Influence of Used Frying Oil Quality and Natural Tocopherol Content on Oxidative Stability of Fried Potatoes

G. Márquez Ruiz[a], M. Martín Polvillo[a], N. Jorge[b], M.V. Ruiz Méndez[a], and M.C. Dobarganes[a,*]

[a]Instituto de la Grasa, CSIC, 41012-Sevilla, Spain, and [b]Depto. de Engenharia e Tecnologia de Alimentos, UNESP. S.J. Rio Preto, São Paulo, Brazil

ABSTRACT: Sunflower oil (SO) and high-oleic sunflower oil (HOSO) were used to prepare fried potatoes by either discontinuous or continuous laboratory frying. Fried potatoes that had been fried in oils of differing quality were stored at 60°C for up to 30 d and evaluated for polar compounds, polymers, peroxide value, oil stability index, and α-tocopherol content. Results obtained through the various methods applied were consistent and indicated that the length of the induction period could not be explained only on the basis of the degree of unsaturation or polar compound levels in fried potatoes before storage. α-Tocopherol content also had a significant influence as potatoes fried in HOSO, with 16% polar compounds and only 10 mg/kg α-tocopherol at the starting point of storage, were oxidized more rapidly than potatoes fried in SO with a comparatively higher degradation level, 19% polar compounds, and 100 mg/kg α-tocopherol.

Paper no. J8714 in *JAOCS 76*, 421–425 (April 1999).

KEY WORDS: Fried potatoes, induction period, oxidative stability, peroxide value, polar compounds, polymers, storage, sunflower oils, tocopherols.

Quality of used frying oils is highly variable and should be controlled as oil degradation often surpasses limitations established for rejection (1–5). Difficulties in controlling oil degradation are due to variables such as continuous or discontinuous frying, surface-to-oil volume ratio, temperature, oil unsaturation degree, and presence of naturally occurring or added minor compounds (6–10). Among these, the influence of fatty acid composition is clearly demonstrated in recent studies on genetically modified oils with low content of polyunsaturated fatty acids, an alternative to saturated fats for fried foods (11–17), and it has been reported that selection of the best oil for frying could even differ depending on which chemical and sensory methods are used for quality evaluation (16,17). Also, previous publications on sunflower oil (SO) and high-oleic sunflower oil (HOSO) as substitutes for palm olein in industrial continuous frying operation demonstrated excellent frying performance of both oils (18) although for fried foods that are stored, stability against oxidation is also required. Therefore, oxidation of fried potatoes was also studied in detail, and chemical (19,20) and sensory (21,22) evaluations indicated, as expected, that shelf life mainly depended on the oil unsaturation degree. However, in this study, the chemical characteristics of the lipids in the fried products did not differ substantially from those corresponding to the unused oils (18) because of the frying equipment used (23), and thus the results obtained could be representative of high-quality fried foods. However, considering the high variability normally found in used frying oil quality, further research is needed to compare stability of fried foods containing used frying oils of different quality.

The objective of this paper was to evaluate the oxidative stability of fried potatoes prepared in oils differing not only in unsaturation degree but also in degradation level of the used frying oils absorbed by the food. Samples for storage were selected with different polar compound levels and tocopherol contents.

MATERIALS AND METHODS

Samples. SO and HOSO were supplied by Medeol (Neuilly sur Seine, France). Fatty acid compositions of major fatty acids for SO and HOSO were: 7.0 and 4.3% palmitic acid; 5.0 and 4.5% stearic acid; 21.5 and 73.0% oleic acid; and 65.1 and 16.4% linoleic acid, respectively. Jaerla variety potatoes were purchased locally.

Frying procedures. (*i*) *Discontinuous frying*. Commercial electric 1 L fryers (Tefal S.A., Barcelona, Spain) each containing 1 L of oil were used to prepare lots of 2 kg of fried potatoes. Potatoes were peeled, cut into homogeneous (0.7 × 0.7 × 6 cm) strips and washed with water. Ten batches of 200 g were fried in each oil for 10 min with 20-min intervals between frying operations. The initial temperature was 175ºC, and no replenishments of oil were made. Total heating period was 6 h, which included an initial heating period (50 min) and a final heating period (30 min). Surface-to-oil volume ratio changed from initially 0.3 to 0.4 cm^{-1} after the tenth frying operation. Samples of frying oils and fried potatoes taken after the tenth frying operation were kept at –30ºC and 60°C, respectively, until further analyses.

