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Changes in breaded chicken and oil degradation during discontinuous frying with cottonseed oil

Alterações em frango empanado e degradação do óleo durante a fritura descontínua em óleo de algodão

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Abstract

Discontinuous frying of breaded chicken in cottonseed oil was evaluated. Three 400 g batches of foodstuff were fried daily in a 28 L fryer at 182 °C for 4.5 minutes for 7-8 days, and the experiment was repeated three times. The total polar compounds in the oil were determined by the conventional method. Changes in the oil were determined by the quick tests *Testo 265, Viscofrit* and *Fri-check* based on physical constants, and the results were compared with those of total polar compounds obtained by the conventional method. The free fatty acids, *conjugated dienes, Lovibond color,* oxidative stability, fatty acid composition, and polymeric compounds were also determined. During frying, the oil samples presented 6.0-39.2% total polar compounds, 0.0-12.9% polymerized triacylglycerols, 1.3-14.5% oxidized triacylglycerols, 2.8-11.0% diacylglycerols, and 1.6-2.6% fatty acids and unsaponifiable polar compounds. The breaded chicken samples lost moisture, absorbed oil up to approximately 6%, and there were small changes in the fatty acid composition and low formation of trans-isomers. The best method for monitoring and discarding the oil was that used for the determination of total polar compounds.

Keywords: frying; fried foods; cottonseed oil.

Resumo

Neste trabalho, foi avaliada a fritura descontínua de frango empanado em óleo de algodão. Três bateladas de 400 g de alimentos foram fritas diariamente em uma fritadeira de 28 L a 182 °C por 4,5 minutos durante 7-8 dias. O experimento foi executado três vezes. Foram realizadas determinações de compostos polares totais no óleo pelo método convencional. As alterações do óleo, baseadas em constantes físicas, foram determinadas por meio dos testes rápidos Testo 265, Viscofrit e Fri-check e seus resultados foram comparados com os resultados de compostos polares totais obtidos pelo método convencional. Foram determinados, também, ácidos graxos livres, dienos conjugados, cor Lovibond, estabilidade oxidativa, composição em ácidos graxos e compostos poliméricos. Durante a fritura, as amostras de óleo apresentaram 6,0-39,2% de compostos polares, 0,0-12,9% de triglicerídios polimerizados, 1,3-14,5% de triglicerídios oxidados, 2,8-11,0% de diglicerídios e 1,6-2,6% de ácidos graxos e polares insaponificáveis. Em relação às amostras de frango empanado, estas perderam umidade, absorveram óleo até aproximadamente 6% e houve pequena alteração na composição em ácidos graxos ou formação de isômeros trans. O melhor método de monitoramento e descarte de óleo foi o de compostos polares totais.

Palavras-chave: frituras; alimentos fritos; óleo de algodão.

1 Introduction

Deep-fat frying is a very important operation since it is a rapid preparation process and offers unique odor and taste characteristics to the products. In this process, a complex series of chemical reactions and alterations take place producing numerous decomposition compounds (FRITSCH, 1981).

During the frying process, the oil or fat is posed to high temperatures in the range from 162 to 196 °C in the presence of air and water. Under such conditions, a series of complex simultaneous reactions occur, such as thermoxidation, polymerization, and hydrolysis, resulting in loss of quality of the frying oil and fried food (DOBARGANES; MÁRQUEZ-RUIZ, 1998).

The rate of formation of decomposition products varies with the food to be fried, type of oil used for frying, fryer design

(relationship between the fryer surface and the volume of oil), and the nature of the operating conditions (STEVENSON; VAISEY-GENSER; ESKIN, 1984; CHOE; MIN, 2007; MACHADO et al., 2007; MACHADO; GARCÍA; ABRANTES, 2008).

Discontinuous frying, adopted in food services, is characterized by heating and cooling cycles. Depending on the menu and the local food patterns, the fryer operates with a total capacity of a few hours per day, working intermittently for a few hours and remaining unused for the remaining time. This intermittent operation is one of the main reasons for the greater oil degradation than that occurring in continuous frying. During the period of low production, the oil is subjected to oxidative and thermal stress (BANKS, 1996).

692

Ciênc. Tecnol. Aliment., Campinas, 32(4): 692-700, out.-dez. 2012

Three repetitions of the frying process were carried out (cycles) under the same experimental conditions, using the same type of fried food and the same type of frying oil. The end of each cycle was defined when the frying oil was condemned by at least two quick tests, since the conventional method of determining the total polar compounds using an open column did not provide the results "in situ" within a few minutes of analysis. For cycles 1 and 2, the experiment was terminated after 9 days of using, and for cycle 3, after 8 days of use.

