Effect of After-Cooking Darkening Inhibitors on Stability of Frying Oil and Quality of French Fries

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The effect of two after-cooking darkening inhibitors, sodium acid pyrophosphate (SAPP) and calcium acetate (CaAc), and their combined effect on frying oil stability and quality of french fries produced were evaluated over a period of 72 h. Samples of frying oil and par-fried french fries were taken at 3-h intervals through each experiment and analyzed for selected chemical and physical parameters. As the frying time increased, all the oil samples contained increased amounts of deterioration products. The color index and free fatty acid (FFA) values were highly correlated with frying time. There were no significant effects on oil properties in terms of FFA until 9 h of frying among the 4 pretreatments. However, from 12 to 72 h of frying, oil used to fry potatoes treated with SAPP contained less FFA than oils exposed to CaAc alone or in combination with SAPP. The fat content of par-fried french fries was approximately 0.11 g/g dry matter and remained relatively constant during extended frying. After-cooking darkening of par-fried french fries and final color of the fries were affected by the pretreatment, but not by the frying time.

KEY WORDS: Calcium acetate, canola oil, color, fat content, free fatty acid, french fries, frying oil, oil stability, SAPP.

Stability and sensory properties of frying oils are influenced by the characteristics of the oil, the product being fried and by the length of time of use. The physical parameters normally monitored to evaluate the stability of frying oils during frying include color, viscosity and smokepoint. The chemical parameters that reflect changes in the stability of oils during frying include free fatty acids (FFA), polar compounds (PC), fatty acid pattern, peroxide value and iodine value (1-7).

Paradis and Nawar (8) reported that the concentration of higher-molecular-weight compounds is a reliable indicator of fat deterioration. The formation and accumulation of these compounds are responsible for chemical changes, such as increase in FFA, carbonyl value and hydroxyl content and decrease in unsaturation; and for physical changes, such as increases in color and viscosity. Most methods for assessing deterioration of frying fats have been based on these chemical and physical changes in the frying oil (7). In North America, many snack food manufacturers and restaurant chains routinely monitor the percentage of FFA in frying oils as an indicator of deterioration (5). Lowry and Tinsley (9) developed a method of rapid colorimetric determination for free fatty acids which can be used as an indicator of excessive amounts of thermal oxidation products in oils.

Several factors affect the rate and degree of oil breakdown. Sebedio *et al.* (10) described the quality assessment of industrial par-fried french fries with palm oil. The effect of various pretreatments of french fried potatoes on the frying medium, however, is largely unknown. The objective of this study was to quantify the influence of four treatments for the control of after-cooking darkening in french fries on the physical and chemical characteristics of frying oil during repeated frying, as well as the effect on the quality of the french fries.

MATERIALS AND METHODS

Process procedures. Russet Burbank potatoes, obtained from local growers, were peeled with a Hobart vegetable peeler, cut mechanically (Hobart, Model A-200F, Hobart Canada Inc., Don Mills, Ontario, Canada) into 0.92 cm × 0.92 cm strips, rinsed with cold water, and water blanched at 82°C for 9 min (Cleveland, Model Ket-5T, Cleveland Range Ltd., Toronto, Ontario, Canada). The blanched potato strips were dipped into four different treatment solutions (as described below) for 1 min, air-dried at 65°C for 15 min, then fried at 189°C for 1 min in a commercial electric deep fryer (Garland SF, #11 Model E18SFBL, Mississauga, Ontario, Canada), and finally drained for 2 min upon removal from the fryer. After par-frying, the potato strips were cooled for 1 h at −15°C, then placed in plastic bags and stored at −20°C until further analysis. The frying oil used in this study was obtained from a local commercial french fry manufacturer and contained primarily hydrogenated canola oil. Typical characteristics of the fresh oil at the onset of the study were: Free fatty acids, 0.037 ± 0.003%; peroxide value, 0.617 ± 0.078 meq/kg (milliequivalents peroxide/1.0 kg sample); and iodine value, 67.4 ± 2.2. For each treatment, 19 L oil was used at the onset of frying. Each day the oil was heated to 185°C and allowed to equilibrate at this temperature for 30 min prior to frying. Four batches of blanched, dipped and dried potato strips (2.0 kg/batch) were fried during a 3-h period. At the end of each day, 500 mL of fresh oil was added, and the fryer was turned off and allowed to cool to room temperature. The frying process was conducted for 4 8-h days for the water treatment, 5 d for the sodium acid pyrophosphate (SAPP) and calcium acetate (CaAc) combination treatment (AcSp) and 9 d for each of the calcium acetate and SAPP treatments, yielding a total oil heating time of 32, 42 and 72 h, respectively. In a controlled experiment, the oil was heated for 5 d (35 h) without frying potatoes. Oil samples were taken at 3-h intervals for each treatment, cooled, flushed with nitrogen and stored at −20°C until subsequent chemical and physical analyses.

