

Formation of polymerization compounds during thermal oxidation of cottonseed oil, partially hydrogenated cottonseed oil and their blends

By C. J. Steel¹, M. C. Dobarganes² and D. Barrera-Arellano^{1*}

¹ Laboratório de Óleos e Gorduras, Departamento de Tecnologia de Alimentos, Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas (UNICAMP) – CEP 13083-18621 – Campinas, SP, BRAZIL

² Instituto de la Grasa (CSIC), Avda. Padre García Tejero, 4 – 41012 – Sevilla, SPAIN

RESUMEN

Formación de compuestos de polimerización durante la termoxidación de aceite de algodón, aceite de algodón parcialmente hidrogenado y sus mezclas.

Muestras de aceite de algodón, aceite de algodón parcialmente hidrogenado y sus mezclas, con índices de yodo de 60 a 110, tratadas o no con óxido de aluminio, fueron sometidas a termoxidación, a 180 °C, durante 10 horas. Se retiraron muestras en los tiempos 0, 2, 5, 8 y 10 horas, para determinación de dímeros y polímeros (compuestos de degradación) y de tocoferoles. Se verificó la influencia del grado de hidrogenación sobre la formación de dímeros y polímeros, y también el papel de los tocoferoles originalmente presentes en el aceite y en las grasas, en la protección contra la degradación térmica. Las curvas de degradación de los tocoferoles mostraron una destrucción bastante rápida de los tocoferoles presentes en el aceite y en las grasas de algodón (α y γ -tocopheroles), con niveles residuales próximos a cero después de 10 horas de termoxidación. Aún así, muestras con sus tocoferoles naturales tuvieron una degradación térmica más lenta. El grado de insaturación parece ser más importante en la protección contra la degradación térmica que el contenido de tocoferoles.

PALABRAS-CLAVE: *Aceite de algodón – Degradación térmica – Grasas hidrogenadas – Termoxidación – Tocopheroles*

SUMMARY

Formation of polymerization compounds during thermal oxidation of cottonseed oil, partially hydrogenated cottonseed oil and their blends

Samples of cottonseed oil, partially hydrogenated cottonseed oil and their blends, with iodine values between 60 and 110, tocopherol-stripped or not by aluminium oxide treatment, were submitted to thermal oxidation, at 180 °C, for 10 hours. Samples were collected at 0, 2, 5, 8 and 10 hours, for the determination of dimers and polymers (degradation compounds) and of tocopherols. The influence of the degree of hydrogenation on the formation of dimers and polymers and the role of originally present tocopherols in the protection of fats and oils against thermal degradation was verified. The degradation curves for tocopherols showed a fast destruction rate for the tocopherols present in cottonseed fats and oil (α and γ -tocopherols), with residual levels close to zero after 10 hours under thermal oxidation conditions. Nevertheless, samples with their natural tocopherols presented a slower rate of thermal degradation. The unsaturation degree was apparently more important in

the protection against thermal degradation than the content of tocopherols.

KEY-WORDS: *Cottonseed oil – Hydrogenated fats – Thermal degradation – Thermal oxidation – Tocopherols*

1. INTRODUCTION

Frying has become one of the most extensively used methods for the preparation of foods in developed countries, making frying fats absorbed by fried products an important component of contemporary diets. The popularity of frying continues to grow and this is demonstrated by the remarkable increase in new fried and pre-fried foods found on the market (Velasco et al., 2004). Oil is the best heat transfer medium for the rapid preparation of foods, adequate for modern lifestyles and food-service systems; also giving the fried product desirable organoleptic characteristics (crispness, flavor, etc.) (Pérez-Camino et al., 1988).

During frying, fats and oils decompose forming volatile and non-volatile products that modify their functional, organoleptic and nutritional properties. The main degradation products absorbed by the food are non-volatile, including triacylglycerol polymers, triacylglycerol dimers, oxidized triacylglycerol monomers, cyclic substances and hydrolytic decomposition products (diacylglycerols, monoacylglycerols and free fatty acids) (Warner, 1997).

There are means to retard degradation, such as: the process of hydrogenation, which reduces the number of double bonds in the fat or oil, reducing reactive sites, concomitantly reducing iodine value; the presence or addition of antioxidants, such as naturally occurring tocopherols (Kamal-Eldin and Appelqvist, 1996) or synthetic tert-butylhydroquinone (TBHQ) (Allam and Mohamed, 2002; Gordon and Kourimska, 1995); and the addition of anti-foaming agents, such as dimethylpolysiloxane (DMPS), which reduce the contact with oxygen (Márquez-Ruiz et al., 2004).