2.1 Fried food analyses

Moisture: carried out based on the AOAC method (HORWITZ, 1980) with modifications. At least 50 g of samples were ground in a food processor and homogenized. Petri plates were codified and placed in an oven at 105 °C for a minimum of 1 hour, followed by cooling in a desiccator. The Petri plates were weighed on an analytical balance and 10 g of ground, homogenized sample were weighed into the petri plate. The plates containing the samples were heated in an oven at 105 °C for 1 hour, cooled in a desiccator, and weighed. They were then placed back in the oven for a further 1 hour at 105 °C, cooled, and weighed; this process was repeated until constant weight.

Oil Content: determined by acid hydrolysis according to the procedures adopted by Osawa (2005). For protein foods with or without significant amounts of carbohydrates, acid hydrolysis is required in order to free the lipids covalently bonded to the proteins and carbohydrates (SHAHIDI; WANASUNDARA, 1998).

Fatty Acid Composition: determined by stearification according to the Hartman and Lago method (1973). The methyl esters obtained by stearification were injected into the Agilent Gas-phase Chromatography 6850 Series GC System, using a 60 m Agilent DB-23 capillary column (50% cyanopropyl – methylpolysiloxane), with an internal diameter of 0.25 mm and 0.25 μm stationary phase. The following temperatures were used: detector at 280 °C, injector at 250 °C, oven at 195 °C for 20 minutes, 195-215 °C (5 °C/min), and 215 °C for 16 minutes. Helium flow was of 1.00 mL/min, rate Split of 1:50, and linear speed of 24 cm/seconds. The volume injected was 1.0 μL (automatic injector). The fatty acids were identified by comparison with a mixture of methyl ester standards (C4-C24).

All determinations were carried out in duplicate. The food samples analyzed were those from the second day of frying (designated as Day 1) and from the last day of frying (designated as Day 7 for cycle 1 and as Day 6 for cycles 2 and 3), considering that the first day of frying was designated as Day 0, and on Day 0, the oil sample was the fresh oil.

2.2 Frying oils analyses

Lovibond color: Method Cc 13e-92 (AMERICAN..., 2004), using the Lovibond Tintometer Model E manual and 5 ¼", 1" or 0.5" cuvettes, in quadruplicate.

Free Fatty Acids: determined according to the method adopted by Osawa, Gonçalves and Ragazzi (2006), in duplicate, using 1.5 g samples for fresh oils, 1.0 g samples for used oils and the *TitroLine easy* titrator (SCHOTT, Germany) adjusted to stop titrating at pH = 8.8.

Conjugated Dienes: spectrophotometric Method Ti 1a-64 (AMERICAN..., 2004) in duplicate.

Total Polar Compounds and fractions (dimerized and polymerized triacylglycerols, oxidized triacylglycerols, diacylglycerols, monoacylglycerols and free fatty acids): determined according to the method developed by Dobarganes, Velasco and Dieffenbacher (2000), in duplicate. The method is based on the elution of non-polar and polar fractions on a silica column, with eluents of different polarity: petroleum ether: diethyl ether 90:10 (v/v), and ethyl ether. The solvents were recovered and the percentage of apolar and polar fractions, respectively, were determined by the difference in weight. The effectiveness of the separation was evaluated by thin-layer chromatography, applying the polar and apolar factions separately and comparing it with the TLC of a refined vegetable oil, which is a sample with both polar and apolar fractions. The polar fraction was dissolved in tetrahydrofuran at a concentration of 0.01 g.mL^{-1} for quantification of the dimerized and polymerized triacylglycerols, oxidized triacylglycerols, diacylglycerols, monoacylglycerols, and free fatty acids. These compounds were separated from the polar fraction by liquid phase chromatography, using a Perkin Elmer chromatograph with a Waters 510 pump and Rheodyne 7725i injector with a 20 μL sampler (Waters Associates, USA). Two gel permeation columns (copolymer styrene divinylbenzene), one of 500 Å and the other 100 Å, were connected in series. Each column had an i.d. of 25 × 0.77 cm, and the mobile phase was chromatographic grade tetrahydrofuran at a flow rate of 1.0 mL. The detector used was a Merck L-7490 refractive index detector (Merck, Germany) together with a Hewlett-Packard HP 3390A integrator (Hewlett-Packard, USA).

Fatty Acid Composition: determined using the same methodology adopted for the oil extracted from the fried foods, in duplicate.