(*ii*) *Simulated continuous frying.* Initial surface-to-oil volume ratio and temperature were similar to those for discontinuous frying. Continuous frying was simulated by using two

*To whom correspondence should be addressed at Instituto de la Grasa (CSIC), Avda. Padre García Tejero, 4, 41012 Sevilla, Spain.
E-mail: cdobar@cica.es

baskets to maintain the presence of the food in the fryer throughout the heating period. Potatoes (6.4 kg) were fried in each oil (32 lots × 10 min). A minimum initial heating period of 20 min was necessary to establish the same temperature in the fryers. Also, 250 mL of oil was added after 21st frying operation to maintain a minimum amount of oil. Surface-to-oil volume ratio changed from the initial 0.3 to 0.5 cm^{-1} after the 32nd frying operation. Samples of used frying oils, taken after the first and 32nd frying operations, were kept at −30°C until further analyses and at 60°C in the case of fried potatoes.

Storage conditions. Samples of 10 g of fried potatoes were wrapped in aluminum foil and stored at 60°C in an oven for up to 30 d.

Analytical methods. Lipids were obtained from ground freeze-dried potatoes by 6-h Soxhlet extraction (24) using diethyl ether as solvent. Quantitation and distribution of polar compounds were determined by a combination of adsorption and high-performance size exclusion chromatography (HPSEC) (25). α-Tocopherol was determined by high-performance liquid chromatography and fluorescence detection (26). Peroxide value was determined by iodometric assay (27). Oil stability index (OSI) was evaluated at 100°C using a Rancimat apparatus (28) with either 2.5 g of oil or 5 g of freeze-dried potatoes.

RESULTS AND DISCUSSION

Table 1 shows evolution of total polar compounds during storage. Samples A, B, and C for SO and HOSO were selected for storage because of their variations in both oil degradation and tocopherol content. Samples A and B corresponded to the first and 32nd frying operations of simulated continuous laboratory frying (30 min and 5.7 h heating, respectively), whereas samples C corresponded to the tenth frying operation in experiments of discontinuous frying (5.5 h heating). Initial contents of polar compounds (day 0) in fried potatoes primarily depended on the type of frying, much more than on the degree of unsaturation (29) since values as low as 8.8 and 6.6% were found after 32 frying operations in continuous frying vs. 19.0 and 16.0% after 10 frying operations in discontinuous frying, for SO and HOSO, respectively. Polar compounds, which represent the increase of total oxidation products during storage, initially showed a slow increase, until a certain point, after which a rapid rise was observed, between 9 and 14 d for SO-A, 7 and 9 d for SO-B, 5 and 7 d for SO-C, 28 and 30 d for HOSO-A, 21 and 28 d for HOSO-B, and 2 and 3 d for HOSO-C. As previously established (19), this point corresponded to initiation of the advanced oxidation stage at the end of the induction period. Surprisingly, the less unsaturated oil underwent the most rapid degradation (HOSO-C), showing a shorter induction period than its counterpart (SO-C).

Figure 1 illustrates the increase of triglyceride polymers, the major group of compounds among polar products in frying fats, during storage. Values for unused oils were 0.6 and 0.2% for SO and HOSO, respectively. It has been reported that, during the early phase of oxidation, only oxidized triglyceride monomers show a gradual increment, in parallel to the development of primary oxidation products, and that triglyceride polymers start increasing at the end of the induction period, indicating that oxidation has accelerated (30). Interestingly, a similar pattern was found here independently of the initial level of polymers in the used frying oil retained in food samples. Again, as observed through polar compounds evaluation, HOSO-C showed the most accelerated degradation. Triglyceride polymers in oils were determined here by HPSEC analysis of the isolated polar fractions (25) but can be also analyzed directly in total oil samples, in only 15 min (31). This easy determination is very valuable to show differences in induction periods.