Treatments for control of after-cooking darkening. One-minute dipping treatments used for the control of after-cooking darkening of french fries were: i) Distilled water; ii(0.8% SAAP; iii) 1% CaAc (calcium acetate); and iv) two-stage dipping in which the samples were first immersed in 0.1% SAPP solution for 30 s, then into 0.5% CaAc solution for 30 s. All solutions were adjusted to pH 5.0 by addition of NaOH or acetic acid. Temperature of the solutions was maintained at 21 ± 2°C.

Analytical methods. The oil samples were analyzed in duplicate for the following parameters: FFA, (AOCS Method Ca 5a-40) (11) and peroxide value (AOCS Method Cd 8-53) (11). Fatty acids were analyzed in a gas chromatography (GC) equipped with a DBWAX column, 15 m × 0.32 mm (Chromatographic Specialties, Inc., Brockville, On-

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tario, Canada). The operating conditions were: Injection port temperature, 275°C; detector temperature, 285°C; column temperature, 200°C; carrier gas flow rate, linear velocity, 49.9 cm/s; and injection volume, 1 μL. Methyl esters of fatty acids were prepared by the boron trifluoride/methanol method of Metcalfe *et al.* (12). Identification of the fatty acids on the chromatogram was made by comparing the retention times of the frying oil methyl esters with those of known mixtures of methyl esters (NuChek Prep, Inc., Elysian, MN; GC reference mixture 17A) run on the same column under the same conditions. The fatty acid composition was expressed as area percentage of the total area from all methyl esters. Iodine value (IV) was calculated as follows (AOCS Method T2.1C-85) (11):

$$IV = 0.857 \times C18{:}1 + 1.726 \times C18{:}1 + 2.607 \times C18{:}3 + 0.783 \times C22{:}1 \tag*{[1]}$$

Color of the oil was determined from absorbance at 460, 550, 620 and 670 nm measured with a Beckman DU-50 spectrophotometer (Beckman Instruments, Orvine, CA), connected to an Epson Rx-80 printer and an IBM personal computer equipped with a "peak pick" program (Beckman Quart 1 soft-pak, Beckman Instruments according the AOCA Method Cc 13c-50 (11).

The nonpolar and polar components were fractionated in Sep-Pak cartridges (Millipore Canada Ltd., Mississauga, Ontario, Canada) (13). Approximately 80–90 mg of oil was placed on a Sep-Pak cartridge, the nonpolar fraction was eluted with 30 mL of petroleum ether/diethyl ether (98:2) and the polar fraction with 30 mL of methanol.

Quality evaluation of french fries. Color evaluation of par-fried french fries was assessed by six panelists using the magnitude estimation method (14). The magnitude estimates of each panelist were transformed and equalized prior to statistical analysis. The moisture content of the potato strips at different stages of processing was determined by air-drying the samples at 110°C for 2 h.