Oxidative Stability: Cd 12b-92 (AMERICAN..., 2004) method, using the *Oxidative Stability Instrument* (OSI) (Omnion Archer – Daniels Midland Company), 5 g of sample, temperature of 110 °C, and air flow of 10 L/hour, in duplicate.

Rapid Tests: Viscofrit, Fri-Check® and Testo 265, according to the manufacturer's instructions, in triplicate.

3 Results and discussion

3.1 Alterations in the foods during frying

Moisture and oil absorption

The moisture content of the frozen breaded skinless chicken was 64.7 ± 0.4%, and the lipid content was 1.6 ± 0.2% (Table 1). With the frying process, there was a reduction in moisture content and incorporation of oil into the food, reaching average levels of 57% moisture and 6% total lipids.

694

Ciênc. Tecnol. Aliment., Campinas, 32(4): 692-700, out.-dez. 2012

The differences in moisture and oil content between the first and last days of frying were almost imperceptible for cycles 1 and 2 (Table 1). The variation in moisture content between the first and last days of frying was from 57.6 ± 0.8% to 57.3 ± 0.1% and from 57.3 ± 0.4% to 57.5 ± 0.2% for cycles 1 and 2, respectively. As for the oil content, the variation was from 7.0 ± 0.1% to 7.3 ± 0.6% (cycle 1) and from 5.8 ± 0.9% to 5.4 ± 0.0% (cycle 2).

However, a significant difference in moisture content was observed for cycle 3 (from 55.1 ± 0.2% to 49.1 ± 0.9%) and in oil absorption (from 6.7 ± 0.1% to 8.6 ± 1.0%) when comparing the first and the last day of frying (Table 1).

Oil absorption may be described by two mechanisms: 1) continuous oil absorption as a replacement for the water evaporated during frying; and 2) an absorption process, occurring mainly at the end of frying (SAGUY; DANA, 2003).

The increase in oil absorption during frying when using oil close to its expiration date may be explained by the surfactant theory. As the oil deteriorates, more surfactants are formed and there is an increase in contact time between the food and the oil. As a result, the quantity of oil absorbed by the food and the rate of heat transfer increases, generating a decrease in moisture evaporation and darkening of the surface, depending on the temperature gradient (PAUL; MITTAL, 1997).

Fatty acid composition and trans isomers

In order to evaluate the fatty acid composition of fried foods, one must first analyze the alterations in the fatty acid composition in the fatty acid fraction of the oils used during frying.

According to Table 2, the fresh cottonseed oil presented a fatty acid composition in agreement with that of the Codex Alimentarius (CODEX..., 2003) for cottonseed oil: 21.4 to 26.4% of palmitic acid (16:0); 2.1 to 3.3% of stearic acid (18:0); 14.7 to 21.7 of oleic acid (18:1); 46.7 to 58.2% of linoleic acid (18:2), and 0.05 to 0.4% of linolenic acid (18:3).

Comparing the fresh oil with samples of the used oil on the last day of frying for each cycle, a slight decrease in the linoleic acid content (18:2) could be observed, more notably for cycle 2 (Table 2). In cycle 1, the 18:2 ratio decreased to 52.2%, while in cycle 2 it decreased to 48.3% (Table 2). The apparent increase from 55.0% to 55.9% in cycle 3 (Table 2) may be attributed to

experimental errors, stemming from the integration area of the chromatographic peak.

The decrease in unsaturated acids is attributed to oxidative reactions occurring during frying, with the formation of total polar compounds. When computing the percent areas of the chromatographic peaks of other fatty acids present in the oils, apparent increases in the percentages of saturated fatty acids and of oleic acid may occur. These apparent increases in percentage are related to the computing tools used to quantify the fatty acids and do not have scientific significance in fried foods. However, comments on the increase in saturated fatty acids or oleic acid are not justified.

The alteration observed in the saturated fatty acids corroborates those found by Machado, García and Abrantes (2008), who explained this experimental mistake in computing the fatty acid composition without considering the losses resulting from the formation of decomposition frying products, which was most perceptible in fried foods. When observing the alterations in the fatty acid composition of the fried foods with time, a significant decrease in linoleic acid (18:2) was noted when comparing the samples from the 2nd day of frying (Day 1) with those from the last day of frying (Day 7 for cycle 1 and Day 6 for cycles 2 and 3). This variation was from 43.8% to 25.9% for cycle 1; from 24.4% to 8.3% for cycle 2, and from 25.1 to 18.3% for cycle 3 (Table 3). This means that the decrease in polyunsaturated fats occurred proportionally to the increase in the total polar compounds of the oils that increased with the time of frying (Tables 2 and 4).

