Effect of Oil Degradation During Frying on the Color of Fried, Battered Squid Rings

R. Baixauli, A. Salvador, S.M. Fiszman, and C. Calvo*

Instituto de Agroquímica y Tecnología de Alimentos (CSIC), 46100 Burjassot, Valencia, Spain

ABSTRACT: Oil degradation caused by the number of fryings performed and the effect of oil degradation on the color of fried battered squid rings were studied. Spectrophotometric techniques with absorbance in the UV and visible ranges, and iodine, peroxide, and acid values were used to determine oil degradation. Determination of various CIELAB parameters in order to study the external color of the fried battered squid rings revealed no differences in color due to the number of fryings. A study of the color of the battered squid rings at various frying times and temperatures showed significant differences for both variables. Although there was some degradation in the oil after 20 fryings, appearing as a slight darkening, it did not affect the final color of the fried, battered squid rings.

Paper no. J10252 in *JAOCS 79*, 1127–1131 (November 2002).

KEY WORDS: Absorbance, batter, color, frying, oil, squid rings.

The process of frying is frequently used in food manufacturing. In frying, oil is heated to temperatures above 180°C in the presence of air for long periods. As a result, degradation of the oil takes place, and volatile and nonvolatile compounds are formed. The main causes of the degradation are oxidation reactions and reactions due to the interaction of oil and food at high temperatures (1,2).

Various authors have studied the physical and chemical changes that take place in oil during frying. Min and Schweizer (3) studied lipid oxidation of oil used to prepare potato chips by measuring PV. To evaluate the quality of the aroma of the oil, they analyzed volatile compounds. Tyagi and Vasishtha (4) and Tsaknis *et al.* (5) studied the chemical changes that took place in oil during the frying of potato chips by evaluating various parameters including iodine index, PV, FFA content, color, and viscosity.

However, the changes that take place in oil during frying can be studied more quickly by the use of spectrophotometric techniques. Absorbance values in the UV range reflect the presence of conjugated double bonds that are due to the formation of peroxides and other by-products of lipid oxidation. On the other hand, measurement of absorbance in the visible range indicates the changes that take place in oil color intensity (6,7), which are related to other parameters that affect oil quality. Studies of color changes are based on quick tests that require only a small sample quantity, and results can be considered as an index of oil quality. The value of this type of test is that it can be applied quantitatively by companies that use frying oil in their processes, and qualitatively by restaurant owners and end users, for oil darkening implies some degree of degradation, even though the dark color of the oil may not affect the fried product's final color.

The aim of the present work was to study the degradation of oil during the frying of battered squid rings using spectrophotometric techniques, and to analyze how this degradation affects the color of the fried battered squid rings.

EXPERIMENTAL PROCEDURES

Batter preparation. A commercial batter formulation supplied by Adin, S.A. (Paterna, Valencia, Spain) was used. It consisted of wheat flour (85%), corn flour (5.8%), salt (5.5%), flavoring (0.6%), and leavening [$Na_2H_2P_2O_7$ (1.32%)/$NaHCO_3$ (1.78%), w/w].

The batter was prepared by blending the dry ingredients with water (1:1.2, w/w) at speed 2 for 2 min in a Kenwood Major Classic mixer (Kenwood Ltd., Havant, United Kingdom), and its apparent viscosity was measured at 20°C (Fluke digital thermometer, Everett, WA) with a Haake Viscotester VT5^R (Crawley, United Kingdom) equipped with a No. 3 spindle at 2 rpm. The viscosity values obtained ranged from 30,360 to 40,120 mPa·s.

Sample coating. Frozen squid rings were obtained from a local supplier. The squid rings were thawed, pre-dusted with wheat flour, and immersed in the batter. After being allowed to drip for 5 min, the battered squid rings were pre-fried at 190°C for 30 s, placed in plastic freezer bags (LDPE film, thickness 150 μm), and stored at −18°C for 1 wk.

Frying. Refined sunflower oil with a high oleic acid content was used (Koipe, S.A., Jaén, Spain). The frying was done in a Fritaurus Professional 4 domestic electric fryer (Taurus, Barcelona, Spain) over a period of 40 d, with one frying being done per day. The oil (4 L) was heated and maintained at 190 ± 2°C for approximately 30 min each day, and during this time three squid rings (6–7 g each before frying) were fried for 3 min. Excess surface oil was allowed to drain on tissue paper after frying.