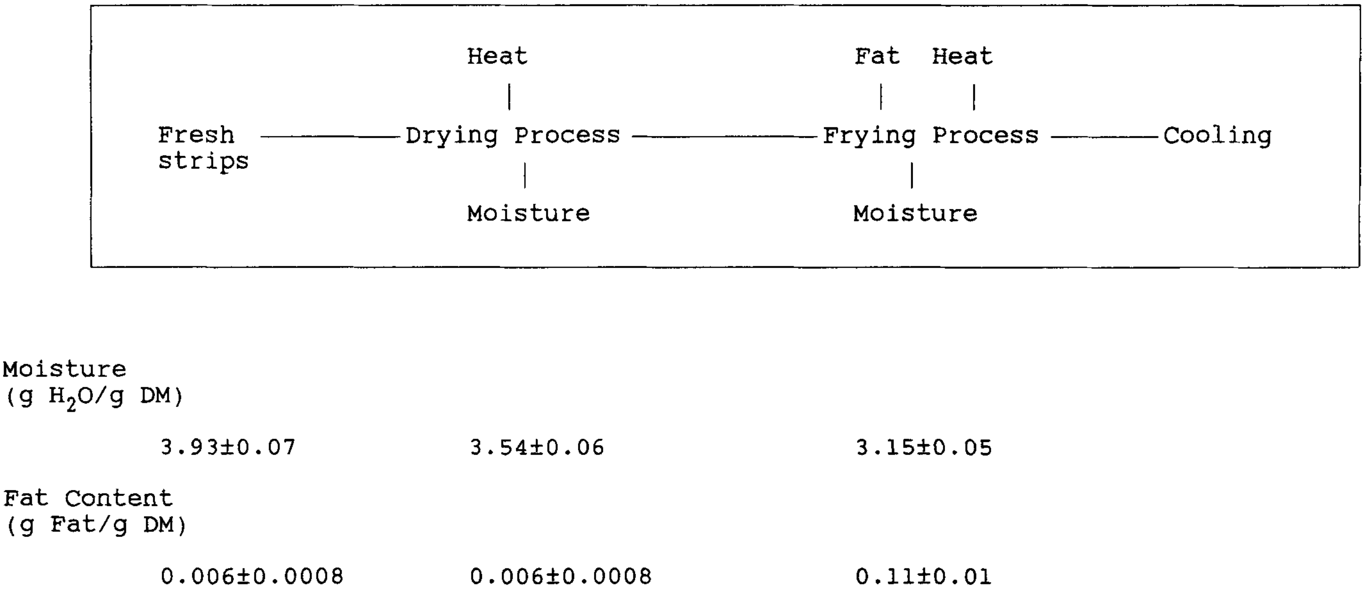
The fat content of par-fried french fries was analyzed by the Soxhlet extraction method (15). Approximately 5 g of ground sample was placed in an extraction thimble eluted with 150 mL of petroleum ether for 12 h. The petroleum ether was evaporated over a water bath in a fumehood. The samples were subsequently dried at 105°C until a constant weight was reached (approximately 2 h). The fat content was gravimetrically determined. The finish frying of par-fried frozen french fries was carried out at 180°C for 5 min. The color of final french fries was determined on a Model M31-A Agtron color meter (Magnuson Corp., Reno, NE) with the red mode scale (disc 00=00 and disc 90=90) and evaluated against the USDA color chart. Experimental data were analyzed by using SAS (Statistical Analysis System).

RESULTS AND DISCUSSION

The moisture and fat balance during the drying and frying operations for the production of par-fried french fries is shown in Scheme 1.

The fat content of the potatoes before frying was 0.2% on a fresh weight basis (FWB), and the total solids (20.3% FWB) remained essentially constant during the washing, peeling, cutting, blanching, dipping and drying operations. However, there was approximately 9% moisture loss (from 79.7 to 71.9%) during the 15-min drying operation and 8% (from 71.9 to 63.9%) during the 1-min par-frying process.

Quality assessment of the frying oil. The fatty acid composition of the frying oil did not exhibit a significant change with frying time (Table 1), which is in agreement with previous results reported in the literature (5). However, there was a slight decrease in the concentrations of linoleic (C18:2) and linolenic acid (C18:3) and an increase in oleic acid (C18:1) for all the treatments as the frying time increased, particularly for the SAPP and CaAc treatments at the frying time of 72 h. This suggests that the frying oil became more saturated with increased frying time. The physical and chemical properties of the frying oils subjected to the four different pretreatments and the



SCHEME 1

TABLE 1

Fatty Acid Composition of Oils Used to Fry Potato Strips Treated with H_2O, SAPP, CaAc and a Combination of SAPP with CaAc