As for the trans fatty acid contents, it is known that frying favors the formation of trans isomers and that ingestion of these fatty acids is detrimental to health (SUNDRAM, 1997). Since the consumption of trans fats is not recommended, independent of the percentage present in the food portion, the amount of trans fats in terms of the percentage of daily values is not mentioned on the nutritional labeling of packaged foods (BRASIL, 2003b; FOOD..., 2009).

The formation of trans isomers in the cottonseed oil during frying was more evident in cycle 2, although at low levels, implying that the oil deteriorated at a faster rate in this cycle than in the others (Table 2). In addition, the total polar compound

Table 1. Moisture and oil contents of the foods fried in cottonseed oil.

Samples		Days of use	Moisture (g.100 g⁻¹)	Oil content (g.100 g⁻¹)
Raw breaded chicken		0	64.7 ± 0.4	1.6 ± 0.2
Fried chicken	Cycle 1	1	57.6 ± 0.8	7.0 ± 0.1
		7*	57.3 ± 0.1	7.3 ± 0.6
	Cycle 2	1	57.3 ± 0.4	5.8 ± 0.9
		6*	57.5 ± 0.2	5.4 ± 0.0
	Cycle 3	1	55.1 ± 0.2	6.7 ± 0.1
		6*	49.1 ± 0.9	8.6 ± 1.0

*Samples corresponding to the last day of frying food.

Table 2. Fatty acid composition in the fatty acid fraction of the cottonseed oil used to fry the breaded chicken (% area).

Fatty acid	Day 0 (Fresh oil)	Cycle 1 Day 9 (Discard)	Cycle 2 Day 9 (Discard)	Cycle 3 Day 8 (Discard)
8:0	-	0.1	0.3	0.3
12:0	0.2	0.1	0.1	0.3
14:0	0.8	0.8	0.9	1.1
16:0	22.8	24.5	25.6	28.7
16:1	0.5	0.5	0.5	0.6
18:0	2.6	2.7	1.7	3.3
18:1	16.8	17.3	19.5	20.1
18:2	55.0	52.2	48.3	55.9
18:3	0.2	0.1	0.1	0.2
Trans	0.7	0.9	2.3	0.5

Ciênc. Tecnol. Aliment., Campinas, 32(4): 692-700, out.-dez. 2012

695

content was greater in the last sample of cycle 2 (39.2 ± 1.0%), when compared with the last samples of cycles 1 and 3 (days 7 and 6, respectively), with 20.2 ± 0.9% and 35.2 ± 0.3% (Table 4), respectively. Since there are changes in the lipids between the food and the frying medium due to the incorporation of lipids originating from the frying oil, it is understandable that on the last day of frying the fried food from cycle 2 presented the highest content of trans isomers (2.5%) if compared to the other fried foods (0.4-1.2% of trans isomers).

However, the samples of used frying oil and the fried food obtained in this study were considered free of trans fatty acids in the recommended daily portion for consumption (Tables 2 and 3), according to current legislation (BRASIL, 2003a; b; FOOD..., 2009), since 2.5% of trans isomers in a lipid fraction of a fried food containing 5.4 ± 0.0% of oil represents less than 0.2 g of trans isomers in the portion of 130 g of the fried breaded chicken (BRASIL, 2003a), which may be declared as zero grams trans-fat in the nutrition facts label. For the trans fat content of the frying oils, the same argument is valid for all samples, except for the cycle 2 sample, whose trans-fat content is around 0.3. However, for this sample, its total polar compounds surpassed 25%, indicating that the oil was not appropriated to be used in deep-fat frying.

Table 3. Fatty acid composition in the fatty acid fraction of the fried foods (% area).

Fatty acid	Cycle 1		Cycle 2		Cycle 3	
	Day 1	Day 7*	Day 1	Day 6*	Day 1	Day 6*
12:0	0.2	0.1	0.2	0.7	0.4	0.8
14:0	1.1	0.6	1.4	1.9	1.1	1.8
16:0	23.9	22.1	39.0	45.4	33.5	41.9
16:1	0.9	0.7	0.8	0.8	1.0	1.1
18:0	4.2	3.9	6.2	9.5	5.9	6.1
18:1	23.7	31.5	23.6	28.5	30.0	27.3
18:2	43.8	25.9	24.4	8.3	25.1	18.3
18:3	0.3	0.7	0.4	0.7	0.6	0.3
20:0	0.3	0.3	0.5	0.6	0.6	0.5
20:1	0.1	0.1	0.8	0.2	0.1	0.3
22:0	0.2	0.2	1.0	0.5	0.4	0.4
22:1	0.0	0.4	0.8	-	-	-
24:0	0.1	0.1	0.2	0.2	0.2	0.3
Trans	0.9	0.4	1.2	2.5	0.9	0.4

*Samples corresponding to the last day of frying.

