A Kinetic Study of Oil Deterioration During Frying and a Comparison with Heating

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ABSTRACT: The thermooxidative alterations of cottonseed oil during frying of potato chips without oil turnover, in a temperature range of 155–195°C, were studied. The results showed that the content of polar compounds, conjugated dienes, conjugated trienes, and *p*-anisidine value (*p*-AV) increased linearly with the time of frying at a rate depending on temperature. The rate constants showed a significant but low increase with temperature, except for the rate constant of conjugated trienes that was not correlated to frying temperature. The alterations induced by heating the oil were also measured and compared with those observed in frying at the same temperature. The major difference observed between frying and heating was related to the *p*-AV increase, which presented a considerably higher rate during heating. The FA content, as a function of process time during frying at 185°C, showed a significant increase in palmitic acid (C16:0) and a significant decrease in linoleic acid (C18:2). Oleic acid (C18:1) also showed a small but significant decrease. The same results were obtained for the oil heated at 185°C. Examination of *p*-AV or conjugated dienes with polar compounds showed that both *p*-AV and conjugated dienes had a linear relationship with total polar compounds, with correlation coefficients of 0.946 and 0.862, respectively.

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KEY WORDS: *p*-Anisidine value, conjugated compounds, frying kinetics, oil deterioration, polar compounds.

In deep-fat frying, a complex series of chemical reactions takes place and results in deteriorative changes in flavor, color, and nutritional value. Several articles have summarized the hydrolytic, oxidative, and thermal changes of frying oils and the methods most used to evaluate their deterioration (1–5). It is well known that hydroperoxides, which are initially formed, are very unstable under frying conditions and decompose further to secondary oxidation products (2,6). Conjugated structures are formed as intermediates through a shift of a double bond of PUFA. Secondary oxidation products include carbonyl compounds and especially aldehydes, formed through decomposition of hydroperoxides, and polar compounds, which contain products of polymerization and of hydrolytic cleavage of TG. Since the rate of oxidation is higher as the extent of unsaturation increases, the content of unsaturated FA is reduced as frying proceeds, while the content of saturated FA increases.

Although there have been many investigations on the identification of separate oxidation products, data related to the accumulation of these substances during frying and to the effect of frying temperature are very limited. The increase of polar compounds was correlated with the numbers of frying (7,8) or days of frying (9) in successive frying experiments. On the other hand, conjugated compounds were reported to increase initially and then reach a plateau (6). Moreover, some published data were obtained through experiments conducted by heating the oil and not actually frying (10). Based on their experimental results, Chang *et al*. (1) commented that chemical reactions that take place during deep-fat frying are different from those during continuous heating. Fritsch (2) observed that some, but not all, oxidation indexes were different when oil was just heated or when potatoes were fried in it. The knowledge of the rate of deterioration during heating, as compared to that during frying, is useful, because the oils are kept heated for various lengths of time at some commercial applications, such as food-service establishments. Therefore, a kinetic study of oxidative alterations during the frying process and a comparative study of the alterations induced by heating was conducted to elucidate these points. The relationships between the studied parameters of oil deterioration were also investigated. Potato chips, which are the major fried-food produce, were used for frying experiments, and the range of frying temperature varied from 155 to 195°C. Cottonseed oil was selected as frying medium, because it is the first vegetable oil considered for deep-frying owing to its high inherent stability to oxidation (11).

MATERIALS AND METHODS

Materials. Sliced potatoes were obtained from a local plant producing potato chips and kept in sealed bags full of water until frying. Refined cottonseed oil was used for heating and frying experiments.

Methyl esters of myristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, and arachidic acids, which were used for FA analysis, were obtained from Sigma-Aldrich (St. Louis, MO).

Experimental procedure. A laboratory fryer that kept the temperature within a range of ±1°C was used. Both heating and frying experiments were conducted with 20 L of cottonseed oil. During heating experiments, 100 g oil was withdrawn every hour until 12 h of heating and further processed for analysis.

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The frying experiments were conducted within a few hours of receiving the sliced potatoes as follows: 100 g of sliced potatoes, after the removal of excess water by blotting with a filter paper, were fried for 3–4 min depending on frying temperature. Successive fryings were run every 15 min with a new batch of 100 g of potatoes each time until 12 h of frying. Oil samples (100 g) were removed from the fryer every hour and processed for analysis. The effect of temperature in frying was estimated in a temperature range of 155–195°C.