Frying oils must be resistant to elevated temperatures, have adequate consistency to ease

handling, have high stability in the finished product and low absorption by the fried product. In Brazil, high performance vegetable frying fats are produced using hydrogenation as an intermediate step, followed by blending with other bases and/or liquid oils (Block, 1997). The two main oils used for producing frying shortenings are soybean oil and cottonseed oil.

Cottonseed fats and oils are often considered superior to other fats and oils in frying applications, due to their higher stability (lower levels of linolenic acid) and better organoleptic characteristics (Warner et al, 1997; NPCA, 2001).

Cottonseed fats used for frying in Brazil have iodine values that vary from 70 to 105, melting points from 24 to 38 °C and may contain tert-butyl-hydroquinone (TBHQ), citric acid and dimethylpolysiloxane to prevent oxidative and thermal degradation.

Naturally occurring tocopherols in cottonseed fats and oils are also a means to retard degradation of the oil. Antioxidant activity of tocopherols is mainly due to their capacity for donating their phenolic hydrogens to lipidic free radicals. But many other factors can affect the *in vitro* activity, such as concentration, light and temperature, type of substrate and solvent, and other chemical species that act as pro-oxidants or synergists in the system (Kamal-Eldin and Appelqvist, 1996).

The objective of this research was to evaluate the formation of polymerization compounds when refined cottonseed oil, partially hydrogenated cottonseed oil and three blends of both were submitted to thermal oxidation conditions. Towards this aim, two series of oils (with and without natural tocopherols) were heated under standard conditions, thus allowing the analysis of the influence of two factors: the degree of fat unsaturation and the level of tocopherols.

2. EXPERIMENTAL PROCEDURE

2.1. Samples

Refined cottonseed oil (Maeda S.A. Agroindustrial, Itumbiara, GO, Brazil) and partially hydrogenated cottonseed oil (PHCO) (Cargill Agrícola S.A., Mairinque, SP, Brazil) were used. Intermediate iodine value samples were prepared by the addition of cottonseed oil to PHCO and corresponded to the proportions 20:80 (w/w), 50:50 (w/w) and 80:20 (w/w) for samples with iodine values of 70, 85 and 100, respectively.

2.2. Sample characterization

The following AOCS or IUPAC Official Methods were used to characterize the samples used: Iodine Value (AOCS Recommended Practice Cd 1c-85, 1993), Oxidative Stability (AOCS Method Cd 12b-92, 1993, using Rancimat equipment at 110 °C), Free Fatty Acids (AOCS Method Ca 5a-40, 1996),

Peroxide Value (AOCS Method Cd 8b-90, 1996), Smoke Point (AOCS Method Cc 9a-48, 1993), Fatty Acid Composition (AOCS Method Ce 1-62, 1993), Tocopherols (IUPAC 2.432, 1992) and Quantitation and Distribution of Polar Compounds (Dobarganes et al., 2000).

2.3. Aluminium oxide treatment

A portion of each sample was treated to remove originally present tocopherols. This stripping procedure was carried out as described by Yoshida et al. (1992), by passing 50 – 100 g of oil through a column with approximately double this amount of activated aluminium oxide (Al₂O₃: aluminium oxide 90, standardised for column chromatographic adsorption analyses, acc. to Brockmann, Merck, item n° 1.01097.1000). Aluminium oxide was activated in an oven at 200 °C for at least 4 hours. After this treatment, each sample had its stripped or treated counterpart.

2.4. Thermal oxidation

8 ± 0.01 g of each sample were weighed in Rancimat tubes and inserted into the heating block previously heated to 180 ± 1 °C. Two samples of approximately 50 mg were collected after 2, 5, 8 and 10 hours heating and kept at –30 °C until analysis.

Rancimat instructions were carefully observed for glassware cleaning. During heating, the tubes were left open and no bubbling of air was applied. This procedure was described in detail, including reproducibility data, in a previous publication (Barrera-Arellano et al., 1997).

2.5. Analysis of thermally oxidized samples

1. Dimers and polymers were quantitated directly in the oil samples, using high performance size-exclusion chromatography (HPSEC), according to the IUPAC Standard Method 2.508 (IUPAC, 1992). Conditions applied for HPSEC were as follows: a Waters 510 HPLC pump and a Rheodyne 7725i injector with a 10 µm sample loop (Waters Associates, Milford, MA, USA), a Merck L-7490 refractive index detector (Merck, Darmstadt, Germany) and a Hewlett-Packard HP 3390A integrator (Hewlett-Packard, Pittsburgh, PA, USA) were used. Two Ultrastaygel columns (Waters Associates, Milford, MA, USA), 100 and 500 Å, connected in series, were used. The columns were 25 cm long x 0.77 cm inner diameter, packed with a porous, highly cross-linked styrenedivinylbenzene copolymer (< 10 µm). High performance liquid chromatography grade tetrahydrofuran was used as mobile phase, with a flow rate of 1 mL/min. Sample solutions of about 50 mg of oil/mL tetrahydrofuran were prepared for analyses.