Absorbance test procedure. In order to discover what changes took place in the oil as the number of fryings increased, its absorbance spectrum was measured with a spectrophotometer

*To whom correspondence should be addressed.
E-mail: ccalvo@iata.csic.es

[Hewlett-Packard (HP) 8452A Diode Array Spectrophotometer], controlled by HP 89532A UV-Vis software. The absorbance of the oil was measured at 20°C, 24 h after each frying. The wavelength range used was 200 to 700 nm. The apparatus was calibrated using an empty cuvette (7). For this study, Elkay Ultra-Vu disposable polystyrene cuvettes with a 10-mm base measurement were used. In each case, three cuvettes were filled with oil from the fryer and the absorbance spectra from each cuvette were recorded. The oil was then emptied back into the fryer.

Photometric Color Index (PCI). The PCI was calculated using the following equation based on AOAC method Cc 13c-50 (8):

$$\text{Photometric Color Index} = 1.29(Ab_{460}) + 69.7(Ab_{550}) + 41.2(Ab_{620}) - 56.4(Ab_{670}) \quad [1]$$

where Ab_{460}, Ab_{550}, Ab_{620}, and Ab_{670} are the absorbance values at the 460, 550, 620, and 670 nm wavelengths, respectively, obtained from the spectrum.

Chemical analyses of oil. AOCS methods (8) were used for determining acid value (Method Cd 3a-63), iodine value (Method Cd 1-25), and PV (Method Cd 8-53).

Measurement of color. The instrumental measurement of the fried battered squid ring color was performed with a Hunter Labscan II colorimeter, and the results were expressed in accordance with the CIELAB system with reference to illuminant D65 and a visual angle of 10°. The measurements were performed through a 6.4-mm diameter diaphragm containing an optical glass. The parameters determined were L^* [$L^* = 0$ (black) and $L^* = 100$ (white)], a^* ($-a^*$ = greenness and $+a^*$ = redness), and b^* ($-b^*$ = blueness and $+b^*$ = yellowness). The total color difference (ΔE^*) and the yellowness index (YI) were calculated according to Reference 9:

$$\Delta E^* = \sqrt{(L_n^* - L_1^*)^2 + (a_n^* - a_1^*)^2 + (b_n^* - b_1^*)^2} \quad [2]$$

$$\text{YI} = 142.86\, b^*/L^* \quad [3]$$

where L_1^*, a_1^*, and b_1^* are the pre-fried sample color parameter values.

Three squid rings were fried each time, and the color of the outer coating of batter was measured. After frying, the rings were left to soften on a tray covered with tissue paper for about 15 min to facilitate color measurement. Each ring was divided into three approximately equal pieces, and six measurements were made with each piece, three on the outer side (contact with oil) and three on the inner side (contact with squid). All the measurements were made by placing the sample directly on the colorimeter diaphragm.

Effect of frying time and temperature on color development. Experiments were carried out for various oil temperatures (160, 170, 180, and 190°C). The frozen battered squid rings were fried for 0.5, 1, 1.5, 2, 2.5, and 3 min to measure color changes during frying.

Statistical analysis. An ANOVA was performed to study the influence of frying on the color of the frozen, battered squid rings, using the SAS software system (10).

RESULTS AND DISCUSSION

Measurement of absorbance. The absorbance values in the UV range (200 to 400 nm) reflect the presence of conjugated double bonds in the structure of the oil molecule. These bonds are probably the result of the formation of peroxides and other by-products of lipid oxidation (11). They are also indicative of the appearance of other, nonoxidized types of bonding formed by isomerization, with maximum absorbance values at 234 nm for dienes and 270 nm for trienes (6,12).

Figure 1A shows that the absorbance value at 234 nm increased with the number of fryings. This indicates an alteration in the oil produced by the conjugation of double bonds as a consequence of a primary oxidation. Figure 1B shows the increase in absorbance at 270 nm, which reflects the appearance of oxidation by-products such as unsaturated α- and β-diketones and β-ketones, typical of oils in the process of going rancid (11). As in the previous case, the absorbance value at 270 nm increased with the number of fryings, with the value increasing in line with frying time. In both cases there were significant differences ($P < 0.05$) after 20 to 22 fryings.