Analytical methods. The percent contents (%w/w) of conjugated dienes and conjugated trienes were calculated according to IUPAC Official Method 2.206 (12) based on measurements of absorbance at 232 and 268 nm according to IUPAC Official Method 2.505 (12). The aldehyde content was estimated by the *p*-anisidine value (*p*-AV), which was determined according to AOCS Official Method Cd 18-90 (13). The content of polar compounds was evaluated by the column chromatographic method of IUPAC 2.505 (12).

The FA content was determined by GC analysis. Samples of the oil were saponified and then methylated according to AOCS Official Method Ce 2-66 (13). Methyl esters were analyzed using a GC 8000 series (Fisons Instruments, Milan, Italy) fitted with a capillary column packed with (50% cyanopropyl) methylpolysiloxane (J&W Scientific, Folsom, CA) and equipped with an FID. The oven temperature was set at 155°C for 2 min and then increased at a rate of 5°C/min up to 225°C, where it was held for 10 min. The injector and the detector blocks were set at 250 and 270°C, respectively. Carrier gas (helium) flow rate was set at 0.7 mL/minute. The methyl esters were identified by comparing their relative and absolute retention times with those of commercial standards.

All analyses were conducted in duplicate, and the results presented are the average of the obtained values.

Statistical analysis. To compare the effect of frying time on FA, the ANOVA (single factor) and Duncan's multiple range test with acceptance at a significance level of 95% were used.

RESULTS AND DISCUSSION

The changes in *p*-AV, conjugated dienes, conjugated trienes, and polar compounds during frying of potato chips were studied at temperatures ranging from 155 to 195°C. The results of *p*-AV, conjugated dienes, and polar compounds at 155, 175, and 195°C are presented in Figure 1. A linear increase with frying time was observed for the studied oxidation indexes at all processing temperatures, according to Equation 1:

$$C = C_o + kt \qquad [1]$$

where C is the value of the index after time t of frying; C_o is the initial value in fresh oil, before frying; k is the rate constant of the reaction; and t is the time of frying (h). The rate constants and the correlation coefficients of Equation 1 are presented in Table 1. The fresh oil contained 0.35% (w/w) conjugated dienes. The experimental results showed a linear increase in the conjugated dienes with frying time. The initial content of conjugated trienes was 0.08% (w/w), and it increased linearly with frying time as well. The increase in conjugated trienes was considerably lower compared to conjugated dienes, as indicated by the values of the rate constants presented in Table 1. The greater increase of conjugated dienes in our experiments is justified by the high content in linoleic acid of the cottonseed oil. The fatty acid analysis of the fresh oil revealed that it contained 55.50% linoleic acid. On the other hand, the linolenic acid content was found to be 0.10%, explaining the minor changes in the conjugated trienes that were observed.

