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Effects of Flour Storage Conditions on the Lipid Oxidation of Fried Products during Storage in the Dark

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Abstract The effect of flour storage conditions on the lipid oxidation of fried products during storage was studied. Wheat flour was stored at 60°C in the dark and at water activity (Aw) of 0.3, 0.5, or 0.8 for 21 days. The square-shaped dough (2×2×0.1 cm) made with the stored flour and water was fried in soybean oil at 160°C for 1 min. The fried products were stored at 60°C for 15 days in the dark. The degree of lipid oxidation of the fried products was evaluated by conjugated dienoic acid (CDA) content and *p*-anisidine value (PAV). Both CDA content and PAV of the fried products increased with lengthening storage time of the fried products, suggesting that longer storage of the fried products raised the lipid oxidation. Furthermore, the lipid oxidation of the fried products made with flour that had been stored for a longer time tended to be higher than that of those made with unstored or short-term-stored flour. However, Aw at which the flour was stored did not significantly affect the lipid oxidation of either flour or the fried products during storage. The storage time of flour clearly exerted a greater effect than Aw on the lipid oxidation of the fried products during storage at 60°C in the dark. This suggests that for the storage stability of fried products, the flour storage time is a more important factor than Aw at which the flour is stored.

Keywords: wheat flour, fried products, storage, lipid oxidation, water activity

Introduction

Lipid oxidation of fried foods is dependent on the composition of foods and frying oil and the storage conditions such as time, temperature, and water activity (Aw) (1, 2). Sugars, especially heated sugars, and proteins decrease lipid oxidation (3-5). Oils containing high amount of unsaturated fatty acids are easily oxidized (6, 7), and the transition metals and oxidized lipids accelerate the lipid oxidation (8-10). With increasing storage time and temperature, the lipid oxidation rate increases (11-13). Lipid oxidation does not show a constant pattern as Aw increases. The rate of lipid oxidation decreases with increasing Aw below the monolayer water region (14). At the intermediate moisture range, the lipid oxidation tends to be minimal because of the dilution of catalysts and collapse of food matrix by water (15). Above the intermediate moisture region, the lipid oxidation rate again increases with increasing Aw (16) due to increased catalyst mobility in the larger liquid volume (17).

Many fried foods are made with grains, such as wheat, corn, and oat, and wheat flour forms a major portion of all fried foods. Flour is exposed for various time periods to many different conditions, intentionally or by accident, before use. During this time, flour, which contains approximately 14% moisture (18), easily absorbs moisture from the humid environment, with a consequent deterioration of its quality by physical and chemical reactions. One of the chemical reactions contributing to quality deterioration in flour is lipid oxidation. Wheat flour lipid has a high content of unsaturated fatty acids (64-71%), mainly linoleic and linolenic acids, although the lipid content of flour is 2-4% (19, 20). Flour stored under different conditions might show different degrees of flour lipid oxidation, and can affect the quality of the fried products made with the stored flour. Very few studies have examined the effects of storage conditions on the flour quality and on the quality of the subsequent flour-based fried products. This study was performed to determine the effects of flour storage conditions on the lipid oxidation of wheat flour-based fried products during storage at 60°C in the dark.

Materials and Methods

Materials and chemicals Wheat flour and refined, bleached, and deodorized soybean oil were products of Daehan Flour Mills Co., Ltd. (Incheon, Korea) and CJ Co. (Seoul, Korea), respectively. Isooctane and n-hexane were purchased from J.T. Bakers, Inc. (Phillipsburg, NJ, USA). BF_3 in methanol, *p*-anisidine, and standard fatty acid methyl esters were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). All other chemicals were of reagent grade.