2. Tocopherols were determined using high performance liquid chromatography (HPLC), according to the IUPAC Standard Method 2.432 (IUPAC, 1992). Conditions applied for HPLC were as follows: a Waters 600 HPLC pump with a 20 μ L sample loop or a Waters Model M45 Solvent Delivery System (Waters Associates, Milford, MA, USA) were used. A LiChrosorb SI 60 (250 x 4 mm) column, packed with silica (average particle size of approximately 5 μ m) (Merck, Darmstadt, Germany), was used. A Hewlett-Packard 1046A programmable fluorescence detector (290 – 330 nm) and a Hewlett-Packard HP 3390A integrator (Hewlett-Packard, Pittsburgh, PA, USA) were used. Oil samples (approximately 50 mg) were dissolved in 1 mL n-hexane. Mobile phase was n-hexane:isopropanol (99:1), with a flow rate of 1 mL/min.

3. RESULTS AND DISCUSSION

Physicochemical characteristics of cottonseed oil and partially hydrogenated cottonseed oil (PHCO) and their blends are shown in Table 1. It can be observed that oxidative stability was iodine value (IV) dependent. Comparing the oxidative stability of the cottonseed samples of this study with those of soybean samples evaluated in previous work (Steel et al., 2005), values close to half can be observed in the present study for the cottonseed samples with similar iodine values. For example, a soybean sample with IV = 60 had a Rancimat oxidative stability, at 110 °C, of 192.1 h, while the stability of PHCO (IV = 60) was of 89.2 h. One of the reasons for this difference could be the difference in the quantities and composition of tocopherols. Levels of 1245 mg/kg and 905 mg/kg total tocopherols were found in the soybean sample and in the PHCO sample, respectively. Apart from this, the soybean sample had a greater quantity of γ - and δ -tocopherols, to which a higher antioxidant activity *in vitro* is attributed (Kamal-Eldin & Appelqvist, 1996). All other quality related analytical indexes were within expected ranges for refined fats and oils.

Table 2 shows the fatty acid composition of cottonseed oil and partially hydrogenated cottonseed oil (PHCO) and their blends. The results clearly show

the effect of blending (oil into PHCO) on the simultaneous increase of iodine value and of the more unsaturated fatty acids, mainly linoleic acid (C18:2), with a concomitant reduction of the monounsaturated and saturated C18 fatty acids (oleic acid, C18:1, and stearic acid, C18:0).

Table 3 presents the tocopherol composition of cottonseed oil, PHCO and their blends. In this work, an abnormally low quantity of tocopherols was observed in cottonseed oil. This could indicate that the oil was intensely deodorized or that it was stored for a very long period. However, the low peroxide value indicates that the oil was recently refined. It can also be observed, in Table 1, that in parallel to the low antioxidant protection, the oxidative stability of the cottonseed oil studied was very low (2.27 h, Rancimat 110 °C).

The levels of tocopherols found in the PHCO sample are close to those reported for crude cottonseed oil (402 mg/kg α -tocopherol and 572 mg/kg γ -tocopherol) (Gunstone et al., 1994) and its oxidative stability is very high when compared to the sample of refined cottonseed oil. Both factors, iodine value and tocopherol content, favored the oxidative stability of the more saturated samples.

Polar compounds (quantitation and distribution) in the samples before and after aluminium oxide treatment can be seen in Table 4. Differences in the levels of polar compounds among the cottonseed samples were observed. Before aluminium oxide treatment, total polar compounds, which represent the degradation compounds in an oil or fat, were present in levels of 10.2% in cottonseed oil (IV = 110) and 6.1% in PHCO (IV = 60). The blends with intermediate iodine values presented intermediate values for polar compounds and correspond to those expected considering the proportions of the two initial fats. Lumley (1988) determined total polar compounds in fifty oil samples without use in frying and found a typical range of 0.4 – 6.4%. Four of the oils analyzed had polar compounds above 7.5%, but these values were considered exceptionally high. In this work, all the cottonseed samples, except the most saturated (PHCO, IV = 60), presented initial polar compound levels above 7.5%.