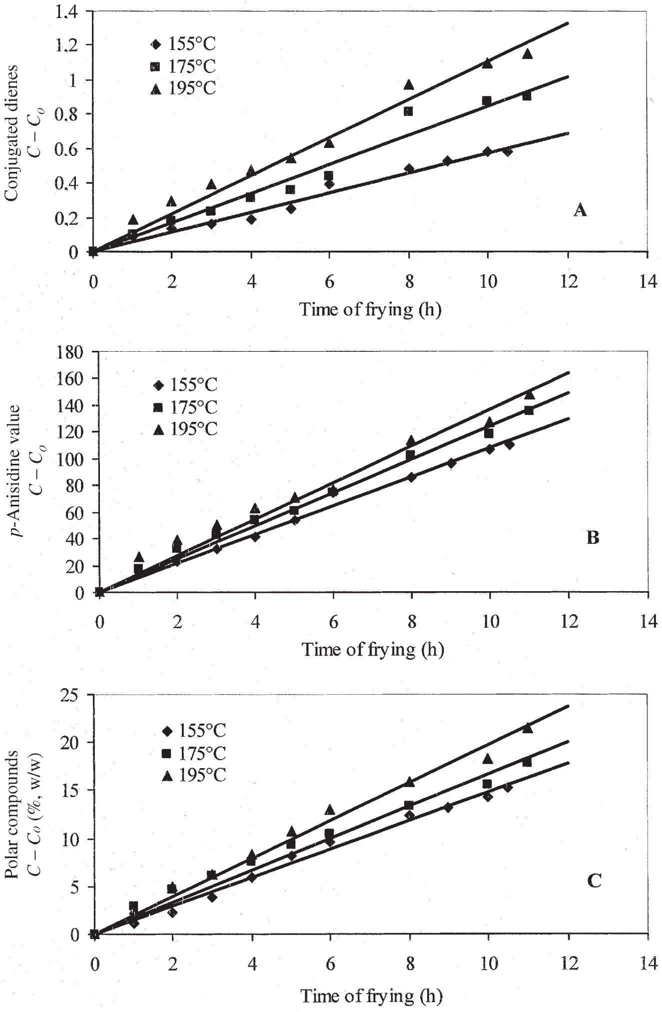

FIG. 1. Increase of conjugated dienes (A), *p*-anisidine value (B), and polar compounds (C) as a function of frying time and temperature. C, concentration at time t; C_o, initial concentration.

The linear increase in *p*-AV indicates a linear increase in the aldehydes accumulated in the oil during frying. The *p*-AV of the fresh oil was 2.6. It is well known that although aldehydes are volatile decomposition products of oil oxidation, a portion of them remains in the frying oil (1,14). The *p*-AV was highly correlated with most of the aldehydes determined in frying oil by headspace analysis and was also highly correlated with the overall odor intensity of the fried oil (15).

Total polar content of the fresh oil was 6.5% and amounted to 28.0% after 11 h of frying at 195°C. Therefore, the oil was

TABLE 1
Rate Constants and Correlation Coefficients of the Changes in Conjugated Dienes, Conjugated Trienes, *p*-Anisidine Value, and Polar Compounds During Frying at Various Temperatures and During Heating the Oil at 185°C

Temperature (°C)	Oxidation indexes: Conjugated dienes k (h^{-1})	r^2	Conjugated trienes k (h^{-1})	r^2	*p*-Anisidine value k (h^{-1})	r^2	% Polar compounds k (h^{-1})	r^2
155	0.058	0.983	0.012	0.978	10.784	0.991	1.476	0.991
165	0.066	0.979	0.013	0.975	11.576	0.938	1.540	0.983
175	0.085	0.970	0.009	0.978	12.033	0.980	1.670	0.973
185	0.094	0.979	0.009	0.989	12.689	0.978	1.765	0.951
195	0.111	0.980	0.012	0.960	13.650	0.969	1.971	0.986
185 (heating)	0.157	0.983	0.039	0.996	20.670	0.985	1.776	0.980

considered unacceptable for further use. National legislation in several countries specifies an acceptable upper limit of total polar content of 25–27% for the frying oils (16). A linear increase with frying time with a good correlation coefficient was observed at any frying temperature as indicated in Table 1. Handel and Guerrieri (10) also found that the total polar content increased linearly with time during heating of various oils at constant temperature. A similar result was observed in frying experiments using successive fryings on repeated days, where the total polar content and the number of fryings (7,8) or days of frying (9) were linearly correlated.

The dependence of the rate constants k of the deteriorative reactions on frying temperature is presented in Figure 2. As can be seen, an Arrhenius-type equation is followed for all three rate constants:

$$\ln k = a - b(1/T) \qquad [2]$$

where a, b are the constants of the equation and T is the absolute temperature (K).

The correlation coefficients were calculated as 0.988 for *p*-AV and conjugated dienes and 0.969 for polar compounds. The rate constants of conjugated trienes were not correlated with temperature. The rate of increase of *p*-AV was slightly affected by temperature. This might be explained by the higher volatility of some of the aldehydes formed at higher temperature that confronts the rate of formation of these substances at elevated temperature and therefore results in a lower accumulation in the oil. A low effect is also observed for the rate constant of the polar compounds. Some of the polar compounds, e.g., FFA and carbonyl compounds, are also volatile and are removed with the steam at higher temperatures. The rate of conjugated diene accumulation showed the highest dependence on temperature. However, these findings suggest that, in the range investigated, the increase of temperature resulted in a significant but not pronounced increase of the altered substances accumulated in the oil. After 70 h of frying at 170, 180, or 190°C, Tyagi and Vasishtha (17) found a remarkable increase in color and some other physical properties but a low increase in conjugated dienes.