Treatment and frying time (h)	C16:0	C18:0	C18:1	C18:2	C18:3	C20:1
Control^{a}						
0	4.1	10.8	69.1	2.6	0.7	1.8
11	4.2	10.7	69.2	3.2	0.4	1.8
23	4.3	10.5	69.1	3.8	0.8	1.8
33	4.2	10.7	69.4	3.3	0.4	1.8
Water						
0	4.7	10.6	67.0	5.3	0.9	1.9
12	4.6	10.7	66.2	5.1	2.3	2.5
23	4.5	10.9	66.5	4.7	2.1	2.3
32	4.4	11.0	68.2	4.5	0.7	2.2
SAPP						
0	4.1	10.9	68.8	2.4	0	2.0
12	4.1	11.0	69.2	2.7	0.4	1.7
24	4.1	10.9	68.6	2.7	0.3	1.9
42	4.2	11.1	69.5	2.7	0	1.7
72	4.0	11.7	71.6	2.3	0	1.8
CaAc						
0	4.0	10.2	69.0	3.1	1.4	1.5
12	4.0	10.5	70.2	2.7	0.1	1.6
24	4.0	10.5	70.4	2.7	0.1	1.6
42	4.0	10.5	70.2	2.6	0.1	1.6
72	4.1	11.0	72.2	2.3	0	1.6
AcSp (SAPP + CaAc)						
0	3.9	10.2	70.2	2.8	0.2	1.6
12	4.1	10.5	70.2	2.7	0	1.7
24	4.0	10.6	70.1	2.7	0	1.8
42	4.0	10.5	69.9	2.7	0	1.7

[a] Oil heated without frying of potato strips.

TABLE 2

Physical and Chemical Properties of Frying Oil Exposed to After-Cooking Darkening Inhibitors and Frying Times^{a}

Treatments and frying time (h)	Color index	Peroxide value (meq)	FFA (%)	Iodine value
Control				
0	0.73^{c}	0.55^{a}	0.04^{d}	66.9
11	1.90^{b}	1.34^{a}	0.05^{c}	67.5
23	$1.37^{b,c}$	1.69^{a}	0.06^{b}	73.4
35	3.17^{a}	1.10^{a}	0.07^{a}	67.8
Water				
0	0.59^{c}	0.72^{b}	0.04^{d}	70.5
12	1.68^{b}	$1.23^{a,b}$	0.10^{c}	71.5
24	$2.16^{a,b}$	$1.00^{a,b}$	0.22^{b}	72.4
32	2.29^{a}	1.75^{a}	0.38^{a}	69.6
SAPP				
0	1.11^{e}	0.62^{c}	0.04^{e}	64.6
12	1.53^{d}	0.90^{c}	0.10^{d}	66.2
24	2.22^{c}	0.91^{c}	0.22^{c}	65.8
42	3.61^{b}	1.94^{b}	0.56^{b}	65.6
72	6.61^{a}	2.55^{a}	1.49^{a}	66.7
CaAc				
0	0.83^{e}	0.66^{c}	0.04^{e}	69.4
12	2.04^{d}	1.44^{b}	0.11^{d}	66.4
24	2.76^{c}	1.82^{b}	0.25^{c}	66.5
42	4.32^{b}	2.80^{a}	0.66^{b}	66.1
72	8.55^{a}	2.58^{a}	1.61^{a}	67.1
AcSp (SAPP + CaAc)				
0	1.67^{d}	0.64^{d}	0.03^{d}	66.8
12	2.08^{c}	1.09^{c}	0.11^{c}	66.1
24	2.75^{b}	2.06^{b}	0.27^{b}	66.1
42	5.33^{a}	$2.51^{a,b}$	0.65^{a}	65.9

[a] Within each treatment each column means followed by the same letter are not significantly different at $P \leqslant 0.05$ using SNK test.

control are shown in Table 2. The color index ranged from 0.6 to 8.5% and increased with increasing frying time. The peroxide value (milliequivalents peroxide/kg) varied from 0.5 for fresh oil to a maximum of 2.8 in the oil exposed to the potatoes treated with CaAc at the frying time of 42 h. The relatively high variability of the peroxide values can likely be attributed to the instability of peroxide during the handling and storage of the oil samples before analysis (16). The amount of FFA in fresh oil ranged from 0.034 to 1.6%, and the iodine value ranged from 64 to 72.