Table 4. Total polar compound content (%) of the cottonseed oil used to fry the breaded chicken.

Days of use	Cycle 1	Cycle 2	Cycle 3
0 (Fresh oil)	8.1 ± 0.4	10.7 ± 1.0	6.0 ± 1.1
3	24.4 ± 1.7	22.9 ± 0.4	23.7 ± 1.4
5	14.5 ± 0.3	28.2 ± 0.2	28.7 ± 0.5
7	17.8 ± 2.3	33.8 ± 0.2	a
8	a	a	35.2 ± 0.3
9 (Discard)	20.2 ± 0.9	39.2 ± 1.0	b

ᵃnot determined. ᵇthe oil in this cycle was used for one day less than in the other cycles. Therefore, the discard for this cycle corresponds to Day 8 of use.

These results confirm the findings of Saguy and Dana (2003), who argued that the concentration of trans isomers formed in frying oils is minimal when considering a recommended 13 mL-daily intake of vegetable edible oils (BRASIL, 2003a), as long as hydrogenated fats are not used. Using canola oil, Aladedunye and Przybylski (2009) did not observe the formation of trans fatty acids at typical frying temperatures although foods cannot be declared free of trans-fats when fried at temperatures above 195 °C.

3.2 Alterations in the oils during frying

Total polar compounds

Observing the values obtained for total polar compounds in the oils used in the various frying cycles (Table 4), it can be seen that frying is not a repetitive process when using the same type of oil to fry the same type of food. On the 9th day of the first cycle of frying chicken in cottonseed oil, the polar content had still not reached the stipulated value of 25%. However, in the 2nd and 3rd cycles the oil was condemned between the 3rd and 5th days of frying.

Oxidative stability

Similarly, since the values for total polar compounds in the oils on the last day of use were closer to each other in cycles 2 and 3, and very different from the value for total polar compounds found in the sample of oil on the last day of use in cycle 1. Similar findings may be observed with respect to the induction periods (Table 5). The discarded oil from cycle 1 presented a period of induction of 3.4 ± 0.1 hours, whereas the induction periods for cycles 2 and 3 were somewhat close to each other with values of 1.6 ± 0.2 hours and 1.5 ± 0.4 hours, respectively.

What can be observed from the results for oxidative stability and total polar compounds is that the oxidative stability has an inverse relationship with the total polar compounds, decreasing with frying time or with oil degradation. For cycle 1, the unused oil presented 8.1 ± 0.4% of total polar compounds and 8.1 ± 0.4 hours of oxidative stability; whereas the discharged sample presented 20.2 ± 0.9% of total polar compounds and 3.4 ± 0.1 hours of oxidative stability. Moreover, the discharged sample from cycle 1 (20.2 ± 0.9% of TPC) presented the highest value for oxidative stability (3.4 ± 0.1 hours) amongst the discharged samples; the other two showed 39.2 ± 1.0% and 35.2 ± 0.3% for total polar compounds and 1.6 ± 0.2 hours and 1.5 ± 0.4 hours for oxidative stability, for cycles 2 and 3, respectively (Table 5). The values for the induction periods of the fresh oils used in the 3 cycles were close to each other (Table 5) in the time period of 5.5 hours (5.6 ± 0.3 hours; 5.2 ± 0.2 hours

Table 5. Oxidative stability of the cottonseed oil used to fry breaded chicken in hours* at 110 °C.

Days of use	Cycle 1	Cycle 2	Cycle 3
Fresh oil	5.6 ± 0.3	5.2 ± 0.2	6.1 ± 0.2
Discard	3.4 ± 0.1	1.6 ± 0.2	1.5 ± 0.4

*5 g of sample with an air flow of 10 L/h.