Peroxide values are presented in Table 2. Data at day 0 do not reflect the degradation oil level of fried potatoes since it is known that at the high temperature of the frying process decomposition of hydroperoxides is more rapid than their formation (32,33). However, during storage at 60°C, evolution of peroxides was consistent with that of polar compounds (Table 1), both measurements being useful to follow the development of oxidation. This was expected considering that,

TABLE 1
Polar Compounds (wt% of oil) in Oils Extracted from Fried Potatoes Stored at 60°C[a,b,c]

	Storage period (d)									
Sample[d]	0	2	3	5	7	9	14	21	28	30
SO-A	5.1	N.A.	N.A.	8.0	N.A.	11.5	50.5			
SO-B	8.8	N.A.	10.5	11.6	14.9	22.5				
SO-C	19.0	19.6	N.A.	22.7	36.6					
HOSO-A	4.6	N.A.	N.A.	N.A.	6.0	N.A.	6.8	7.5	9.6	15.2
HOSO-B	6.6	N.A.	N.A.	N.A.	6.9	N.A.	11.0	12.8	54.0	
HOSO-C	16.0	18.5	30.2							

[a]Abbreviations: SO, sunflower oil; HOSO, high-oleic sunflower oil; N.A., intermediate sample not analyzed.
[b]Content of polar compounds for initial oils was 2.8 and 3.1% for SO and HOSO, respectively.
[c]Moisture and lipid contents of fried potatoes were 20.2 and 28.6% on average, respectively.
[d]Samples A and B corresponded to the first and 32nd frying operations of simulated continuous laboratory frying (30 min and 5.7 h heating, respectively), whereas samples C corresponded to the tenth frying operation in experiments of discontinuous frying (5.5 h heating).

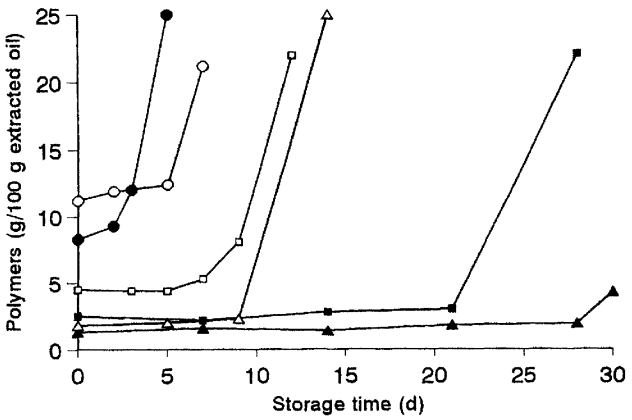

FIG. 1. Evolution of polymers (wt% on extracted oil) in fried potatoes stored at 60°C. (△) Sunflower oil (SO) Sample A, corresponding to first frying operation of simulated continuous laboratory frying (30 min); (□) SO sample B, corresponding to 32nd frying operation of simulated continuous laboratory frying (5.7 h); (○) SO sample C, corresponding to the tenth frying operation in experiments of discontinuous frying (5.5 h); (▲) high-oleic sunflower oil (HOSO), treatment A; (■) HOSO, treatment B; (●) HOSO, treatment C.

as previously reported, at ambient temperature and 60°C, the increase in oxidation compounds before the end of the induction period is primarily attributable to the accumulation of oxidized triglyceride monomers containing acyl hydroperoxides groups (30). On the other hand, the sudden rise in peroxide values closely paralleled the sharp increase of polymers (Fig. 1) at the end of the induction period.

OSI (Table 3) was determined directly in freeze-dried fried potatoes throughout the storage period. Such results cannot be compared with those obtained for oils since values have been found higher when determined in foods (29,34). Thus, the real decrease of stability due to frying cannot be directly deduced from the initial values for the unused oils (9.1 and 20.4 h for SO and HOSO, respectively) and the results on fried potatoes at the starting point of storage. However, data on initial fried potatoes were consistent with results of polar compounds and peroxide values. Also, the decrease observed throughout the storage period was parallel to the increase in the other quality parameters, thus indicating that stability at 100°C provided a good indication of the evolution of oxidation at 60°C.

