Evolution of oxidation during storage of crisps and french fries prepared with sunflower oil and high oleic sunflower oil

By M. Martín-Polvillo, G. Márquez-Ruiz, N. Jorge, M. V. Ruiz-Méndez and M. C. Dobarganes

Instituto de la Grasa (CSIC). Avda. Padre García Tejero, 4. 41012-Sevilla

SUMMARY

Evolution of oxidation during storage of crisps and french fries prepared with sunflower oil and high oleic sunflower oil

Storage studies were carried out to define the behaviour of both conventional and high oleic sunflower oils in the industrial preparation of crisps and prefried french fries. Samples of crisps and prefried french fries were stored during 6 and 21 months, respectively, and evolution of oxidation was compared with that of the more saturated fats normally used for the preparation of both products, i.e., palm olein and hydrogenated rapeseed/palm oil mixture. Total oxidation compounds, α-tocopherol content, as well as monomeric and dimeric triglycerides, were quantitated in lipids from fried products after different time periods. Results obtained for crisps at room temperature indicated that only conventional sunflower oil underwent significant oxidation after 6 months. In the case of prefried french fries, maintained at freezer temperatures, no appreciable changes were found after 21 months storage, thus indicating that both sunflower oils can be good alternatives to saturated fats.

KEY-WORDS: Crisps – French fries – High oleic sunflower oil – Oxidation – Storage – Sunflower oil

1. INTRODUCTION

Results of industrial trials demonstrated that conventional and high oleic sunflower oils had an excellent behaviour in the preparation of crisps and french fries due to the good manufacturing practices applied (Niemelä et al., 1996; Sebedio et al., 1996). However, for using sunflower oils as an alternative to saturated fats it is necessary not only to guarantee a good frying performance but also to ensure an appropiate shelf life of the fried products.

Crisps and french fries are normally stored at room and freezer temperature, respectively, and a high quality of the products has to be maintained at least during their commercialization period, normally 3 and 18 months, respectively. Thus, chemical evaluation of oxidation during storage, complementary to sensory analyses (Gemert, 1996; Raoux et al., 1996), is of great interest to definitively evaluate the behaviour of sunflower oils as substitutes for saturated fats.

Towards this end, an useful methodology has been developed, which allows follow-up of oxidation during the early stages, before appearance of rancidity (Márquez-Ruiz et al., 1996). It was found that quantitation of oxidized triglyceride monomers, comprised of all triglyceride monomers with at least one fatty acyl oxidized, regardless of the type of functional group, is of great utility as it provides a direct measurement of the primary and secondary oxidation products during the first stages of oxidation. On other hand, the increase in polymerization compounds denotes the end of the induction period and the onset of advanced stages of oxidation.

In this paper, total oxidation products as well as monomeric and dimeric triglycerides as good indicators of the early and advanced stages of oxidation, have been quantitated in lipids from crisps and french fries prepared with conventional and high oleic sunflower oils. Samples were stored for 6 and 21 months, respectively, and evolution of oxidation during storage has been compared with that of saturated fats, normally used for the preparation of both products.

2. EXPERIMENTAL

Samples and storage conditions

Crisps were prepared industrially with sunflower oil (SO) and high oleic sunflower oil (HOSO), both without and with 2 mg/kg of dimethylpolysiloxane (DMPS) added. Crisps fried in palm olein (PO) were used as reference samples. Initial food lipids as well as those obtained after storage of crisps at room temperature for 15 and 25 weeks were analysed.

An accelerated test at 60°C in an oven was also carried out during 35 days. Samples of food lipids were analysed after several storage periods.

French fries were prepared with SO and HOSO and stored in a freezer at -20°C. For these products, two partially hydrogenated rapeseed-palm oil mixtures (RP1 and RP2) were used as reference fats. Lipids from french fries were analysed after storage for 8 and 21 months.

Vol. 47 Fasc. 1-2 (1996) 55

Samples of crisps and french fries were taken out after 20 and 48 hours of continuous frying, respectively (Niemelä et al, 1996), and the period controlled under normal storage conditions was 3 months longer than the maximum commercialization period for both products.