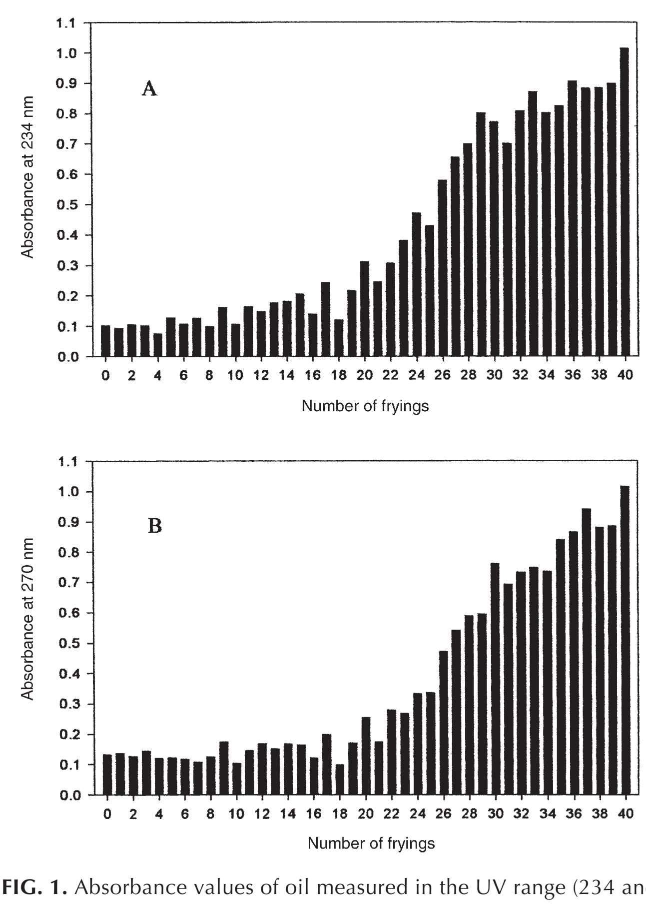

FIG. 1. Absorbance values of oil measured in the UV range (234 and 270 nm) in relation to number of fryings.

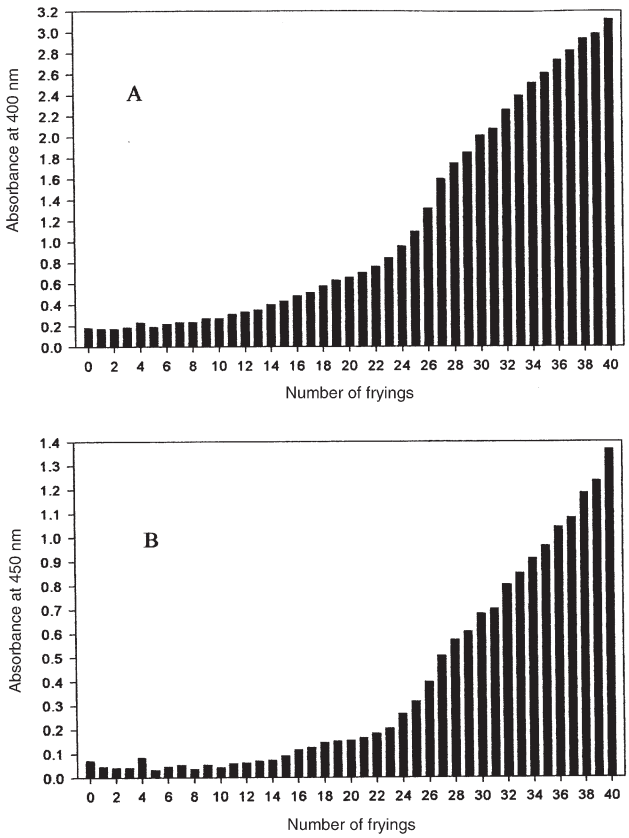

FIG. 2. Absorbance values of oil measured in the visible range (400 and 450 nm) in relation to number of fryings.