Sample preparation and storage Wheat flour was spread on No. 2 Whatman filter paper (Whatman International Ltd., Maidstone, Kent, UK) placed over three salt solutions in desiccators. The salt solutions were saturated $MgCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and $(NH_4)_2SO_4$ equivalent to Aw of 0.3, 0.5, and 0.8, respectively (21). The flour-containing desiccators were wrapped with aluminum foil and then placed in a 60°C incubator for 7 or 21 days. Stored flour (100 g) at Aw of 0.3, 0.5, or 0.8 was removed from the desiccator and mixed with distilled water (35 g) in a dough mixer (Aicohsha Manufacturing Co., Ltd., Saitama, Japan). The flour dough was sheeted at 0.1 cm thickness and then cut into squares (2×2 cm). One batch of square-shaped dough (120 g) was fried in an electric fryer (Phillips, Madrid, Spain) holding 3 L of soybean oil at 160 °C for 1 min. The fried dough was put in a 1 L glass

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bottle, which was then screw-capped, wrapped with aluminum foil, and stored at 60°C for 15 days. Samples were taken out every 3 days for analysis of lipid oxidation. All samples were prepared in duplicate.

Lipid oxidation analysis of wheat flour and fried products Lipids of wheat flour and fried products were extracted by Folch method (22) and their conjugated dienoic acid (CDA) content and *p*-anisidine value (PAV) were determined by AOCS methods Ti 1a-64 and Cd 18-90, respectively (23). Fatty acid compositions of soybean oil, wheat flour, and fried products were analyzed by gas chromatography after esterification of lipid with BF_3 in methanol (24). A Younglin M600D gas chromatograph (Younglin Co., Seoul, Korea), equipped with a Supelcowax™ capillary column (30 m × 0.53 mm, 1.0 μm thickness; Bellefonte, PA, USA) and a flame ionization detector, was used. Temperatures of the oven, injector, and flame ionization detector were 200, 270, and 280°C, respectively. The nitrogen gas flow rate was 5 mL/min and the split ratio was 33:1. Each fatty acid in the GC chromatograms was identified by comparing the retention times of standard fatty acid methyl esters.

Statistical analysis Duncan's multiple range test of the SAS System (25) was performed to analyze the differences among samples. The significance level was 5%.

Results and Discussion

Lipid oxidation of wheat flour during storage in the dark The wheat flour contained 2.71% lipid before storage, which was within the range reported by Chung *et al.* (26). The lipid contents of flour decreased to 1.44, 1.51, and 1.42% after 7-day storage, and to 1.30, 1.44, and 1.22% after 21-day storage at Aw 0.3, 0.5, and 0.8, respectively. Before storage the flour lipid consisted of palmitic (17.9%), stearic (1.4%), oleic (14.5%), linoleic (62.1%), and linolenic (4.0%) acids. Storage of flour in the dark changed the fatty acid composition; after 7-day storage at Aw 0.3, 0.5, and 0.8, linolenic acid content decreased to 35.1, 39.3, and 23.1%, respectively, of the original. Most of the linolenic acid had disappeared after 21-day storage and was reduced to only 5.7, 4.7, and 5.9%, respectively, of the original amount. The decrease in linoleic acid content after 21-day storage, to 50, 56, and 47% of the original, respectively, was less than that in linolenic acid content. This clearly shows that flour storage decreased the linolenic acid content in the flour, which could be due to flour lipid oxidation. Linolenic acid was oxidized faster than linoleic or oleic acid (27).

CDA content and PAV of flour lipid, shown in Table 1, increased after storage at 60°C in the dark, and CDA content and PAV of flour stored at Aw 0.8 were significantly higher than those of flour stored at Aw 0.3 or 0.5 ($p < 0.05$). This suggested that lipid oxidation of the flour was higher at Aw 0.8 than at Aw 0.3 or 0.5. Higher lipid oxidation at Aw 0.8 than that at Aw 0.5 has been observed in other studies (28, 29). CDA values generally increase during lipid oxidation due to shifts of nonconjugated double bonds to thermodynamically more stable conjugated forms (29). PAV is a measure of the formation of aldehydes, which are secondary products from the primary oxidation products (27, 30). Since flour contained lipid at 2.71%, the sum of linoleic and linolenic acid contents could be estimated as 1.8% of the flour, and these fatty acids may have contributed to the increase in CDA and PAV. The flour stored at Aw 0.5 tended to show the lowest lipid oxidation, in agreement with a previous report (14).