In the distribution of polar compounds, it can be seen that in PHCO (IV = 60), the sample with the

Table 1

Physicochemical characteristics of cottonseed oil, partially hydrogenated cottonseed oil and their blends

	PHCO IV = 60	Blend IV = 70	Blend IV = 85	Blend IV = 100	Cottonseed oil IV = 110
Iodine value	60.95	70.24	84.83	98.98	109.39
Oxidative stability, 110 °C (h)	89.2	23.5	10.6	5.0	2.3
Free fatty acids (% oleic acid)	0.04	0.03	0.04	0.04	0.04
Peroxide value (meq/kg)	0.3	0.6	0.6	1.0	1.1
Smoke point (°C)	217	226	224	219	220

PHCO: partially hydrogenated cottonseed oil; IV: iodine value

Table 2
Fatty acid composition of cottonseed oil, partially hydrogenated cottonseed oil and their blends

Fatty acids	PHCO IV = 60	Blend IV = 70	Blend IV = 85	Blend IV = 100	Cottonseed oil IV = 110
C 14:0	0.9	0.8	0.8	0.8	0.8
C 16:0	23.8	23.3	23.0	23.1	23.3
C 16:1	0.5	0.5	0.6	0.6	0.5
C 18:0	9.8	8.6	6.5	4.5	3.0
C 18:1	59.3	51.9	39.8	27.3	17.7
C 18:2	4.8	13.7	28.2	42.5	53.3
C 18:3	0.4	0.4	0.4	0.4	0.3
C 20:0	0.3	0.3	0.3	0.3	0.3
C 20:1	0.2	0.2	0.2	0.2	0.2
C 22:0	0.2	0.1	0.2	0.1	0.2
C 22:1 (n9)	–	0.1	0.1	0.1	0.2
C 22:1 (n11)	–	0.1	0.1	0.1	0.2
Saturated	34.8	33.1	30.7	28.8	27.5
Monounsaturated	65.1	66.9	69.2	71.2	72.5
Polyunsaturated	4.8	13.7	28.2	42.5	53.3

PHCO: partially hydrogenated cottonseed oil; IV: iodine value.

lowest quantity of total polar compounds, the predominant species were oxidized triglycerides (oxidized monomers) and diglycerides. As the unsaturation of the samples increased (and also their total polar compound level, in this case), the level of oxidized triglycerides increased, from 2.7% in PHCO (IV = 60) to 4.0% in cottonseed oil (IV = 110), and also the levels of triglyceride polymers, from 0.8% in PHCO (IV = 60) to 4.0% in cottonseed oil (IV = 110). In general, the results found for the blends are those expected from the proportions of the cottonseed oil and PHCO. Also, as commented above, the presence of a high amount of polymerization compounds in the cottonseed oil, would justify its low tocopherol content, as these compounds are mainly nonpolar dimers formed during the deodorization step of the refining process. The higher the amount of these compounds, the more severe the deodorization conditions and the more probable the loss of minor compounds like tocopherols, due to their volatility (Ruiz-Méndez et al., 1997).

The absence of tocopherols in aluminium oxide treated samples demonstrates the efficacy of the procedure in their removal, while fatty acid composition was not affected by the treatment (data not included). The percentages of total polar compounds in the treated samples varied from 2.4% in the blend with IV = 70 to 4.9% in cottonseed oil (IV = 110). As can be observed in Table 4, the lower concentration of polar compounds in the treated samples was mainly due to the adsorption on the aluminium oxide of two groups of compounds: oxidized triglycerides and diglycerides.

As expected, a drastic reduction in the oxidative stability of tocopherol-stripped samples was observed (Table 5). Higher oxidative stability was observed for the more saturated samples, but the removal of tocopherols caused a drastic reduction in oxidative stability, demonstrating the enormous influence of natural antioxidants on the stability against oxidation. Also, differences in stability of the series (OR or TR) increased as the iodine value decreased.

Table 3
Tocopherol composition of cottonseed oil, partially hydrogenated cottonseed oil and their blends

	PHCO IV = 60	Blend IV = 70	Blend IV = 85	Blend IV = 100	Cottonseed oil IV = 110
Total tocopherols (mg/kg)	905	782	502	282	85
α -tocopherol (mg/kg)	423	367	244	146	55
β -tocopherol (mg/kg)	0	0	0	0	0
γ -tocopherol (mg/kg)	476	413	258	136	30
δ -tocopherol (mg/kg)	6	2	0	0	0

PHCO: partially hydrogenated cottonseed oil; IV: iodine value.