Analytical determinations

- Potatoes were ground and freeze-dried, and the lipids were obtained by 6 hours Söxhlet extraction (AENOR, 1991), using diethyl ether as solvent.
- Total oxidation compounds were evaluated by means of polar compound determination (IUPAC, 1987). Formation of dimers and oxidized monomers during storage was determined by size-exclusion chromatography of total oxidation compounds isolated previously (Dobarganes et al, 1988).
- $-\alpha$ -tocopherol was quantitated by IUPAC Standard method (IUPAC, 1992).
- Oil stability index (OSI) was evaluated by means of a Rancimat apparatus at 100°C (AOCS, 1994) using 5g of crisps or ground, freeze-dried french fries.

3. RESULTS AND DISCUSSION

Table I shows the evolution of total oxidation compounds and oxidized triglyceride monomers (oxTGM) in crisps stored at room temperature. The other groups of specific compounds separated by means of exclusion chromatography, i.e. triglyceride polymers, dimers, oxidized monomers, diglycerides and fatty acids, are not included in the table since they remained practically at the initial levels. By comparing the results for the different oils, it is clearly deduced that only sunflower oil (SO and SODMPS) crisps showed a considerable rise in oxidation compounds specifically attributable to an increase in oxTGM and changes from initial values were significant even at 15 weeks. In contrast, high oleic sunflower oil (HOSO and HOSODMPS) samples presented roughly the same oxidation levels as initially after 25 weeks, thus showing an excellent shelf-life at room temperature. Parallel results for α-tocopherol contents and oil stability index values are given in Table II wherein the loss of stability against oxidation in sunflower oil crisps (2.5 h and 2.6 h vs. 9.3 h at the starting point) can be noted even if α -tocopherol levels after 25 weeks remained high. For high oleic sunflower oil samples only a slow decrease in stability was observed, while PO crisps did not change during the controlled period.

Comparison of samples without and with DMPS added also allowed evaluation of DMPS action during storage. In previous studies, variable results were obtained. For instance, Rhee found that flavor, peroxide value and color of the oils were similar after storage of 95% soybean/5% cotton oil for one year

without and with DMPS added (Rhee, 1978). Nevertheless, Kusaka et al; in storage at room temperature and 55°C reported a slight antioxidative effect on peroxide values in oils with DMPS added, suggesting that it may be active at both low and high temperatures (Kusaka et al., 1980). Finally, Snyder et al. evaluated the oxidative and thermal stability of hydrogenated soybean oils and found that DMPS addition to the oils had practically no effect on volatile and peroxide values after storage at 60°C for 8 days. However, after storage of bread fries for 4 days at 60°C, DMPS showed a great effect (Snyder et al., 1986). Although no explanation is given on such differences between oils and bread fries, the latter results do not seem to be due to a positive effect of DMPS during storage but to the previous action of DMPS during frying. Protection of the oil against oxidation at high temperature clearly prolongs the subsequent storage period of the fried product, as we have recently found (Jorge et al., 1995). However, under the conditions used in the present study, samples without and with DMPS added where practically identical before and after storage, thus indicating that DMPS had not been active neither during industrial continuous frying at high temperature (Sebedio et al., 1996) nor during storage.

Table I
Evolution of total oxidation compounds
and oxidized triglyceride monomers (oxTGM)
during storage of crisps at room temperature
(wt% on oil)

		Initial	15 weeks	25 weeks
SO	Total	5.2	7.5	10.2
	oxTGM	1.5	3.7	6.1
SO DMPS	Total	5.6	8.0	10.3
	oxTGM	1.6	4.1	6.4
HOSO	Total	4.9	4.8	5.2
	oxTGM	1.2	1.2	1.6
HOSO DMPS	Total	5.2	5.2	5.6
	oxTGM	1.3	1.5	1.7
PO	Total	8.9	8.6	8.9
	oxTGM	1.1	1.2	1.1

Abbreviations: SO, sunflower oil; HOSO, high oleic sunflower oil; DMPS, dimethylpolysiloxane; PO, palm olein

Results obtained here at room temperature were in agreement with those of peroxide values and hexanal contents (Lahtinen et al., 1996) as well as for sensory evaluation (Gemert, 1996; Raoux et al., 1996). Overall, they indicate that HOSO would be an excellent oil for the preparation of crisps while SO, as expected, was much more sensitive to oxidation during storage. Considering that high quality oils and good frying practice were applied in this study, it is evidenced that conventional

56 Grasas y Aceites

sunflower oils should only be used for frying in case of short commercialization periods which could ensure the consumption of high quality crisps.