Decrease of α-tocopherol, included in Table 4, was essential to complete information on the progression of oxidation in fried potatoes. As levels of α-tocopherol for unused oils were of the same order (603 and 650 mg/kg for SO and HOSO, respectively), changes during frying (data at day 0) clearly showed that α-tocopherol was lost more rapidly in the less unsaturated oil, as previously reported (35–38). Furthermore, concomitantly with higher losses of α-tocopherol, HOSO reached lower degradation levels than their counterparts SO (Table 1). However, as expected, the decrease of α-tocopherol during storage was more rapid for the more unsaturated oils as shown for samples with practically identical initial contents of α-tocopherol (SO-B and HOSO-A). In particular, HOSO-C had a remarkably low content of α-tocopherol (10 mg/kg) which was insufficient to delay oxidation, and this may explain the results obtained for polar compounds and polymers. These findings reveal some insight into the different

TABLE 2
Peroxide Value (meq O_2/kg oil) in Oils Extracted from Fried Potatoes Stored at 60°C

	Storage period (d)									
Sample[a]	0	2	3	5	7	9	14	21	28	30
SO-A	12	N.A.	30	N.A.	68	120	532			
SO-B	26	N.A.	62	101	158	323				
SO-C	21	34	48	52	354					
HOSO-A	8	N.A.	N.A.	N.A.	21	N.A.	35	47	82	108
HOSO-B	14	N.A.	N.A.	N.A.	32	N.A.	68	140		
HOSO-C	33	81	303							

[a]For abbreviations see Table 1.

TABLE 3
Oil Stability Index (h) in Fried Potatoes Stored at 60°C

	Storage period (d)									
Sample[a]	0	2	3	5	7	9	14	21	28	30
SO-A	8.7	N.A.	N.A.	N.A.	4.9	2.2				
SO-B	6.6	N.A.	4.6	3.0	1.3	0				
SO-C	4.5	4.6	2.8	2.6	0	N.A.				
HOSO-A	20.4	N.A.	N.A.	N.A.	16.8	N.A.	13.3	7.2	4.1	2.8
HOSO-B	16.1	N.A.	N.A.	N.A.	12.3	N.A.	4.0	1.1		
HOSO-C	3.8	2.9	0							

[a]For abbreviations see Table 1.

TABLE 4
α-Tocopherol (mg/kg oil) in Oils Exctracted from Fried Potatoes Stored at 60°C

	Storage period (d)									
Sample[a]	0	2	3	5	7	9	14	21	28	30
SO-A	545	N.A.	550	405	245	73	N.D.			
SO-B	390	N.A.	356	285	119	N.D.				
SO-C	100	78	55	44	N.D.					
HOSO-A	392	N.A.	N.A.	N.A.	375	N.A.	302	210	70	32
HOSO-B	188	N.A.	N.A.	N.A.	201	N.A.	75	13	N.D.	
HOSO-C	10	N.D.								

[a]N.D., not detected. For other abbreviations see Table 1.

behavior of α-tocopherol depending on the temperature applied, and stresses the importance of the remaining level of natural antioxidants in oils to stop a rapid initiation of oxidation after frying.

A practical conclusion drawn from this study is that, during frying, the absence of tocopherols might be compatible with intermediate, still acceptable levels of degradation in monounsaturated oils. It is well-known that frying oil degradation should be limited. Moreover, these results indicate that antioxidant protection is essential for preparation of fried foods that require storage before consumption to avoid rapid development of oxidation. In fact, susceptibility to oxidation of the fried products may be more dependent on the protection provided by the remanent antioxidants than on the unsaturation degree. Hence it is difficult to define the best oil for frying without knowledge of the characteristics of the frying process and the later destination of the fried food.

ACKNOWLEDGMENTS

This study was funded by CICYT (Project ALI-95-0736) and EC (Project AIR1 CT92-0687). The authors thank Mercedes Giménez for assistance. Neuza Jorge was supported by a fellowship from CNPq (Brazil).

