisture       | 0.489***  | 0.490***   | 0.652***    | 0.544*** | 0.572*** |       |       |       |
| CD             | 0.989***  | 0.418**    | 0.631***    |       |       |       |       |       |
| CT             |          | 0.401**    | 0.590***    |       |       |       |       |       |
| PV             |          |            |   0.648***  |       |       |       |       |   0.706*** |
| p-AV           |          |            |            |       |       |       |   0.997*** |

Significant differences by Duncan’s multiple range test at *P<0.05, **P<0.01, and ***P<0.001.

CD, conjugated diene; CT, conjugated triene; PV, peroxide value; p-AV, p-anisidine value; TOTOX, total oxidation.

during deep-frying, and it could be evidenced by the increase in the yellowness of PSPP oils (Table 4). Jiang et al. (2019) reported that the loss of anthocyanin was well correlated with the polymeric color characteristics, such as an increase in yellowness or brownness. Second, this was presumably due to the ability of antioxidants to reduce transition metals, such as Cu and Fe (Laguerre et al., 2011). Considering the higher antioxidant activity of polar extracts from PSPP powder, PSPP oils might have contained the association colloids where polar antioxidants were more concentrated at the interface (Fig. 2). Therefore, oxidized metals within association colloids in PSPP oils could be more easily reduced; their action as pro-oxidants might have been much facilitated compared to SPP oils. Last, lower carotene content in PSPP than in SPP might have affected the higher TOTOX value of PSPP oils.

Correlations among lipid oxidation indices depending on coating powders and frying repetition

CD, CT, PV, p-AV, and TOTOX reflecting primary and/or secondary LOPs were significantly correlated (Table 7). Among the color values, yellowness was positively correlated with all LOP indices (P<0.001). It could be attributed to the anthocyanin decomposition and subsequent brownish polymer formation (Patras et al., 2010; Jiang et al., 2019). The moisture content in the frying oils was positively correlated with the primary and secondary LOP indices (P<0.001). Initially, the moisture in the frying oil was expected to prevent oil oxidation, as it could form association colloids and load polar antioxidants at the interface where lipid oxidation might occur (Frankel et al., 1994). The unexpected positive correlation was presumably due to the presence of transition metals. The water in the frying oils acted as a reservoir of not only polar antioxidants but also transition metals (Laguerre et al., 2011). Results demonstrated that the polar paradox hypothesis was not always applicable to real foods because other environmental factors, such as transition metals, might interact with antioxidants and affect lipid oxidation in bulk oil.

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AUTHOR DISCLAIMER STATEMENT

The authors declare no conflict of interest.

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