Table II

Evolution of α -tocopherol contents (α -toc)(mg/Kg) and oil stability index (OSI) (hours) during storage of crisps at room temperature

		Initial	15 weeks	25 weeks
SO	α-toc	606	545	497
	OSI	9.3	3.9	2.5
SO DMPS	α -toc	580	528	507
	OSI	9.3	4.1	2.6
HOSO	α-toc	571	589	576
	OSI	21.8	18.6	18.5
HOSO DMPS	α-toc	584	568	554
	OSI	21.7	19.6	16.6
PO	α-toc	207	209	198
	OSI	38.5	42.0	42.2

For abbreviations, see Table I

Accelerated oxidative assays at 60°C were carried out in oven to examine the course of oxidation at more advanced stages. Results obtained for total oxidation products are shown in Table III, while evolution of α -tocopherol levels and oil stability index values during storage are included in Table IV. Samples of SO and SODMPS crisps after 11 days had similar oxidation levels as those reached after 25 weeks at room temperature, and stability against oxidation was almost lost. This point (11 days) was very close to the end of the induction period, as indicated by the large increase of total oxidation products in just three days (from day 11 to day 14) in SODMPS crisps.

For HOSO and HOSODMPS, the rise in total oxidation compounds was gradual but, unlike SO and

SODMPS, oxidation had still not entered the accelerated stage after 35 days, thus indicating that the end of the induction period had not been reached yet. Palm olein, as expected, showed the slowest oxidation rate.

Table III

Evolution of total oxidation compounds during storage of crisps at 60°C (wt% on oil)

	Initial	6 days	11 days	14 days	21 days	28 days	35 days
SO	5.5	7.7	11.1	_	87.3	_	89.0
SO DMPS	5.6	7.4	12.5	71.3	_	84.5	_
HOSO	4.9	5.6	5.7	_	7.5	_	14.6
HOSO DMPS	5.2	4.9	5.6	6.4	_	10.7	_
PO	8.9	9.5	9.3	_	-	11.9	10.7

For abbreviations, see Table I

Figure 1 shows evolution of oxidized triglyceride monomers, the only group of compounds formed in HOSO, HOSODMPS and PO after 35 days. In contrast, in the case of SO and SODMPS crisps, oxTGM contents increased drastically after 11 days even though the maximum amount obtained was around 30% lower than that of total oxidation compounds due to the parallel formation of polymerization compounds. This is well illustrated in Figure 2 where data for both sunflower oils, SO and SODMPS, have been combined given the similar evolution followed by both oils as a result of the lack of effect of DMPS. As can be observed, as a consequence of the sharp increase in oxidation monomers, oxidative polymerization occurred in parallel and, as oxidation progresses, intermediate compounds, i.e. oxidized monomers and dimers, tended to stabilize or even decrease because of their participation in the formation of the most stable compounds, triglyceride polymers.

Table IV Evolution of α -tocopherol (α -toc) (mg/Kg) and oil stability index (OSI) (hours) during storage of crisps at 60°C

		Initial	6 days	11 days	14 days	21 days	28 days	35 days
SO	α–toc OSI	595 9.4	394 4.1	201 1.8	-	n.d. 0		
SO DMPS	α–toc OSI	561 9.6	315 3.7	73 1.1	n.d. 0			
HOSO	α–toc OSI	597 24.0	575 18.9	487 14.7	- -	365 7.4	_ _	n.d. 1.2
HOSO DMPS	α–toc OSI	581 23.7	562 18.2	454 13.2	409 10.2	-	312 2.3	_ _
РО	α–toc OSI	207 48.3	199 -	201 44.1		<u>-</u> -	_ 26.5	64 20.4

For abbreviations, see Table I

Vol. 47 Fasc. 1-2 (1996) 57

Table IV shows changes in α -tocopherol and induction times during accelerated storage test at 60°C. Oil stability index at 100°C for SO and SODMPS was close to 0 after 11 days thus denoting that the end of the induction period was being reached. Similar values were found for HOSO after much longer storage, 35 days, while PO was the most stable oil.