Table 4
Total polar compounds (%) and their distribution in cottonseed oil, partially hydrogenated cottonseed oil and their blends before and after aluminium oxide treatment

	PHCO IV = 60		Blend IV = 70		Blend IV = 85		Blend IV = 100		Cottonseed oil IV = 110	
	OR	TR	OR	TR	OR	TR	OR	TR	OR	TR
PC (%)	6.1	2.7	7.8	2.4	8.2	3.5	9.3	4.1	10.2	4.9
Polar Compound Distribution:										
TGP	0.8	0.6	1.6	0.6	2.4	1.8	3.3	2.6	4.0	3.5
TGox	2.7	1.5	3.3	1.3	3.3	1.3	3.7	1.2	4.0	1.1
DG	1.9	0.3	2.2	0.2	2.0	0.2	2.0	0.1	2.0	0.2
MG	0.1	–	0.1	–	–	–	–	–	–	–
FA	0.6	0.3	0.6	0.3	0.5	0.2	0.3	0.2	0.2	0.1

OR: original; TR: treated with aluminium oxide to remove tocopherols; PHCO: partially hydrogenated cottonseed oil; IV: iodine value; PC: total polar compounds; TGP: triglyceride polymers; TGox: oxidised triglycerides; DG: diglycerides; MG: monoglycerides; FA: fatty acids + unsaponifiable polar fraction.

Table 5
Oxidative stability in hours (Rancimat, 110 °C) of cottonseed oil, partially hydrogenated cottonseed oil and their blends, with and without aluminium oxide treatment

	PHCO IV = 60	Blend IV = 70	Blend IV = 85	Blend IV = 100	Cottonseed oil IV = 110
OR	89.2	23.5	10.6	5.0	2.3
TR	16.9	5.1	1.9	1.2	0.9
OR/TR	5.3	4.6	5.6	4.2	2.6

OR: original; TR: treated with aluminium oxide to remove tocopherols; PHCO: partially hydrogenated cottonseed oil; IV: iodine value.

Table 6 shows the evolution of dimers and polymers in cottonseed fat samples, during 10 hours under thermal oxidation conditions. In the first place, aluminium oxide treated samples, without their natural tocopherols, all showed greater degradation than their original counterparts after 2 h, demonstrating the importance of tocopherols in retarding thermal degradation. At time 0 h, dimers and polymers were lower for the treated samples as most of the polar compounds present in the original samples were retained in the aluminium oxide column. Secondly, the effect of iodine value was also observed; the higher the iodine value, the greater the thermal degradation (more oligomeric compounds formed). An exception was the blend with IV = 70, which will be commented below. However, the differences were lower than expected, considering the enormous differences in oxidative stabilities shown in Table 5. Results were in agreement with those reported for used frying fats and oils where differences in unsaturation degree were translated into low differences in degradation (Márquez-Ruiz et al., 1995; Warner et al., 1997).

The blend with IV = 70 showed an unexpected behavior: having a higher IV than PHCO (IV = 60), thus a higher unsaturation degree, it degraded less than PHCO under the thermal oxidation conditions

applied in this study. The quantity of D+P in the original blend with IV = 70, after 10 h, 4.6%, was notably lower than the quantity (8.2%) found in original PHCO.

The relationship between the amount of polymers and time fitted a pseudo-zero order kinetic in all the experiments. Table 7 shows the parameters of the lines (slopes and intercepts) as well as the correlation coefficients found. As can be observed, not only correlation coefficients higher than 0.99 were found, but also the intercept increases with iodine value, parallel to the experimental data found for the initial samples. Also, the slopes corresponding to the data of thermoxidation assays without original tocopherols were, as expected, higher than their counterparts with original tocopherols. Finally, with the exception of the sample with IV = 70, the slopes increased with iodine values.

For those experiments carried out with original oils, Figure 1 shows the formation of polymers (the amounts in Table 6 minus the amount at the initial time) and the loss of natural tocopherols expressed as residual percentages. With the exception of the sample with IV = 70 commented above, the loss of tocopherols was very rapid in all the samples and they were exhausted at the end of the heating