The measurement of absorbance in the visible range (400 and 450 nm) indicates the changes that took place in the intensity of the color of the oil. As frying time increased there was a darkening of the oil, owing mainly to particles of food that caramelized and released soluble compounds into the fats (7). Figure 2 shows that the absorbance at 400 (A) and 450 nm (B) increased with the number of fryings. As with the measurements in the UV range, there were significant differences after 20 fryings.

Figure 3 shows the complete spectrum of the oil for fryings 1, 20, and 40. Although all three curves have a maximal absorbance at 312 nm, as the number of fryings increases the maximum band becomes wider at higher wavelengths (300 to 400 nm) and the curve for frying no. 40 even shows two peaks (300 and 500 nm). These changes in the absorbance curves are due to degradation of the oil during frying.

PCI. The PCI is a combination of the absorbance values at wavelengths of 460, 550, 620, and 670 nm; wavelengths between 530 and 795 nm are appropriate for measuring the degradation of fats (13). The PCI was calculated for the oil of each of the 40 fryings studied, and the regression model obtained was as follows:

$$\text{PCI} = 0.63 - 0.43[n_f] + 0.02[n_f]^2;\ R^2 = 0.9696 \qquad [4]$$

where n_f is the fry number.

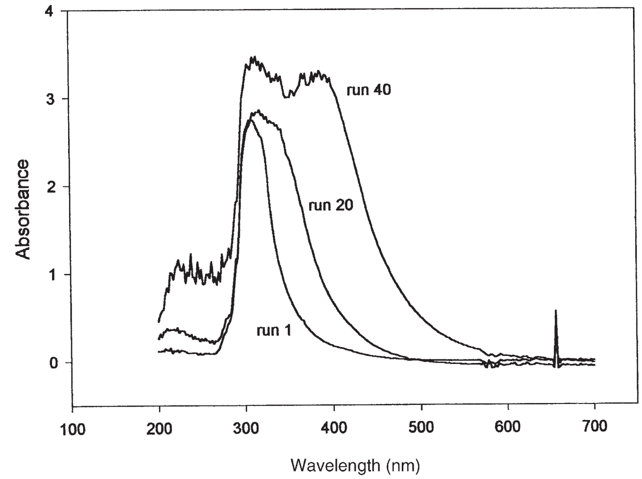

FIG. 3. Spectrum obtained for fryings nos. 1, 20, and 40 between 200 and 700 nm.

As can be seen in Figure 4, there was practically no variation in this index until frying no. 20, and from then on there was a significant linear increase. This indicates that after 20 fryings the degradation of the oil began to be detectable, a result that agrees with the absorbance measurements discussed earlier. The PCI provides a practical way of detecting the beginning of deterioration as a result of thermal exposure.

Chemical analyses of oil. To monitor the properties of the oil, the values of the classic indices (iodine, peroxide, and acid values) used for determining oil degradation were obtained after 0, 5, 10, 15, 20, 25, 30, 35, and 40 fryings (Table 1). As can be seen, the changes in the indices are continuous, and none of them reflects the inflection detected by the use of the PCI or the absorbance spectrum analysis.

Measurement of color. The results of the measurements performed on the fried, battered squid rings were expressed in accordance with the CIELAB system, and the rectangular

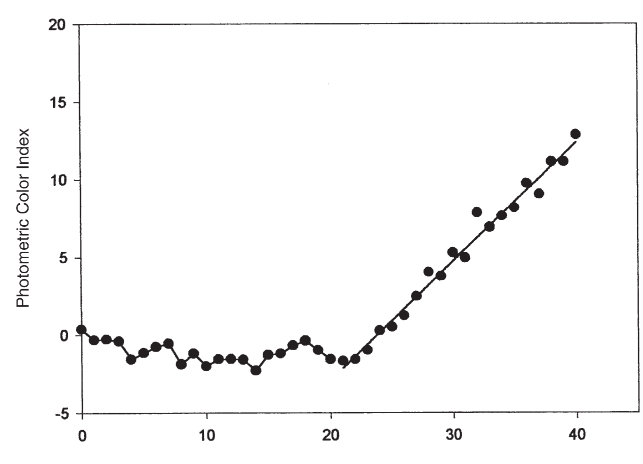

FIG. 4. Photometric Color Index values obtained in relation to the number of fryings.