It is interesting to note that results for α -tocopherol contents at 60°C clearly differed from those obtained at room temperature. By comparing Tables II and IV for SO and SODMPS, it is easily deduced that the loss

of α -tocopherol was much more rapid at 60°C and that there is not a clear relationship between tocopherol content and either total oxidation products or oil stability index values. Levels of α -tocopherol remaining after storage of sunflower oils for 6 days were much lower than those found after 25 weeks even though oil stability index values were significantly higher. This would indicate that evolution of oxidation clearly depended on temperature, and hence it is difficult to extrapolate results obtained at different temperatures (Frankel, 1993).

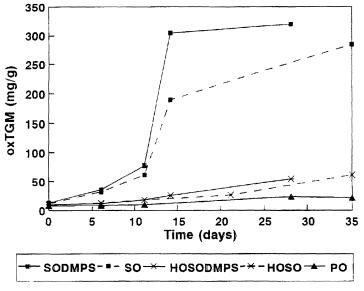


Figure 1

Evolution of oxidized triglyceride monomers (oxTGM) in crisps prepared with sunflower oil, without (SO) and with DMPS added (SODMPS), high oleic sunflower oil, without (HOSO) and with DMPS added (HOSODMPS) and palm olein (PO), during storage at 60°C

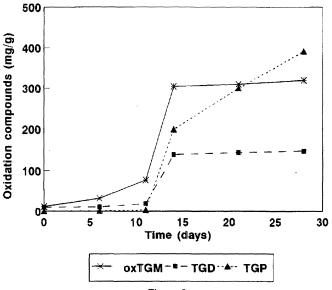


Figure 2

Evolution of oxidized triglyceride monomers (oxTGM), dimers (TGD) and polymers (TGP) in crisps prepared with sunflower oil, during storage at 60°C

58 Grasas y Aceites

Finally, Table V includes values of total oxidation compounds and oxTGM in french fries after 8 and 21 months at -20°C. Initial data correspond to the frying oils as french fries were provided after 7 months storage at freezer temperature and, consequently, could not be analysed at the initial point. As can be observed, only in the case of SO was a small increase in oxidized triglyceride monomers obtained. Nevertheless, after 21 months, oil stability index was still 5 h and α -tocopherol remained at the initial levels thus indicating that the end of the induction period was far from being reached. The other oils did not undergo any appreciable change during the period controlled.

Table V
Evolution of total oxidation compounds and oxidized triglyceride monomers (oxTGM) during storage of french fries at freezer temperature (wt% on oil)

		Initial	8 months	21 months
so	Total	7.4	8.5	8.7
	oxTGM	2.2	2.5	3.5
HOSO	Total	7.4	7.8	7.9
	oxTGM	2.2	2.4	2.7
RP1	Total	7.0	7.1	7.1
	oxTGM	2.1	2.0	2.1
RP2	Total	7.5	7.8	7.4
	oxTGM	2.2	2.1	2.2

Abbreviations: SO, sunflower oil; HOSO, high oleic sunflower oil; RP, partially hydrogenated rapeseed–palm oil mixture.

Based on the data obtained, it is concluded that both oils could be used as alternatives to saturated fats for products maintained at freezer temperatures. Moreover, due to the high increase in the consumption of prefried products, the use of liquid oils for the prefrying step would be of particular utility in countries where prefried foods are subjected to a second frying operation before comsumption and liquid oils are used for this final preparation. Otherwise, the concentration of saturated fat in the frying medium would increase because of the high proportion of fats solubilized from the prefried food (Pérez-Camino et al, 1991).

ACKNOWLEDGEMENTS

This work was funded by EC (Proyect AIR1-CT92-0687) and CICYT (Project ALI 95-0736). The authors would also like to thank M. Giménez and M. Serrano for assistance. Neuza Jorge was supported by a fellowship from CNPq (Brazil).