Figure 1 illustrates the increase in the color index with increase in frying time of the oil. This indicates that the quantity of chemicals formed as the oil is heated during frying results in an increase in the UV absorption spectrum. The percentage of FFA in the frying oil as a function of frying time is shown in Figure 2. The concentration of FFA increased significantly as the frying time increased for all treatments. Equations [2] and [3] describe the change in FFA as function of time for the oil used to fry the potatoes treated with SAPP and CaAc, respectively:

$$Y = 0.04 + 5 \times 10^{-4} X + 2.6 \times 10^{-4} X^2 \qquad [2]$$

$$Y = 0.04 + 13 \times 10^{-4} X + 2.8 \times 10^{-4} X^2 \qquad [3]$$

where Y represents % FFA in the oil and X represents the frying time. There was a significant difference between the X coefficients in these two equations. This indicates that development of FFA during frying of potatoes treated with the two inhibitors is significantly different, especially after extended frying times. The sharp decrease in % FFA at 42 h (Fig. 2) was expected, as 2 L of fresh oil was added at that time to maintain a sufficient oil level in the fryer for further frying. The concentration of FFA in the oil not used for frying of potatoes (control) changed little. Together, these results show strong interaction between oil and the frying potato strips, but only a limited effect of the pre-treatment of potatoes. There was no significant difference in the FFA content among the four treatments until 9 h frying and between CaAc and AcSp treatments at frying times before 15 h (Table 3). FFA appeared lower for CaAc than for AcSp at further frying times. SAPP and water treatments generally had low FFA levels as compared with other treatments. This suggests that the presence of CaAc may affect the stability of frying oil. The concentration of polar compounds, determined with the Sep-Pak cartridges, ranged from 3.9% in fresh oil to 19% for the oil used for 72 h to fry potato strips treated with CaAc. Some studies have reported a strong correlation between the concentration of FFA and the amount of polar compounds in the frying oils. According to Stevenson *et al.* (5), the relationship between FFA and PC of canola oil can be expressed by the equation Y = 4.48 + 6.99X, where Y represents the amount of polar components and X the amount of FFA. From this equation, the predicted level of PC in the fresh oil used in this study would be 4.74%, and that of oil used to fry potatoes treated with CaAc for 72 h would be 15.8% PC. A value of 27% PC was suggested by Paradis and Nawar (8) as a usage end-point for oils.

The correlation between color index, peroxide value, FFA value and IV of the frying oil and frying time are