REFERENCES

1. Croon, L.B., A. Rogstad, T. Leth, and T. Kiutamo, A Comparative Study of Analytical Methods for Quality Evaluation of Frying Fat, *Fette Seifen Anstrichm. 88*:87–91 (1986).
2. Gertz, C., Chromatographische Methoden bei der Untersuchung Von Fritierfetten, *Ibid. 88*:475–480 (1986).
3. Sebedio, J.L., A. Grandgirard, C. Septier, and J. Prevost, Etat d'altération de quelques huiles de friture prélevées en restauration, *Rev. Fr. Corps Gras 36*:15–18 (1987).
4. Dobarganes, M.C., and G. Márquez Ruiz, Calidad de las Grasas de Fritura en el Sector de Restauración de Andalucía, *Grasas Aceites 46*:115–120 (1995).
5. Skrökki, A., Test Used for Examining the Quality of Frying Oils, *Fat. Sci. Technol. 97*:384–386 (1995).
6. Gere, A., Decrease in Essential Fatty Acid Content of Edible Fat During the Frying Process, *Z. Ernährungswiss. 21*:191–201 (1982).
7. Gere, A., Study of Some Factors Affecting Frying Fat Deterioration, *Fette Seifen Anstrichm. 85*:18–23 (1983).
8. Varela, G., Current Facts About Frying of Foods, in *Frying of Food: Principles, Changes, New Approaches*, edited by G. Varela, A.E. Bender, and I.D. Morton, Ellis Horwood, Chichester, 1988, pp. 9–25.
9. Boskou, D., Stability of Frying Oils, *Ibid*. pp. 174–182.
10. Dobarganes, M.C., and G. Márquez Ruiz, Dimeric and Higher Oligomeric Triglycerides, in *Deep Frying, Chemistry, Nutrition and Practical Applications*, edited by E.G. Perkins and M.D. Erickson, American Oil Chemists' Society, Champaign, 1996, pp. 89–111.
11. Liu, H.-R. and P.J. White, High-Temperature Stability of Soybean Oils with Altered Fatty Acid Composition, *J. Am. Oil Chem. Soc. 69*:533–537 (1992).
12. Dobarganes, M.C., G. Márquez Ruiz, and M.C. Pérez-Camino, Thermal Stability and Frying Performance of Genetically Modified Sunflower Seed (*Helianthus annuus* L.) Oils, *J. Agric. Food Chem. 41*:678–681 (1993).
13. Warner, K., and T.L. Mounts, Frying Stability of Soybean and Canola Oils with Modified Fatty Acid Compositions, *J. Am. Oil Chem. Soc. 70*:983–988 (1993).
14. Mounts, T.L., K. Warner, and G.R. List, Performance Evaluation of Hexane-Extracted Oils from Genetically Modified Soybeans, *Ibid. 71*:157–161 (1994).
15. Mounts, T.L., K. Warner, G.R. List, W.E. Neff, and R.F. Wilson, Low-Linolenic Acid Soybean Oils—Alternatives to Frying Oils, *Ibid. 71*:495–499 (1994).
16. Warner, K., P. Orr, L. Parrot, and M. Glyn, Effects of Frying Oil Composition on Potato Chip Stability, *Ibid. 71*:1117–1121 (1994).
17. Warner, K., P. Orr, and M. Glynn, Effect of Fatty Acid Composition of Oils on Flavor and Stability of Fried Foods, *Ibid. 74*:347–356 (1997).
18. Sebedio, J.L., M.C. Dobarganes, G. Márquez, I. Wester, W.W. Christie, G. Dobson, F. Zwobada, J.M. Chardigny, T. Mairot, and R. Lahtienen, Industrial Production of Crisps and Prefried French Fries Using Sunflower Oils, *Grasas Aceites 47*:5–13 (1996).
19. Martín-Polvillo, M., G. Márquez Ruiz, M.V. Ruiz Méndez, and M.C. Dobarganes, Evolution of Oxidation During Storage of Crisps and French Fries Prepared with Sunflower Oil and High Oleic Sunflower Oil, *Ibid. 47*:54–58. (1996).
20. Lahtinen, R.M., I. Wester, and J.R.K. Niemelä, Storage Stability of Crisps Measured by Headspace and Peroxide Value Analyses, *Ibid. 47*:59–62 (1996).
21. Raoux, R., O. Morin, and F. Mordret, Sensory Assessment of Stored French Fries and Crisps Fried in Sunflower and High Oleic Sunflower Oils, *Ibid. 47*:63–74 (1996).
22. Van Gemert, L., Sensory Properties During Storage of Crisps and French Fries Prepared with Sunflower Oil and High Oleic Sunflower Oil, *Ibid. 47*:75–80 (1996).
23. Niemelä, J.R.K., I. Wester, and R.M. Lahtinen, Industrial Frying Trials with High Oleic Sunflower Oil, *Ibid. 47*:1–4 (1996).
24. *Asociación Española de Normalización*, Norma UNE 55-062-80, Madrid, 1991.