Table 1. Duncan's multiple range test for the effects of water activity (Aw) of flour storage on the conjugated dienoic acid (CDA, %) content and *p*-anisidine value (PAV) of flour during storage at 60°C in the dark

Storage time of flour (days)	Aw	CDA[1]	PAV[1]
0		0.86±0.04	1468±0.00
7	0.3	1.39±0.05^b	1723±0.00^b
	0.5	1.31±0.11^b	1296±0.00^c
	0.8	2.86±0.03^a	2786±0.00^a
21	0.3	1.32±0.00^b	1533±0.00^b
	0.5	1.34±0.03^b	1456±0.00^c
	0.8	1.58±0.07^a	2150±0.00^a

[1] Different superscript means a significant difference among samples stored under different water activity at α=0.05.

CDA content and PAV of the flour stored for 21 days were lower than those of the flour stored for 7 days at Aw 0.3 or 0.8. This may have been partly due to rapid loss of linolenic and linoleic acids in the flour during 7-day storage in the flour at Aw 0.3 or 0.8, and the lack of linoleic and linolenic acids might have produced less CDA in the flour (31, 32).

Lipid oxidation of fried products made with stored flour during storage in the dark Lipid contents of the fried products made with flour stored at 60°C and at Aw 0.3, 0.5, and 0.8 were 33.0, 33.5, and 32.7%, respectively, which were not significant differences among the samples ($p > 0.05$). Soybean oil consisted of palmitic (11.9%), stearic (4.6%), oleic (25.0%), linoleic (52.3%) and linolenic (5.9%) acids before frying.

Fatty acid compositions of the fried products made with stored flour are shown in Table 2. Fried products contained palmitic (11%), stearic (4-5%), oleic (25-26%), linoleic (51-52%), and linolenic (6-7%) acids, which was a similar composition to that of soybean oil. When foods with low lipid content are fried, the fried foods show similar fatty acid composition to the frying oil (33-35). Fatty acid compositions among fried products made with the flour stored at different conditions were slightly different. Linolenic acid contents were lower in the fried products made with stored flour than in those made with unstored flour.

CDA content changes in the lipids of fried products during storage at 60°C in the dark are shown in Fig. 1. CDA contents of the fried products increased with increased fried product storage time as was expected. Figure 1 also shows that CDA contents of the fried products made with flour stored for 21 days (mean value; 1.1-3.8%) were higher than those of the fried products

Table 2. Effects of wheat flour storage conditions on the fatty acid composition of fried products before storage

Flour storage conditions		Relative content (%)[1]				
Aw	Time (days)	C16:0	C18:0	C18:1	C18:2	C18:3
	0	11.2±0.53^{a}	4.9±0.10^{a}	24.9±0.07^{b}	51.3±0.01^{d}	7.1±0.22^{a}
0.3	7	10.7±0.27^{a}	5.2±0.19^{a}	25.7±0.40^{a}	51.7±0.22^{cd}	6.1±0.19^{b}
	21	10.8±0.60^{a}	4.9±0.15^{a}	25.5±0.22^{ab}	52.1±0.51^{c}	6.4±0.26^{b}
0.5	7	11.5±0.30^{a}	5.0±0.10^{a}	25.1±0.25^{ab}	51.8±0.10^{cd}	6.1±0.08^{b}
	21	10.4±0.49^{a}	4.5±0.15^{b}	25.3±0.37^{ab}	53.7±0.40^{a}	6.0±0.18^{b}
0.8	7	10.9±0.42^{a}	5.1±0.07^{a}	25.2±0.05^{ab}	51.8±0.25^{cd}	6.4±0.05^{b}
	21	10.9±0.24^{a}	4.5±0.06^{b}	25.2±0.05^{ab}	53.0±0.08^{b}	6.1±0.38^{b}

[1] Different superscript means a significant difference among samples for each fatty acid at α=0.05.