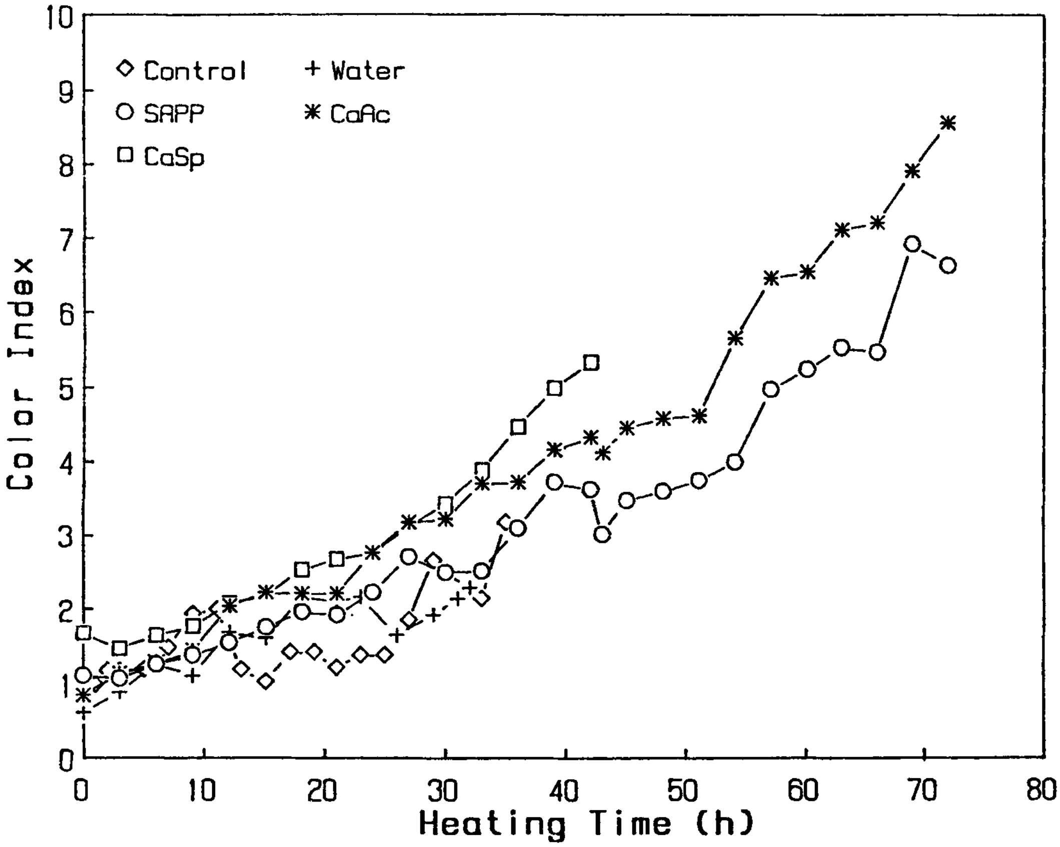


FIG. 1. Color index of the frying oil as a function of heating time.

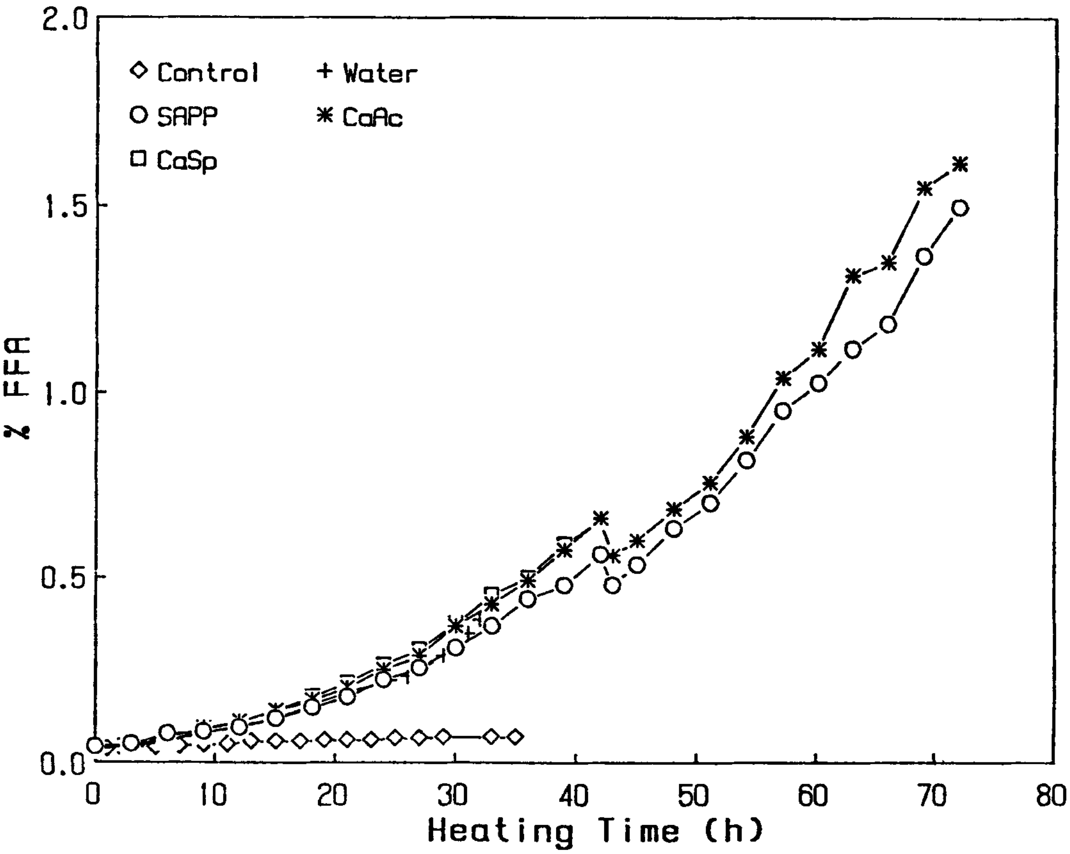


FIG. 2. Percent FFA of the frying oil as a function of heating time.