696

Ciênc. Tecnol. Aliment., Campinas, 32(4): 692-700, out.-dez. 2012

and 6.1 ± 0.2, respectively, for cycles 1, 2, and 3). With respect to the total polar compounds in the fresh oils (Table 4), although not so close to each other, it is possible that the initial quality of the cottonseed oil had no influence on the lack of repeatability of the frying process. Besides, there are other factors that should be analyzed. In the three frying cycles, the foods used and the cottonseed oil were from the same batch, the frying time and temperature were the same, the time interval between one frying and another was the same, and the same fryer was used. This was done because the rate of formation of decomposition products in frying oils varies with the food fried, the oil used, the choice of fryer, the nature of the operating conditions (time and temperature), the oil level replenishment, quality of the oil and the presence of antioxidants (STEVENSON; VAISEY-GENSER; ESKIN, 1984; CHOE; MIN, 2007; MACHADO et al., 2007; MACHADO; GARCÍA; ABRANTES, 2008).

The fryer used in the experiments was sufficiently potent to recover in a few minutes (around 2 minutes) after the lowering of the temperature of the oil by the addition of frozen food; although there may be minimal temperature variations throughout the process. A fryer with a large volume was chosen so that the daily lowering of the oil level, caused by sample taking for analysis and the incorporation of oil into the fried foods, would not significantly affect the relationship between the fryer surface and oil volume. This ratio should preferably be small enough to reduce oil oxidation (CHOE; MIN, 2007).

The use of different fryers may induce unequal heating and cooling periods, due to the sensor in each fryer and the use of varied initial temperatures, resulting in unequal temperatures in the oil during the various periods of the process (before and after addition of the food and before and after frying), for the same time of heating, causing different levels of alteration of the oil (MACHADO; GARCÍA; ABRANTES, 2008).

The lack of repeatability of the frying process may be explained by the following uncontrollable factors: differences in the time of cooling of the oil that was subject to the environmental conditions; the presence of residues of flour from the breading that detached from the food (a variable that was neither quantified nor controlled), the time of recovery of the temperature after addition of the food to the fryer, the absorption of oil by the foods, which altered the oil level and, minimally, the ratio between the surface of the fryer and the oil volume.

Quick tests

None of the quick tests used to determine when to discard the oil provided data with 100% precision (Table 6). The differences amongst the results obtained using the three quick tests compared to those of the official method can be attributed to the different principles of analysis of each one.

Among the quick tests used, Viscofrit can be considered the most reliable, with 1 error in 14 samples. It condemned sample 9 of cycle 1 although this sample only presented 21.2 ± 0.9% total polar compounds (Table 6).

It can be seen in Table 6 that if only Testo 265 was taken into account without considering the conventional method, the moment the frying oil should be discarded would be before attaining 25% of total polar compounds for all cycles. The measurements made by Testo 265 are based on variations in the dielectric constant (TESTO, 2009), and hence the presence of water in the food influences the results, overestimating them, since water increases the dielectric constant (MARMESAT et al., 2007).

With respect to the Fri-check test, no uniform behavior could be predicted from its results, when compared to those obtained by the official method for the determination of the total polar compounds.

Table 6. Comparison of the results obtained by determining the total polar compounds with those obtained using the quick tests for the cottonseed oil used to fry the breaded chicken.

Sample		Official method[a]	Testo 265[a]	Fri-check[a]	Viscofrit: pol. >25%?[b]
Frying cycle	Days of frying				
Cycle 1	0 (Fresh)	8.1 ± 0.4	14.2 ± 0.3	0.8 ± 1.3	-
	3	24.4 ± 1.7	19.2 ± 0.3	2.5 ± 0.2	No
	5	14.5 ± 0.3	22.2 ± 0.3	3.7 ± 1.1	No
	7	17.8 ± 2.3	25.5 ± 0.0	7.2 ± 0.8	No
	9 (Discard)	20.2 ± 0.9	28.0 ± 0.0	11.4 ± 1.7	Yes
Cycle 2	0	10.7 ± 1.0	16.3 ± 0.3	0.8 ± 1.3	-
	3	22.9 ± 0.4	26.5 ± 0.0	6.0 ± 1.6	No
	5	28.2 ± 0.2	34.3 ± 0.3	17.8 ± 1.5	Yes
	7	33.8 ± 0.2	42.0 ± 0.9	29.5 ± 1.2	Yes
	9 (Discard)	39.2 ± 1.0	41.7 ± 0.3	36.2 ± 4.4	Yes
Cycle 3	0	6.0 ± 1.1	16.8 ± 0.6	1.5 ± 1.3	-
	3	23.7 ± 1.4	28.0 ± 0.0	8.0 ± 0.9	No
	5	28.7 ± 0.5	34.7 ± 0.8	26.0 ± 1.0	Yes
	8 (Discard)	35.2 ± 0.3	38.8 ± 0.6	27.8 ± 0.8	Yes

[a]Results in % total polar compounds, without correcting them by a factor of 1.25. [b]TPC > 25%? = is the TPC content superior to 25%? YES = Yes, the TPC content is superior to 25% and the oil should be discarded. No = No, the TPC content is inferior to 25% and the oil may be continuously used.