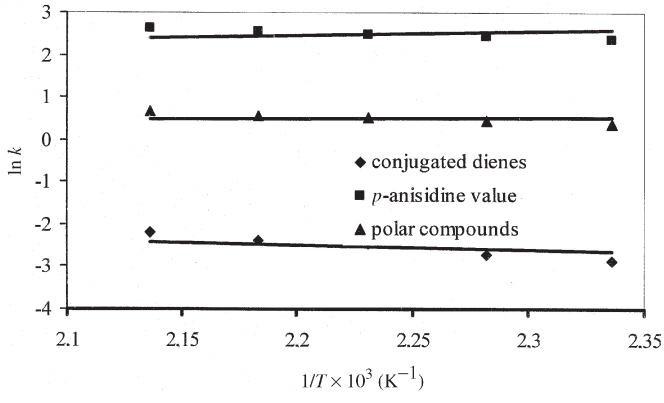

FIG. 2. Effect of temperature on the oxidation rate constants.

In Table 1 the rate constants of the deteriorative changes found during heating the oil at 185°C are also presented. The major difference observed between frying and heating concerns the *p*-AV increase, which presented a considerably higher rate during heating. This might be attributed to partial removal of aldehydes with steam during frying. A comparative study of oils obtained from commercial frying establishments with corn oil heated at 180°C showed that aldehyde content was much lower in the fried oils (6). The increase of conjugated compounds also showed a higher rate constant during heating, while no significant difference was observed for the polar compounds. Fritsch (2) reported no difference between heating and frying in polar compounds or in conjugated dienes.

The FA content as a function of process time during frying at 185°C is presented in Table 2. A significant increase was observed in palmitic acid (C16:0), and a significant decrease in linoleic acid (C18:2). Oleic acid (C18:1) also showed a small but significant decrease. The same results, with no significant difference, were obtained for the oil heated at 185°C. The decrease in linoleic acid amounted to 8.60% of the initial value after 12 h. White (4) refers to a drop of 7–11.5% in soybean oils heated at 180°C for 40 h and comments that this value is low compared with results from lightly hydrogenated frying oils. Soybean oil is rich in linolenic acid, which presented a decrease of 27–46% in the same experiments. Augustin *et al.* (18) in heating and frying experiments with refined, bleached, deodorized olein observed a drop of C18:2/C16:0 from 0.271 to 0.094 and suggested that the ratio of 18:2/16:0 could be used for the evaluation of oil deterioration. Their experiments were extented to very high polar

TABLE 2
Changes in Fatty Acid Content of Frying Oil with Process Time at 185°C^{a}

	Frying time (h)						
Fatty acids	0	2	4	6	8	10	12
14:0 (myristic)	0.80^{a}	0.80^{a}	0.80^{a}	0.80^{a}	0.80^{a}	0.90^{a}	0.90^{a}
16:0 (palmitic)	23.25^{a}	23.40^{a}	23.65^{a}	23.75^{a}	$23.95^{a,b}$	$24.30^{a,b}$	25.00^{b}
16:1 (palmitoleic)	0.50^{a}	0.50^{a}	0.50^{a}	0.50^{a}	0.50^{a}	0.50^{a}	0.50^{a}
18:0 (stearic)	2.10^{a}	2.10^{a}	2.10^{a}	2.20^{a}	2.20^{a}	2.20^{a}	2.20^{a}
18:1n-9 (oleic-n-9)	$15.90^{a,b}$	$15.75^{a,b}$	15.70^{b}	$15.55^{b,c}$	$15.55^{b,c}$	15.45 c	15.45^{c}
18:2 (linoleic)	55.50^{a}	55.25^{a}	$54.45^{a,b}$	$53.80^{a,b,c}$	$52.65^{b,c}$	$52.25^{b,c,d}$	50.75^{d}
18:3 (linolenic)	0.10^{a}	0.10^{a}	0.10^{a}	0.10^{a}	0.10^{a}	0.10^{a}	0.10^{a}
20:0 (arachidic)	0.20^{a}	0.20^{a}	0.30^{a}	0.30^{a}	0.30^{a}	0.30^{a}	0.30^{a}
18:2/16:0	2.39^{a}	2.36^{b}	2.30^{c}	2.26^{c}	2.20^{d}	2.15^{e}	2.03^{f}

[a] Values in the same row bearing a different superscript roman letter are significantly different ($P < 0.05$, Duncan's multiple-range test).

content, namely 47.40%. This ratio in our experiments was reduced from 2.39 to 2.03 as indicated in Table 2.