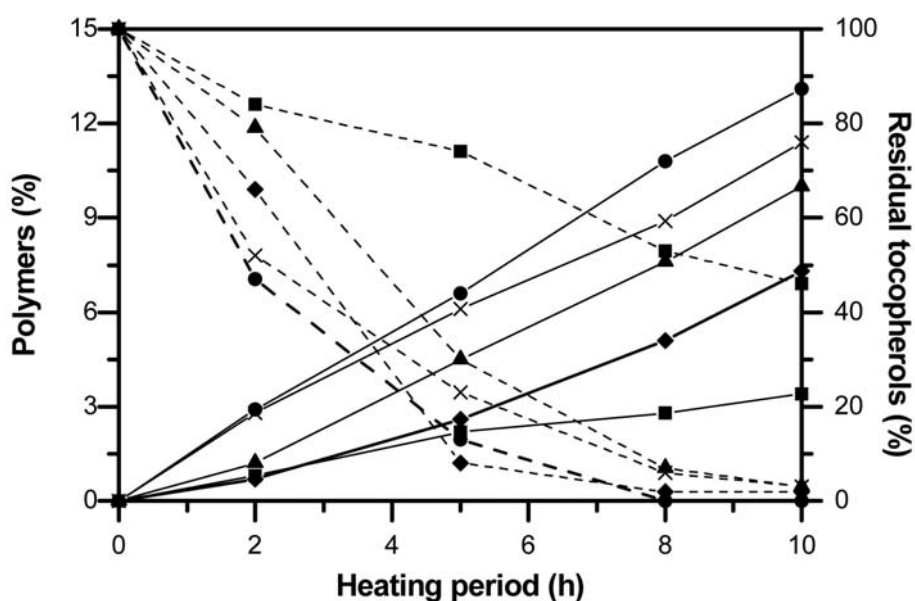


Figure 1
Formation of polymerization compounds (solid lines) and loss of natural tocopherols (dashed lines) in cottonseed oil, partially hydrogenated cottonseed oil (PHCO) and their blends submitted to thermal oxidation conditions (Symbols: ◆ IV 60 ■ IV 70 ▲ IV 85 × IV 100 ● IV 110).

period (10 hours). On the other hand, polymer formation was higher when the unsaturation degree increased. As high polymerization involves high oil degradation, these results suggest that fats of low unsaturation degree would become unprotected at low degradation levels. Consequently, fat degradation should be controlled in saturated fats used for the preparation of fried foods to be stored, as they have to maintain a significant part of antioxidants in order to delay oxidation before consumption (Márquez-Ruiz et al., 1999).

A possible explanation of the results obtained for the samples with IV = 60 and 70 could be related to the complex relationship between the formation of new compounds and the loss of natural antioxidants, considering that tocopherols are lost very rapidly in highly saturated fats at frying temperatures (Yuki and Ishikawa, 1976). As can be observed in Figure 1, the total loss of tocopherols

was very rapid, around 5 hours, for the most saturated sample (IV = 60). After 5 hours, the increase in polymers was exponential and justifies the fact that the lowest correlation coefficient among those shown in Table 7 was found for the linear fitting of this sample. The existence of an uncontrolled variable, for example, a higher content of pro-oxidants in the sample with IV = 60 could accelerate the rapid loss of tocopherols and the subsequent rapid decomposition of the main substrate. Moreover, when tocopherols were still present in both samples (2 and 5 hours), it can be observed that there were no differences in practice between the samples with IV = 60 and 70.

In Figure 2, the degradation of individual tocopherols in cottonseed samples, submitted to thermal oxidation conditions, can be observed. Alpha-tocopherol was destroyed faster than γ -tocopherol. This can be seen at time 5 h, where

Table 6
Evolution of dimers and polymers (%) in cottonseed oil, partially hydrogenated cottonseed oil and their blends, with and without aluminium oxide treatment, submitted to thermal oxidation conditions

Time (h)	PHCO IV = 60		Blend IV = 70		Blend IV = 85		Blend IV = 100		Cottonseed oil IV = 110	
	OR	TR	OR	TR	OR	TR	OR	TR	OR	TR
0	0.9	0.5	1.2	0.6	2.5	1.4	3.5	2.3	3.9	3.7
2	1.6	2.3	2.0	2.7	3.6	5.0	5.9	6.1	6.6	7.1
5	3.6	5.4	3.0	5.3	6.6	9.3	9.2	11.2	10.3	12.1
8	6.0	9.1	4.0	7.7	9.8	12.2	12.0	15.0	14.5	16.8
10	8.2	10.7	4.6	9.2	12.3	14.3	14.5	17.5	16.8	19.5

OR: original; TR: treated with aluminium oxide to remove tocopherols; PHCO: partially hydrogenated cottonseed oil; IV: iodine value.