Ciênc. Tecnol. Aliment., Campinas, 32(4): 692-700, out.-dez. 2012

697

Given the small number of samples, other studies are necessary to consider them as valid tools or otherwise. However, a tendency for Testo 265 to overestimate the results was observed by presenting false positive results, which would entail economic losses, since frying oil could be discarded unnecessarily before hitting the 25% total polar compound mark, a limit internationally established for the discarding of frying oils (PAUL; MITTAL, 1997).

The results obtained from the Viscofrit and Fri-check tests were more similar to those of the conventional method, despite the fact that the correction factor of 1.25 recommended by Osawa, Gonçalves and Grimaldi (2005) had not been applied to the Fri-check results. After applying the correction factor, the number of false positive or false negative results did not change.

Even though it was not possible to carry out correlation studies between the results obtained using the rapid tests and those obtained by conventional methods, Viscofrit was considered to be a reliable method for the evaluation of frying oils. The numbers of false positives and false negatives in one study involving 105 samples of frying oils of different origins were, respectively, 4.8% and 1.9%, values low enough to be considered tolerable (MARMESAT et al., 2007).

Polar fractions

In addition to the increase in total polar compounds during frying, there was an increase in polymerized triacylglycerols (dimers and polymers), resulting from polymerization of the oil, from oxidized triacylglycerols, and from diacylglycerols, as shown in Table 7. Table 7 shows the amounts of polar fractions and polymeric compounds in terms of percentages of the oil sample, although the polymeric compounds were separated from the polar fraction of the samples.

Analyzing the limits for dimerized and polymerized triacylglycerols established by several countries, it was observed that they vary from 10% to 16% (PAUL; MITTAL, 1997; BASTIDA; SÁNCHEZ-MUNIZ, 2002). If the limit of 10% of dimerized and polymerized triacylglycerols were adopted, the same samples that were condemned for their contents of total polar compounds would be condemned by this criterion. This confirms that alterations in frying oils can be efficiently verified by a quantitative determination of the polymers (MACHADO; GARCÍA; ABRANTES, 2008).

Free fatty acids

The free fatty acid contents of the condemned oils were relatively low, 0.09% in oleic acid, and hence not reaching

2.5% (PAUL; MITTAL, 1997). This indicates that in the case of discontinuous frying, the monitoring of free fatty acids is not a good parameter for evaluation, and that the alterations attributed to thermoxidation of the oil prevail over the hydrolytic alterations.

The hydrolysis of frying oil, common in continuous processes, causes an increase in free fatty acids, monoacylglycerols, diacylglycerols, and glycerols, whereas oxidation causes the formation of hydroperoxides as intermediary products, plus low molecular weight volatile compounds, such as aldehydes and ketones, carboxylic acids, and short chain alkanes and alkenes. Dimers, polymers, oxidized monomers, and oxidized fatty acids, such as hydroxyacids, ketoacids, and epoxyacids, are also formed in oxidized oil via reactions with radicals and Diels-Alder reactions during frying (FRITSCH, 1981; STEVENSON; VAISEY-GENSER; ESKIN, 1984; CHOE; MIN, 2007; MACHADO et al., 2008).

Color

The evolution of a red color during frying can be seen in Figure 1. In the method adopted to evaluate the color of the oils during frying, the intensity of yellow was considered less important than that of red. A proportion of 10 units of yellow for each unit of red may be adopted for oils, in which the red color is below 3.5, and more elevated levels of yellow are specified for darker oils (O'BRIEN et al., 2005). However, in the present study, complete freedom was given to the judges by not fixing the patterns of yellow.
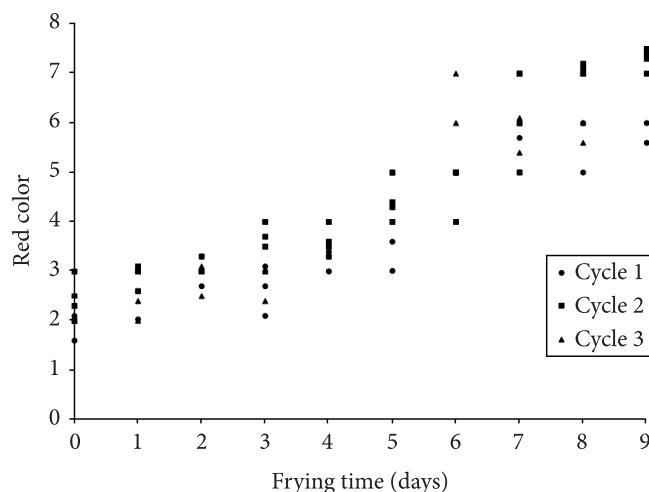
Figure 1. Evolution of the red color in the cottonseed oil during the frying of breaded chicken, using a 5 ¼" cuvette.