According to several investigators, the determination of total polar compounds in a frying oil or fat provides the most reliable measure of the extent of deterioration in most cases (2,4,5). The measurement of total polar compounds is a laborious and expensive method; therefore, it is useful to correlate total polar compounds with other oxidation indexes that allow for easier and more successful determinations of the degradation of oils. Several attempts have been made to correlate these with rapid and simpler measurements of oxidation (9,19,20).

To examine the relationship between *p*-AV or conjugated dienes and polar compounds, we plotted all the experimental data obtained during heating and frying experiments at all temperatures. The results are presented in Figures 3A and 3B for conjugated dienes and *p*-AV, respectively. As can be seen, *p*-AV and conjugated dienes have a linear relationship with total polar compounds. The respective correlation coefficients are 0.946 and 0.862. Al-Kahtani (21), in his investigation of the oxidative deterioration of used frying oils from various restaurants, also found a significant linear correlation of *p*-AV and absorbance at 232 nm with total polar compounds, but correlation coefficients were considerably lower (0.670 and 0.630, respectively). However, he referred to higher correlation coefficients obtained by other investigators.

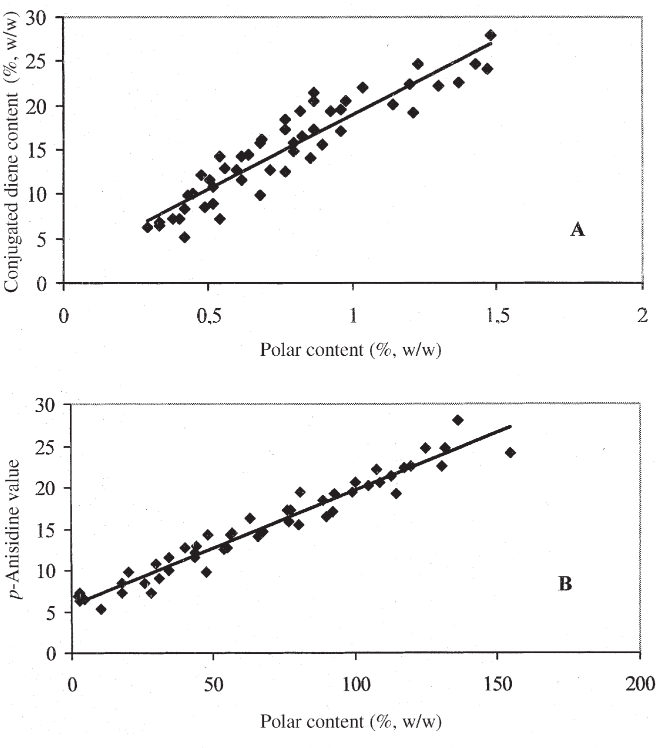

FIG. 3. Correlation of conjugated dienes (A) and *p*-anisidine value (B) with polar compounds.

The examination of the relationship of the ratio C18:2/C16:0 to polar compounds showed that it was correlated linearly with total polar compounds too, although with a lower correlation coefficient (0.843). Al-Kahtani (21) observed a poor correlation of these indexes, as well. Augustin *et al.* (18), on the other hand, found that the ratio of C18:2/C16:0 was highly significantly linearly correlated (r^2, 0.990) with total polar compounds, as far as the same frying or heating system was maintained. It should be noted, however, that the change in the ratio of C18:2/C16:0 is limited, especially in the early stages of frying, as indicated in Table 2; therefore we do not consider the change of fatty acid profile suitable for the estimation of frying oil deterioration. On the contrary, both *p*-AV and conjugated dienes presented considerable changes throughout frying, were sufficiently well correlated to polar compounds, and could be used for the estimation of oil deterioration in a frying system.

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