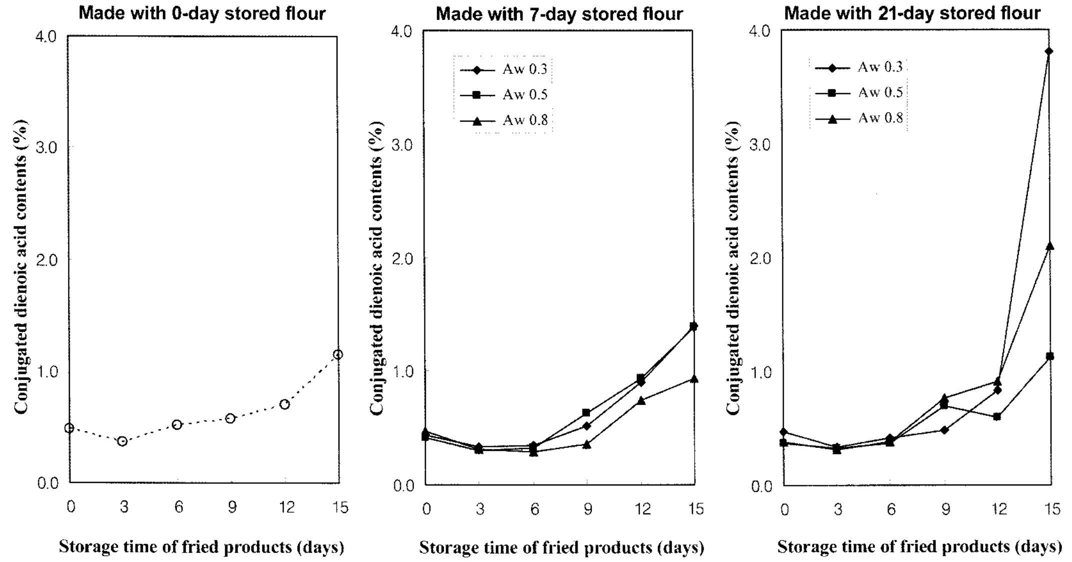

Fig. 1. Effects of water activity (Aw) of flour storage on the conjugated dienoic acid content of fried products of flour during storage at 60°C in the dark.

made with 7-day stored flour (mean value; 0.9-1.4%) during 15-day storage. This suggests that increased flour storage time also increased the CDA contents in the fried products during storage in the dark. However, there was no significant difference (p>0.05) in CDA content during 15-day storage among fried products made with flours stored at different Aw (Table 3). Since flour storage time, but not Aw, affected the CDA formation in the fried products, the mean induction periods (IP) in the lipid oxidation were estimated for fried products made with flour that had been stored for different times. Estimated IP in the lipid oxidation of fried dough made with unstored flour, 7-day stored flour, and 21-day stored flour was 9.4, 7.6, and 6.7 days, respectively. This indicates that flour storage time significantly affected the lipid oxidation of the fried products, and that the fried products were more susceptible to the lipid oxidation during storage when they were made with flour stored for longer.

Table 3. Duncan's multiple range test for the effects of water activity (Aw) of flour storage on the mean conjugated dienoic acid (CDA, %)[1] content of fried products during storage at 60 °C in the dark

Storage time of flour (days)	Mean value of CDA (%)		
	Aw 0.3	Aw 0.5	Aw 0.8
0		0.63±0.27	
7	0.66±0.40^{a}	0.67±0.41^{a}	0.52±0.28^{a}
21	1.06±1.30^{a}	0.58±0.29^{a}	0.81±0.65^{a}

[1] Different superscript means significant differences among samples stored under different water activity at α=0.05.