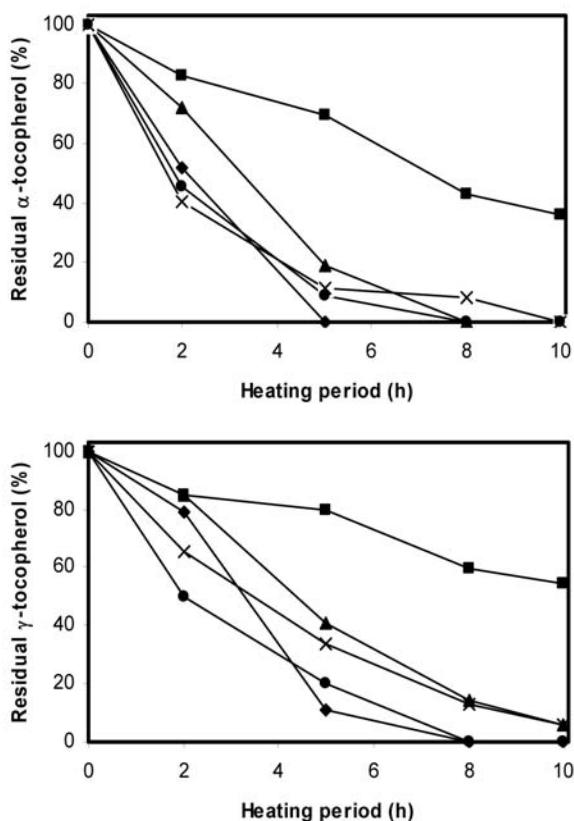


Figure 2
Evolution of α - and γ -tocopherols (residual %) in original cottonseed oil, partially hydrogenated cottonseed oil (PHCO) and their blends submitted to thermal oxidation conditions (Symbols: \blacklozenge IV 60 \blacksquare IV 70 \blacktriangle IV 85 \times IV 100 \bullet IV 110).

residual α -tocopherol was lower than 20% and residual γ -tocopherol ranged from 10.7 to 41.1% for all samples, excluding the blend with IV = 70 which contained 69.5% residual α -tocopherol and 79.4% residual γ -tocopherol. Yoshida et al. (1991), using

microwaves, and Barrera-Arellano et al. (1999), working with triglyceride model systems, had already observed this difference in the destruction rate of α - and γ -tocopherols.

The blend with IV = 70 was the less degraded sample considering the formation of polymerization compounds (D+P). It also kept its tocopherols longer (had higher percentages of residual tocopherols): approx. 50% α -tocopherol and 60% γ -tocopherol after 10 h under thermal oxidation conditions.

Overall, these results suggest the complexity of degradation at high temperatures. In contrast to what occurs at low or medium temperatures, substrates of low iodine values, more stable at high temperatures, may be unprotected from natural antioxidants very rapidly and at low levels of polymerization.

ACKNOWLEDGEMENTS

This study was funded by the Ministerio de Educación y Ciencia (Project AGL 2004-00148) and the Junta de Andalucía. Caroline Joy Steel was supported by a doctoral fellowship (98/14729-0) from Fundação de Apoio à Pesquisa do Estado de São Paulo (FAPESP). The authors thank Mercedes Giménez for assistance.

BIBLIOGRAPHY

Allam S.S.M., Mohamed H.M.A. 2002. Thermal stability of some commercial natural and synthetic antioxidants and their mixtures. *J. Food Lipids* 9 (4), 277-293.
 AOCS – American Oil Chemists’ Society. 1993. *Official Methods and Recommended Practices of the American Oil Chemists’ Society*, 4th ed., AOCS, Champaign.
 Barrera-Arellano D., Márquez-Ruiz G., Dobarganes, M.C. 1997. A simple procedure to evaluate the performance

Table 7
Parameters of the equation (Polymers (%) = a t (h) + b) and correlation coefficients

Iodine Value	Tocopherols	Slope (a)	Intercept (b)	Correlation coefficient
60	OR	0.75	0.29	0.9916
	TR	1.03	0.46	0.9979
70	OR	0.33	1.32	0.9998
	TR	0.80	1.23	0.9996
85	OR	1.01	1.81	0.9970
	TR	1.20	2.56	0.9963
100	OR	1.11	3.40	0.9981
	TR	1.45	3.32	0.9980
110	OR	1.31	3.82	0.9996
	TR	1.59	3.89	0.9993

OR: original; TR: treated with aluminium oxide to remove tocopherols.