BIBLIOGRAPHY

- AENOR (1991). Norma UNE 55-062-80, Catálogo de Normas UNE, Asociación Española de Normalización, Madrid.
- AOCS (1994). Method Cd 12b-92 in «Official methods and recommended practices of the American Oil Chemists' Society», 4th ed.- AOCS, Champaign.
- Dobarganes, M.C., Pérez-Camino, M.C. and Márquez-Ruiz, G. (1988).- "High-performance size-exclusion chromatography of polar compounds in heated and non-heated fats".- Fat Sci. Technol. 90, 308-311.
- Frankel, E.N. (1993).- «In search of better methods to evaluate natural antioxidants and oxidative stability in food lipids».- Trends Food Sci. Technol. **4**, 220-225.
- Gemert Van, L.J. (1996).- «Sensory properties during storage of crisps and french fries prepared with sunflower oil and high oleic sunflower oil».- Grasas y Aceites 47, 75-80.
- IUPAC. (1987). Method 2.507. «Standard methods for the analysis of oils, fats and derivatives».- 7th edition, Pergamon Press, Oxford.
- IUPAC. (1992). Method 2.432.- «Standard methods for the analysis of oils, fat and derivatives».- 1st supplement to 7th edition, Pergamon Press, Oxford.
- Jorge, N., Martín-Polvillo, M., Ruiz-Méndez, M.V., Márquez-Ruiz, G. and Dobarganes, M.C. (1995).- «Influence of dimethylpolysiloxane on frying performance of sunflower oils in discontinuous frying and on storage of fried potatoes» in «Proceedings of the 6th Latin Congress and Exhibit on Fats and Oils Processing» p. 311-315.- D. Barrera-Arellano, M.A.B. Regitano d'Arce and L.A.G. Çonzalves (Ed).- SBOG, Campinas (Brasil).
- Kusaka, H., Kakizaki, J., Shinozaki, T.A. and Ohta, S. (1980).-«On functions of silicone in frying oil. II: Antioxidative effect of silicone oil on autoxidation of edible oil».- J. Japan Oil Chem Soc. 5, 341-344.
- Lahtinen, R.M., Wester, I. and Niemelä, J.R.K. (1996).- «Storage stability of crisps measured by headspace and peroxide value analyses».- Grasas y Aceites 47, 59-62.
- Márquez-Ruiz, G., Martín-Polvillo, M. and Dobarganes, M.C. (1996).- "Quantitation of oxidized triglyceride monomers and dimers as an useful measurement for early and advanced stages of oxidation".- Grasas y Aceites 47, 48-53.
- Niemelä, J.R.K., Wester, I. and Lahtinen, R.M. (1996).-«Industrial frying trials with high oleic sunflower oil».-Grasas y Aceites 47, 1-4.
- Pérez-Camino, M.C., Márquez-Ruiz, G., Ruiz-Méndez, M.V. and Dobarganes, M.C. (1991).- «Lipid changes during frying of frozen prefried foods».- J. Food Sci. **56**, 1644-1647.
- Raoux, R., Morin, O. and Mordret, F. (1996).- «Sensory assessment of stored french fries and crisps fried in sunflower and high oleic sunflower oils».- Grasas y Aceites 47, 63-74.
- Rhee, J.S. (1978).- «Effect of methyl silicone, TBHQ and BHA/BHT on frying and storage stabilities of the vegetable salad oil in high density polyethylene bottles».- Korean J. Food Sci. Technol. 10, 250-257.
- Sebedio, J.L., Dobarganes, C., Márquez, G., Wester, I., Christie, W.W., Dobson, G., Zwobada, F., Chardigny, J.M., Mairot, Th. and Lahtinen, R. (1996).- «Industrial production of crisps and prefried french fries using sunflower oils».- Grasas y Aceites 47, 5-13.
- Snyder, J.M., Frankel, E.N. and Warner, K. (1986).- «Headspace volatile analysis to evaluate oxidative and thermal stability of soybean oil. Effect of hydrogenation and additives».- J. Am. Oil Chem Soc. **63**, 1055-1058.