Figure 2 shows PAV changes in the lipids of fried products during storage at 60°C in the dark. During the storage of the fried products, their PAV initially decreased but then increased, as shown in other studies (35-37). The high PAV of the fried dough in the beginning of storage until the 3rd day may have resulted from the aldehydes formed in the oil during frying and transferred to the fried products (2). When fried products are bottled, the aldehyde compounds are volatilized to the headspace of the bottle until an equilibrium is reached, which decreases the concentration of aldehyde compounds in the fried products (38), as seen in the beginning stage of storage in this study. With increasing lipid oxidation, unstable primary oxidation

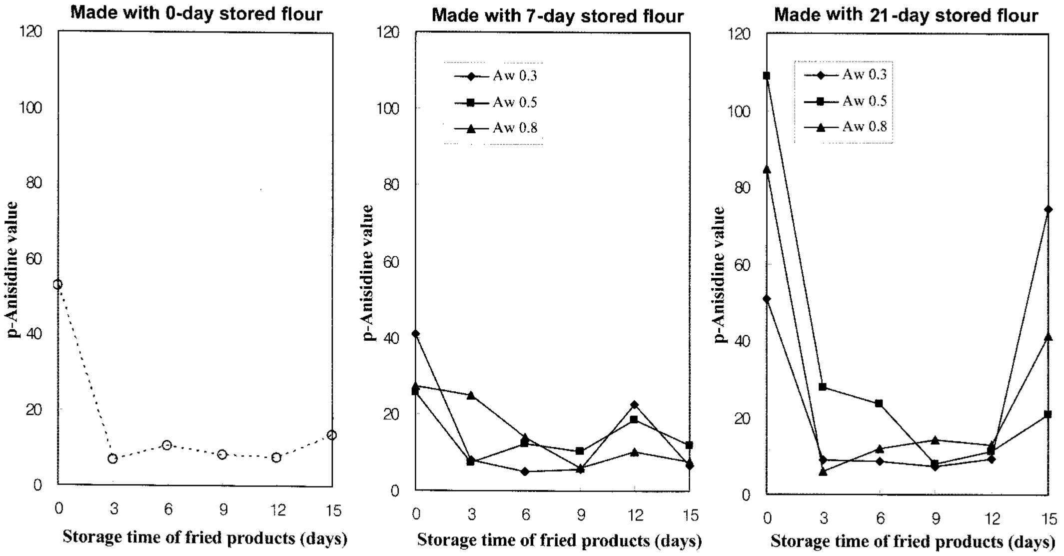

Fig. 2. Effects of water activity (Aw) of flour storage on the *p*-anisidine value of fried products of flour during storage at 60°C in the dark.

products of lipid are often decomposed which leads to the production of many volatile compounds such as aldehydes. The newly formed aldehydes, formed in the fried products by lipid oxidation during storage, could increase PAV in the later period of storage of the fried products.

Since PAV of the fried products in this study decreased until 3 days of storage, only PAV changes after 3-day storage were considered in evaluating the decomposition of oxidized lipids in the fried products during storage. Mean PAVs of fried products made with 7- and 21-day stored flour at Aw 0.8 during 15-day storage of the fried products were 12.49±6.93 and 17.25±13.23 respectively, which were significantly (p<0.05) higher than those of fried products made with unstored flour (9.16±3.69). However, mean PAVs of the fried products made with 7-day stored flour at Aw 0.3, 0.5, and 0.8 were 9.54±7.64, 12.12±4.53, and 12.49±6.93, respectively, during 15-day storage in the dark, which were not significantly different (p>0.05). This suggests that storage time, rather than Aw of the flour, affected the decomposition of oxidized lipids in the fried products during storage.

The results clearly indicate that lipid oxidation of both flour and its subsequent fried products increased with increasing storage time, and that the flour storage time affected the lipid oxidative stability of the fried products during storage by decreasing the CDA content and aldehyde compounds formation. The lipid oxidation of fried products made with flour stored for longer was higher than that of fried products made with unstored or short-term-stored flour. However, Aw for flour storage did not significantly affect the lipid oxidative stability of the fried products of flour during storage in the dark. This suggests that wheat flour storage time is crucial to control the lipid oxidation of fried products during storage in the dark.

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