- of fats and oils at frying temperatures. *Grasas y Aceites* **48**, 231-235.
- Barrera-Arellano D., Ruiz-Méndez M.V., Márquez-Ruiz G., Dobarganes M.C. 1999. Loss of tocopherols and formation of degradation compounds in triacylglycerol model systems heated at high temperature. *J. Sci. Food Agric.* **79**, 1-6.
- Block J.M. 1997. Formulação de gorduras hidrogenadas através de redes neurais. PhD Thesis. Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas. 146 p.
- Dobarganes M.C., Velasco J., Dieffenbacher A. 2000. The determination of polar compounds, polymerised triacylglycerols, oxidised triacylglycerols and diacylglycerols in fats and oils. *Pure and Appl. Chem.* **72**, 1563-1575.
- Gordon M.H., Kourimska L. 1995. The effect of antioxidants on changes in oils during heating and deep frying. *J. Sci. Food Agric.* **68** (3), 347-353.
- Gunstone F.D., Harwood J.L., Padley B.P. 1994. *The Lipid Handbook*, 2nd ed., Chapman & Hall, London, 551 p.
- IUPAC – International Union of Pure and Applied Chemistry. 1992. Methods 2.432 and 2.508 in *Standard Methods for the Analysis of Oils, Fats and Derivatives*, 7th edition, Pergamon Press, Oxford.
- Kamal-Eldin A., Appelqvist L. 1996. The chemistry and antioxidant properties of tocopherols and tocotrienols. *Lipids* **31**, 671-701.
- Lumley I.D. 1988. Polar compounds in heated oils, in Varela G., Bender A.E., Morton I.D. (Eds.) *Frying of Food: Principles, Changes, New Approaches*. Ellis Horwood Ltd., Chichester, pp. 166-182.
- Márquez-Ruiz G., Tasioula-Margari M., Dobarganes M.C. 1995. Quantitation and distribution of altered fatty acids in frying fats. *J. Am. Oil Chem. Soc.* **72**, 1171-1176.
- Márquez Ruiz G., Martín Polvillo M., Jorge N., Ruiz Méndez M.V., Dobarganes, M.C. 1999. Influence of used frying oil quality and natural tocopherol content on oxidative stability of fried potatoes. *J. Am. Oil Chem Soc.* **76**, 421-425.
- Márquez-Ruiz G., Velasco J., Dobarganes M.C. 2004. Effectiveness of dimethylpolysiloxane during deep frying. *Eur. J. Lipid Sci. Technol.* **106**, 752-758.
- NPCA – National Cottonseed Products Association. 2001. Cottonseed oil: naturally the right choice. Available at: <<http://www.cottonseed.com>>. Accessed on: 13 Oct. 2001.
- Pérez-Camino M.C., Márquez-Ruiz G., Salgado Raposo A., Dobarganes, M.C. 1988. Alteración de grasas usadas en fritura. III. Correlación entre índices analíticos y métodos de evaluación directa de compuestos de degradación. *Grasas y Aceites* **39**, 72-76.
- Ruiz-Méndez M.V., Márquez-Ruiz G., Dobarganes M.C. 1997. Relationships between quality of crude and refined edible oils based on quantitation of minor glyceridic compounds. *Food Chem.* **60**, 549-554.
- Steel C.J., Dobarganes M.C., Barrera-Arellano D. 2005. The influence of natural tocopherols during thermal oxidation of refined and partially hydrogenated soybean oils. *Grasas y Aceites* **55**, 46-52.
- Velasco J., Marmesat S., Márquez-Ruiz G., Dobarganes M.C. 2004. Formation of short-chain glycerol bound oxidation products and oxidised monomeric triacylglycerols during deep-frying and occurrence in used frying fats. *Eur. J. Lipid Sci. Technol.* **106**, 728-735.
- Warner K. 1997. Chemistry of frying fats in Akoh C.C., Min D. B. (Eds.) *Food Lipids: Chemistry, Nutrition and Biotechnology*, Marcel Dekker, New York, pp. 167-180.
- Warner K., Orr P., Glynn M. 1997. Effect of fatty acid composition of oils on flavor and stability of fried foods. *J. Am. Oil Chem. Soc.* **74**, 347-356.
- Yoshida H., Tatsumi M., Kajimoto G. 1991. Relationship between oxidative stability of vitamin E and production of fatty acids in oils during microwave heating. *J. Am. Oil Chem. Soc.* **68**, 566-570.
- Yoshida H., Kondo I., Kajimoto G. 1992. Participation of free fatty acids in the oxidation of purified soybean oil during microwave heating. *J. Am. Oil Chem. Soc.* **69**, 1136-1140.
- Yuki E., Ishikawa Y. 1976. Tocopherol contents of nine vegetable frying oils, and their changes under simulated deep-fat frying conditions. *J. Am. Oil Chem. Soc.* **53**, 673-676.

Recibido: Mayo 2005
Aceptado: Febrero 2006