TABLE 1
Acidity Value, Iodine Value, and PV in Relation to Number of Fryings[a]

Number of fryings	Acidity value (% as oleic acid)	Iodine value (g of I_2/100 g of oil)	PV (meq. O_2/kg of oil)
0	0.205[a]	134.2[a]	5.69[a]
	(0.006)	(1.8)	(0.08)
5	0.276[b]	139.3[b]	11.58[d]
	(0.003)	(2.4)	(0.32)
10	0.296[b]	134.8[a,b]	7.95[b,c]
	(0.006)	(1.4)	(0.06)
15	0.332[c]	126.420[c]	7.12[a,b,c]
	(0.009)	(1.848)	(0.31)
20	0.352[c]	122.7[c,d]	6.24[a,b]
	(0.011)	(0.6)	(0.02)
25	0.552[d]	125.0[c,d]	6.71[a,b,c]
	(0.006)	(1.8)	(2.74)
30	0.592[e]	120.6[d]	5.08[a]
	(0.011)	(1.8)	(0.44)
35	0.663[f]	121.3[c,d]	8.45[c]
	(0.017)	(0.7)	(0.05)
40	0.704[g]	104.4[e]	10.88[d]
	(0.023)	(4.0)	(0.15)

[a]Means in the same column without a common superscript letter differ ($P < 0.05$) according to the least significant difference multiple range test. Values within parentheses are SD.

coordinates (L^*, a^*, b^*) were defined. To study the effect of the number of fryings on the color parameters, an ANOVA was carried out.

The parameters used to determine the color of the squid rings were a^* (redness), b^* (yellowness), YI (yellowness index), and ΔE^*. Figure 5 shows these four parameters in relation to the number of fryings. As can be seen, they all followed a similar pattern. There was a significant increase in the value of the parameters between the pre-fried product (frying no. 0) and frying no. 1, although no significant differences were found as the number of fryings in the same oil increased.

Visual comparison of the fried, battered squid rings corresponding to frying no. 1, fried in fresh oil, and the fried battered squid rings corresponding to frying no. 40, fried in oil that had been used 40 times, also did not reveal differences in color between the two batches.

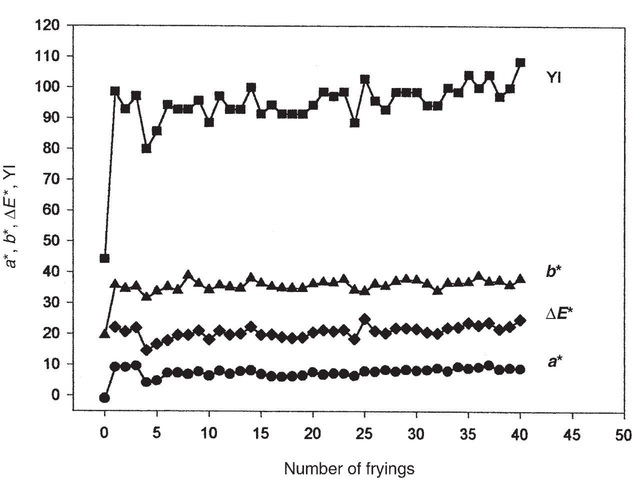

FIG. 5. Values of the color parameters a^* (redness), b^* (yellowness), ΔE^* (total color difference), and YI (yellowness index) in relation to number of fryings.

TABLE 2
Values of b^* in Relation to Frying Time and Temperature[a]

Time (min)	160°C	170°C	180°C	190°C
0.5	25.9[a,A]	24.4[a,A]	25.8[a,A]	29.2[a,A]
	(2.9)	(3.8)	(2.0)	(2.8)
1.0	25.4[a,A]	26.8[a,b,A]	26.9[a,A]	31.0[a,A]
	(1.0)	(4.0)	(2.8)	(4.1)
1.5	29.4[a,b,B]	29.6[b,c,B]	32.5[b,B]	38.6[b,A]
	(2.2)	(1.4)	(2.2)	(2.2)
2.0	28.9[a,b,C]	29.7[b,c,B,C]	35.0[b,A,B]	38.8[b,A]
	(5.7)	(1.6)	(0.3)	(2.3)
2.5	31.6[a,b,B]	31.9[b,c,B]	32.8[b,B]	38.7[b,A]
	(3.7)	(3.3)	(0.9)	(0.5)
3.0	33.2[b,B]	32.0[c,B]	34.7[b,B]	39.6[b,A]
	(3.6)	(1.6)	(0.5)	(1.7)