25. Dobarganes, M.C., M.C. Pérez-Camino, and G. Márquez Ruiz, High-Performance Size-Exclusion Chromatography of Polar Compounds in Heated and Non-heated Fats, *Fat Sci. Technol. 90*:308–311 (1988).
26. *Standard Methods for the Analysis of Oils, Fats and Derivatives*, 1st supplement to 7th edn., Pergamon Press, Oxford, 1992, IUPAC Method 2.432.
27. *Asociación Española de Normalización*, Norma UNE 55-023-73, Madrid,1991.
28. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., American Oil Chemists' Society, Champaign, 1989, Method Cd 12b-92.
29. Jorge, N., G. Márquez Ruiz, M. Martín Polvillo, M.V. Ruiz Méndez, and M.C. Dobarganes, Influence of the Addition of DMPS to Frying Oils: Performance of Sunflower Oils in Discontinuous and Continuous Laboratory Frying, *Grasas Aceites 47*:20–25 (1996).
30. Márquez Ruiz, G., M. Martín Polvillo, and M.C. Dobarganes, Quantitation of Oxidized Triglyceride Monomers and Dimers as a Useful Measurement for Early and Advanced Stages of Oxidation, *Ibid.47*:48–53 (1996).
31. *Standard Methods for the Analysis of Oils, Fats and Derivatives*, 7th edn., Pergamon Press, Oxford, 1992, IUPAC Method 2.508.
32. Stevenson, S.G., M. Vaisey-Genser, and N.A.M. Eskin, Quality Control in the Use of Deep Frying Oils, *J. Am. Oil Chem. Soc. 61*:1102–1108 (1984).
33. Masson, L., P. Robert, N. Romero, M. Izaurieta, S. Valenzuela, J. Ortiz, and M.C. Dobarganes, Comportamiento de Aceites Poliinsaturados en la Preparación de Patatas Fritas para Consumo Inmediato: Formación de Nuevos Compuestos y Comparación de Métodos Analíticos, *Grasa Aceites 48*:273–281 (1997).
34. Barrera-Arellano, D., and W. Esteves, Oxidative Stability of Potato Chips Determined by Rancimat, *J. Am. Oil Chem. Soc. 69*:335–338 (1992).
35. Yuki, E., and Y. Ishikawa, Tocopherol Contents of Nine Vegetable Frying Oils, and Their Changes Under Simulated Deep-Fat Frying Conditions, *Ibid. 53*:673–676 (1976).
36. Pongracz, G., Hitzestabiliät der Tocopherole, *Fat Sci. Technol. 90*:247–251 (1988).
37. Yoshida, H., N. Hirooka, and G. Kajimoto, Microwave Energy Effects on Quality of Some Seed Oils, *J. Food Sci. 55*:1412–1416 (1990).
38. Kajimoto, G., Y. Kanomi, H. Yoshida, and A. Shibahara, Influence of Fatty Acid Composition in Oil on the Thermal Decomposition of Tocopherols, *J. Jpn. Oil Chem. Soc. 40*:196–201 (1991).

[Received November 24, 1997; accepted March 6, 1999]