Table 7. Composition of the polar fraction in % sample of the frying oils.

	Cycle 1		Cycle 2		Cycle 3	
	Day 0 (Fresh)	Day 9 (Discard)	Day 0 (Fresh)	Day 9 (Discard)	Day 0 (Fresh)	Day 8 (Discard)
Total Polar fraction (%)	8.1 ± 0.4	20.2 ± 0.9	10.7 ± 1.0	39.2 ± 1.0	6.0 ± 1.1	35.2 ± 0.3
Polymerized TG (%)	0.0 ± 0.0	4.8 ± 0.6	0.4 ± 0.1	10.9 ± 2.9	0.4 ± 0.1	12.9 ± 0.8
Oxidized TG (%)	1.4 ± 0.0	7.1 ± 0.3	2.1 ± 0.0	14.5 ± 0.8	1.3 ± 0.2	11.1 ± 0.2
DG (%)	4.3 ± 0.0	6.1 ± 0.3	5.8 ± 0.0	11.0 ± 0.4	2.8 ± 0.1	8.6 ± 0.3
FA + unsap. polar (%)	2.4 ± 0.0	2.2 ± 0.6	2.3 ± 0.0	2.8 ± 0.4	1.6 ± 0.1	2.6 ± 0.6

The oil, initially showing approximately 2.0 units of red, showed 6.4 ± 0.7; 7.3 ± 0.2 and 6.4 ± 0.7 units of red at the end of the frying cycles 1, 2, and 3, respectively. For these samples, the yellow color was, respectively, 56 ± 15; 45 ± 6 and 36 ± 14 units, and the initial samples presented approximately 20 units of yellow. The increase in red color was due to particles of breading flour that contaminated the frying oil, and since the oil was not filtered, they just remained there. With the high temperatures of the oil, the particles underwent caramelization, forming carbonized particles in suspension, which darkened the oil (PAUL; MITTAL, 1997). One should also take into consideration the formation of products from the Maillard reaction in the darkening of the oil (BELITZ; GROSCH, 1999), and also the contribution of polymers to the color of the frying oil (STEVENSON; VAISEY-GENSER; ESKIN, 1984).

Additionally, the increase in color could be related to conjugated double bonds formed during frying. Conjugated double bonds induce the absorption of greater quantities of blue, causing an increase in the orange and brown colors in the oil (LIMA; GONÇALVES, 1994).

Conjugated dienes

In the present study, the discarded frying oils showed smaller conjugated diene contents (all with 0.06%) than that of the fresh oil (0.82%), which is not in agreement with the literature (LIMA; GONÇALVES, 1994; HOUHOULA; OREOPOULOU; TZIA, 2002; GERDE et al., 2007). This can be explained by the fact that equilibrium was established between the rate of formation of conjugated dienes and the rate of formation of polymers involving the conjugated dienes, and hence the absorption at 232 nm did not show large variation during the course of frying (PAUL; MITTAL, 1997). Thus, the determination of conjugated dienes is not a precise parameter to predict the moment the frying oil should be discarded. The decrease in conjugated dienes can be explained by their degradation to form other secondary products (GERDE et al., 2007).

4 Conclusions

Since frying is a rather complex and irreproducible operation, the "in situ" monitoring of the oil used in frying is essential, in order to define the moment it should be discarded.

The measurement of the total polar compounds is the most indicated method to verify alterations in the oil during discontinuous frying. The polymerized triacylglycerol content was proven to be a good method for the quality control of frying oils although there is no agreement between researchers about it. However, such determinations are costly and time consuming, and thus, validated quick tests, which produce results while the oil is in use, are necessary.

This study indicated that the Testo 265 and Viscofrit tests are strong potential candidates to replace the determinations of total polar compounds by the conventional method.

Other determinations, such as those of color, fatty acid composition, oxidative stability, free fatty acid contents, and the conjugated dienes are important parameters for quality control, but they cannot be used to predict the right moment to discard the oil.

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699

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