[a]Superscript lowercase letters correspond to the analysis by columns. Superscript capital letters correspond to the analysis by rows. Means without a common superscript letter differ ($P < 0.05$) according to the least significant difference multiple range test. Values within parentheses are SD.

The results obtained previously showed that the oil began to degrade after 20 fryings, but this degradation did not affect the color of the outer layer of batter on the fried squid.

Effect of frying time and temperature on color development. The parameters b^* and a^* were used to study the effect of frying time and temperature on the color of fried battered squid rings because they best represent the variations in this product's color (golden yellow). Tables 2 and 3 show the values of b^* and a^* for all the times and temperatures studied. The color of the fried, battered squid rings was affected by both frying temperature and frying time. Both b^* and a^* increased as frying time increased, and this difference was significantly greater at 190°C. In general, after 1.5 min of frying there were significant differences in relation to temperature, and the values of the parameters increased as the temperature increased. These results agree with the studies carried out by Krokida *et al.* (14), who measured the color of potatoes fried for different times and at different temperatures.

TABLE 3
Values of a^* in Relation to Frying Time and Temperature[a]

Time (min)	160°C	170°C	180°C	190°C
0.5	0.5[a,A]	0.7[a,A]	1.1[a,b,A]	1.2[a,A]
	(0.4)	(0.3)	(0.5)	(0.4)
1.0	0.7[a,B]	1.7[a,b,A,B]	1.1[a,A,B]	2.1[a,A]
	(0.5)	(0.2)	(0.7)	(0.7)
1.5	2.2[a,b,B]	2.7[b,B]	2.4[b,B]	6.2[b,A]
	(1.0)	(1.0)	(0.5)	(0.9)
2.0	3.1[b,C]	2.7[b,B,C]	4.6[c,A,B]	6.3[b,A]
	(0.6)	(0.9)	(0.9)	(1.1)
2.5	3.5[b,B]	3.0[b,B]	3.9[c,B]	5.8[b,A]
	(1.3)	(0.8)	(0.3)	(0.3)
3.0	3.5[b,A,B]	3.0[b,B]	4.2[c,A,B]	6.2[b,A]
	(2.0)	(0.7)	(1.1)	(0.1)

[a]Superscript lowercase letters correspond to the analysis by columns. Superscript capital letters correspond to the analysis by rows. Means without a common superscript letter differ ($P < 0.05$) according to the least significant difference multiple range test. Values within parentheses are SD.

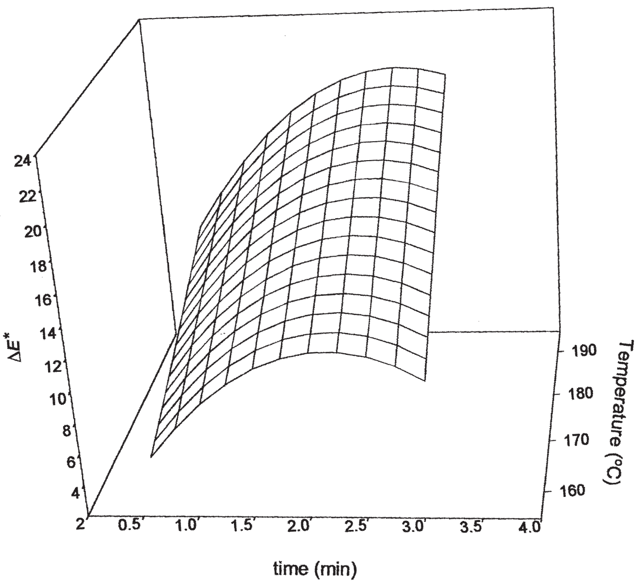

FIG 6. Response surface of the color parameter ΔE^* in relation to frying time and temperature.