TABLE 3

Free Fatty Acids (g/g) in Frying Oil Exposed to Four Different Treatments

Time (h)	Control	Treatments[a] Water	SAPP	CaAc	AcSp
0	3.8^{a}	3.6^{a}	4.0^{a}	3.6^{a}	3.4^{a}
3	4.1^{b}	4.5^{a}	4.9^{a}	4.7^{a}	4.7^{a}
6	4.4^{a}	6.2^{a}	7.9^{a}	6.7^{a}	5.8^{a}
9	4.9^{b}	8.0^{a}	8.5^{a}	9.0^{a}	8.8^{a}
12	5.2^{c}	10.0^{b}	9.7^{b}	11.2^{a}	11.0^{a}
15	5.5^{c}	12.1^{b}	12.1^{b}	14.1^{a}	13.9^{a}
18	5.8^{e}	15.1^{c}	14.9^{d}	16.9^{b}	17.8^{a}
21	6.1^{d}	18.0^{c}	17.8^{c}	20.4^{b}	21.5^{a}
24	6.4^{d}	21.9^{c}	22.2^{c}	25.1^{b}	26.5^{a}
27	6.7^{d}	25.5^{c}	25.6^{c}	$28.9^{a,b}$	30.6^{a}
30	6.9^{c}	31.0^{b}	31.1^{b}	36.8^{a}	37.3^{a}
33	7.0^{d}	37.0^{c}	36.9^{c}	42.8^{b}	45.0^{a}
36	7.7^{c}	44.1^{b}	44.0^{b}	49.1^{a}	50.0^{a}
39	8.1^{d}	48.0^{c}	47.9^{c}	57.3^{b}	59.0^{a}
42	8.4^{d}	57.0^{b}	56.4^{c}	66.0^{a}	65.3^{a}

[a] Within each row means followed by the same letter are not significantly different ($P \leqslant 0.05$) by the SNK test.

shown in Table 4. A high correlation ($r > 0.83$) between color index and frying time was observed for all treatments except for the control. The peroxide value correlated highly with frying time for CaAc ($r = 0.97$) and AcSp ($r = 0.90$), as well as SAPP treatment ($r = 0.77$), and was not significant for the water treatment and control. FFA values were significantly correlated with frying time ($r > 0.96$) for all of the treatments, including the control, indicating that FFA is a critical factor in determining the extent of deterioration of the frying oil. Iodine value was negatively and nonsignificantly correlated with frying time for all treatments except for the water treatment, which was positive.

Quality assessment of par-fried french fries. Table 5

TABLE 4

Correlation Coefficients Between Color Index, Peroxide Value, FFA, Iodine Value and Frying Time for Four Different Treatments

Treatments	Color index	Peroxide value (meq)	FFA (%)	Iodine value
Control	0.52	0.44	0.98	−0.20
Water	0.83	0.48	0.96	0.13
SAPP	0.94	0.77	0.96	−0.14
CaAc	0.98	0.96	0.97	−0.52
AcSp (SAPP + CaAc)	0.96	0.90	0.96	−0.44

TABLE 5

Fat Content and After-Cooking Darkening of Par-Fried French Fries and the Color of Refried French Fries Subjected to Four Different Treatments[a]