A second-order polynomial model was developed to show the effect of time (t) and temperature (T) on the change in color (ΔE^*) that took place in the fried, battered squid rings. The equation obtained was:

$$\Delta E^* = -14.803 + 0.566.10^{-3}\,T^2 - 2.463t^2 + 0.067Tt \qquad [5]$$

The coefficient of regression obtained (R^2) was 0.8898, indicating a good fit with the model. In this case, both frying temperature and frying time had a significant effect on ΔE^*. In using this model, ΔE^* was plotted against time and temperature (Fig. 6). As can be seen, the effect of temperature was greater than that of time. As the frying temperature increased there was an increase in the value of ΔE^*, whereas as frying time increased there was an increase in ΔE^* at shorter times and then it stabilized at about 2 min.

Although under the conditions employed the frying oil began to degrade at frying no. 20, its darkening did not significantly affect the color of the fried, battered squid rings, which were of the same color in the 40 fryings studied. This result indicates that the color of fried, battered products cannot be associated with the darkening of the oil employed, and that degradation of the oil cannot be detected without making a more profound analysis.

ACKNOWLEDGMENTS

The authors are indebted to the Comisión de Ciencia y Tecnología for financial support (projects AGL 2000-1553-C02-01). We are also grateful to Adin, S.A. for the supply of samples.

REFERENCES

1. Chang, S.S., R.J. Peterson, and C.-T. Ho, Chemical Reactions Involved in the Deep-Fat Frying of Foods, *J. Am. Oil Chem. Soc. 55*:718–727 (1978).
2. Fritsch, C.W., Measurements of Frying Fat Deterioration: A Brief Review, *Ibid. 85*:272–274 (1981).
3. Min, D.B., and D.Q. Schweizer, Lipid Oxidation in Potato Chips, *Ibid. 60*:1662–1665 (1983).
4. Tyagi, V.K., and A.K. Vasishtha, Changes in the Characteristics and Composition of Oils During Deep-Fat Frying, *Ibid. 73*: 499–506 (1996).
5. Tsaknis, J., V. Spiliotis, S. Lalas, V. Gergis, and V. Dourtoglou, Quality Changes of *Moringa oleifera*, Variety Mbololo of Kenya, Seed Oil During Frying, *Grasas Aceites 50*:37–48 (1999).
6. Peers, K.E., and P.A.T. Swoboda, Deterioration of Sunflower Seed Oil Under Simulated Frying Conditions and During Small-Scale Frying of Potato Chips, *J. Sci. Food Agric. 33*:389–395 (1982).
7. Vijayan, J., D.C. Slaughter, and R.P. Singh, Optical Properties of Corn Oil During Frying, *Int. J. Food Sci. Technol. 31*:353–358 (1996).
8. AOCS, *Official Methods and Recommended Practices of the American Oil Chemists' Society*, edited by D. Firesone, American Oil Chemists' Society, Champaign, 1986, Cc 13c-50.
9. Francis, F.J., and F.M. Clydesdale, *Food Colorimetry: Theory and Applications*, AVI, Westport, CT, 1975.
10. SAS, *SAS/Stat User's Guide*, version 6.0, 4th edition, SAS Institute, Cary, NC, 1990.
11. Fernández, R., E. Llorca, I. Hernando, I. Pérez-Munuera, and M.A. Lluch, Características químicas de los aceites sometidos a estrés térmico durante la fritura de calamares rebozados congelados, *III Congreso Iberoamericano de Ingeniería de Alimentos,* Universidad Politécnica, Valencia, 2001, 3C-09.
12. Abdel-Aal, M.H., and H.A. Karara, Changes in Corn Oil During Deep-Fat Frying of Foods, *Lebens. Wiss. Technol. 19*:323–327 (1986).
13. Paul, S., and G.S. Mittal, Dynamics of Fat/Oil Degradation During Frying Based on Optical Properties, *J. Food Eng. 30*:389–403 (1996).
14. Krokida, M.K., V. Oreopoulou, Z.B. Maroulis, and D. Marinos-Kouris, Colour Changes During Deep-Fat Frying, *Ibid. 48*:219–228 (2001).

[Received February 18, 2002; accepted July 2, 2002]