Treatment time (h)	Fat content		ACD		Final color	
	% (tw)	g/g (DM)	Score	Log (ME)[b]	Agtron	Chart
Water						
1	4.32^{a}	0.12^{a}	1.80^{a}	0.27^{a}	52.8^{a}	54.3^{b}
9	3.71^{b}	0.11^{b}	1.60^{a}	0.22^{a}	46.3^{b}	54.3^{b}
15	4.01^{b}	0.11^{b}	1.70^{a}	0.24^{a}	50.5^{a}	56.0^{a}
21	3.77^{b}	0.11^{b}	1.00^{b}	0.16^{b}	50.0^{a}	56.3^{a}
26	4.51^{a}	0.13^{a}	2.00^{a}	0.31^{a}	49.5^{a}	57.6^{a}
31	4.31^{a}	0.12^{a}	2.10^{a}	0.33^{a}	47.3^{b}	56.3^{a}
SAPP						
1	4.70^{a}	0.12^{a}	8.10^{a}	0.73^{a}	56.3^{a}	58.7^{a}
24	5.01^{a}	0.11^{b}	7.70^{a}	0.71^{a}	54.7^{a}	57.7^{a}
36	3.25^{b}	0.09^{b}	8.68^{a}	0.76^{a}	55.0^{a}	59.0^{a}
48	4.67^{a}	0.13^{a}	8.05^{a}	0.73^{a}	55.2^{a}	59.3^{a}
63	3.63^{b}	0.10^{b}	8.10^{a}	0.73^{a}	53.5^{a}	59.0^{a}
72	3.27^{b}	0.09^{b}	9.03^{a}	0.78^{a}	50.0^{b}	59.3^{a}
CaAc						
1	$4.04^{b,c}$	$0.12^{b,c}$	5.83^{a}	0.61^{a}	50.7^{b}	54.0^{a}
24	$4.04^{b,c}$	$0.12^{b,c}$	6.70^{a}	0.67^{a}	52.5^{b}	54.0^{a}
36	$3.88^{b,c}$	$0.11^{b,c}$	8.35^{a}	0.69^{a}	54.0^{a}	57.7^{a}
48	5.03^{a}	0.14^{a}	7.65^{a}	0.71^{a}	52.7^{b}	55.3^{a}
63	3.29^{d}	0.09^{d}	7.25^{a}	0.72^{a}	54.2^{a}	55.7^{a}
72	3.58^{d}	0.10^{d}	6.65^{a}	0.58^{a}	52.2^{b}	55.7^{a}
AcSp (SAPP + CaAc)						
1	3.83^{a}	0.11^{a}	6.60^{a}	0.67^{a}	57.0^{a}	58.2^{a}
9	4.11^{a}	0.12^{a}	6.25^{a}	0.61^{a}	54.3^{b}	55.0^{b}
16	3.91^{a}	0.11^{a}	8.50^{a}	0.70^{a}	53.5^{b}	$55.8^{a,b}$
27	3.86^{a}	0.11^{a}	7.35^{a}	0.72^{a}	51.0^{c}	54.8^{b}
36	2.98^{b}	0.09^{b}	8.65^{a}	0.81^{a}	50.3^{c}	57.0^{a}
42	4.02^{a}	0.11^{a}	6.40^{a}	0.65^{a}	54.0^{b}	56.3^{a}

[a] Within each treatment each column means followed by the same letter are not significantly different at $P \leqslant 0.056$ by the SNK test.

[b] Logarithm magnitude estimate.

summarizes the results of par-fried and refried french fries. The fat content in potatoes prior to any frying was less than 0.2% (0.006 g fat/g DM). The fat content of the par-fried french fries prepared by the different treatments changed little with frying time of the oils, and ranged from 0.09 to 0.13 g fat/g DM (Table 5). Sebedio *et al.* (17) also found that the percentage of lipids in par-fried french fries was not affected by the continuous production process. For par-fried french fries, the average fat content was 0.11 ± 0.01 g fat/g dry matter (3.9 ± 0.4%). Lamberg *et al.* (15) studied the relationship between fat content and moisture content. They found that the fat uptake depends greatly upon the preprocessing conditions, especially the surface moisture content of potato strips prior to frying. In this investigation, the process conditions were standardized and the average moisture content of dried potato strips remained relatively constant (around 65 ± 2%) for all the treatments. Due to identical drying conditions, the same surface moisture content of dried potato strips could be achieved, resulting in a similar fat content in par-fried french fries over the frying time.

The results of the sensory evaluation for after-cooking darkening of par-fried french fries are presented in Table 5, both as color scores as scored on a line scale and as the logarithm magnitude estimates. There was no significant difference among the potato strips within each treatment as the frying time of the oil increased. Similarly, the final color of french fries measured both by Agtron and USDA charts did not indicate any consistent change as a result of frying time.

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