Effect of Heating on the Characteristics and Chemical Composition of Selected Frying Oils and Fats

Gary R. Takeoka,* Gerhard H. Full, and Lan T. Dao

Western Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 800 Buchanan Street, Albany, California 94710

Seven commonly used frying oils and fats (beef tallow, canola oil, partially hydrogenated canola oil, corn oil, cottonseed oil, soybean oil, and partially hydrogenated soybean oil) were heated at two different temperatures (190 and 204 °C) for 8 h/day until they reached a critical level of polar constituents. Iodine value, color index, and the levels of polar compounds and of dimeric and polymeric triglycerides were monitored daily using AOCS official methods. In general, oils with higher levels of unsaturated fatty acids produced more polar compounds compared to the more saturated oils. Cottonseed oil had the fastest rate of formation of polar material and of polymeric triglycerides at 190 °C. For all seven oils and fats, total polar material was highly ($r \ge 0.99$) and significantly (P < 0.001) correlated with the dimeric and polymeric triglyceride content and also highly ($r \ge 0.94$ and $r \le -0.97$) and significantly (P < 0.001 for the majority of cases; P < 0.05 for the poorest correlation) with the color index and iodine value, respectively. Despite its significant correlations with total polar material, color index was not a reliable indicator of oil quality.

Keywords: Frying oils; total polar material; polymeric triglycerides; iodine value; oil quality

INTRODUCTION

Oils and fats constitute one of the three major classes of food constituents besides proteins and carbohydrates (Lawson, 1995). Deep-fat frying is one of the most popular procedures for food preparation since it is rapid and desirable flavor and texture are developed. It is estimated that commercial deep-fat frying is a \$75 billion industry in the United States with a value at least double that for the rest of the world (Blumenthal, 1996). However, the repeated use of frying oils can produce undesirable constituents which not only compromise the quality of the food but also pose a potential hazard to human health and nutrition. During deepfat frying, fats and oils are continuously or repeatedly heated at high temperatures for prolonged periods in the presence of air. This leads to a variety of chemical reactions which can be categorized as hydrolysis, oxidation, and polymerization of the triacylglycerol molecule. The decomposition products formed by these processes may be volatile or nonvolatile and undergo further degradation. There is some evidence that highly oxidized and heated oils exhibit deleterious health effects when fed to laboratory animals. The observed effects range from weight loss, growth suppression, increased liver and kidney weights to cellular damage to liver, thymus, epidydimides, and testes (Andia and Street, 1975; Billek, 1980; Alexander, 1981; Alexander et al., 1987; Clark and Serbia, 1991).

Detailed research has been performed to link chemical parameters of the oil to the state of degradation and quality of frying oils. Several analytical methods for monitoring frying oil quality have been reported such as measurement of viscosity (Chang et al., 1978), polymers (Peled et al., 1975), dielectric constant (Fritsch et al., 1979), smoke point, carbonyls and free fatty acids

(Bhalerao et al., 1961), polar compounds by column chromatography (Billek et al., 1978), dimers by GC (Paradis and Nawar, 1981), cyclic monomers (Melzer et al., 1981), and short-chain fatty acids (Márquez-Ruiz and Dobarganes, 1996). Some of the methods mentioned are now official AOCS methods. One method for the evaluation of the degradation of frying oil is the measurement of petroleum ether insoluble oxidized fatty acids. A limit of 0.7-1% oxidized fatty acids was recommended in Germany as early as 1973. However, the analysis of petroleum ether insoluble oxidized fatty acids is a very labor intensive procedure. Additionally, Billek et al. (1978) reported that the accuracy of this method is poor. These workers suggested a column chromatographic method for the evaluation of the total polar compounds formed in the oil. This analytical method had a very good correlation to the content of oxidized fatty acids. More recently, several quick tests have been developed to measure the degradation state of oils (Oxifrit-Test [Merck] which determines the amount of oxidized compounds, Fritest [Merck] which uses the alkali color count principle to measure carbonyl compounds, Spot test [Robern and Gray, 1981], and test kits from Libra Laboratories, Inc. [Metuchen, NJ] measure the level of alkaline material [VERI-FRY TAM], FFAs [VERI-FRY FFA], and total polar material [VERI-FRY TPM]). There is also an instrument for measuring the dielectric constant (Foodoil sensor, FOS) for quality assessment of used frying oils (White, 1991). High performance size exclusion chromatography (HPSEC) appears to be the most useful method for the analysis of polymerized triglycerides (White and Wang, 1986; Dobarganes et al., 1988; Hopia et al., 1992; Hopia, 1993; Dobarganes and Márquez-Ruíz, 1993). The proportion of polymerized triglycerides provides a good measurement of the extent of alteration of frying oils. Determination of total polar material (TPM) as well as the analysis of dimeric and polymeric triglycerides (DPTG) are now official AOCS methods and determination of TPM is widely recognized as the most accurate

^{*} Author to whom correspondence should be addressed [telephone (510) 559-5668; fax (510) 559-5828; e-mail grt@pw.usda.gov].

method for assessing the degradation status of frying oils (Billek et al., 1978; Fritsch, 1981; Blumenthal, 1996). Many European countries such as Spain, Portugal, France, Germany, Belgium, Switzerland, Italy, and the Netherlands have established regulatory limits for TPM in frying oils (Blumenthal, 1996). Most of these countries have set a limit for 25% TPM and in some countries the content of DPTG is set to 16% (Firestone et al., 1991).

The aim of this study was to evaluate the heat stability of oils under repeated and discontinuous heating operations (without food) by measuring the polymerized triglycerides content, total polar material, photometric color index, and iodine number of different types of commercial oils. Previous studies on the thermal stability of frying oils have used temperatures of 190 °C or lower. The upper temperature range of 204 °C was used in this study since it has been reported that a similar frying temperature (205 °C) was observed in over 100 food processing locations (Blumenthal, 1996).

EXPERIMENTAL PROCEDURES

Materials. Canola salad oil, canola liquid frying shortening, corn oil, soybean salad oil, soybean liquid frying shortening, and cottonseed oil were obtained from Premier Foods (Richmond, CA). The canola liquid frying shortening and soybean liquid frying shortening were partially hydrogenated oils which also contained *tert*-butylhydroquinone (TBHQ), citric acid, and dimethylpolysiloxane. Beef tallow was obtained from a local retailer in Berkeley, CA. All chemicals used were of p.A. quality; solvents were redistilled before use.

Heating Cycles. The oil heating operations were conducted in two commercial electric fryers, a Cecilware Model 250 (fryer tank: 20.3 cm width \times 30.5 cm length; Cecilware Corp., West Palm Beach, FL) and an Intedge Model F175 (fryer tank: 31.1 cm width \times 49.5 cm length; Intedge Industries, Inc., Woodruff, SC) that contained approximately 6.8 and 5.6 kg of each oil, respectively. The Cecilware fryer was heated to 190 \pm 5 °C while the Intedge fryer was heated to 204 \pm 5 °C. The oils were heated for 8 h/day (five days per week) until the percentage of polymerized triglycerides passed 20% or until the oils began to smoke severely. One hundred milliliters of heated oil was withdrawn after each day of heating and stored in a freezer (-7 °C) until used. The volume of oil was not replenished during the heating operations.

Determination of Polar Components. Determination of polar components was conducted according to AOCS official method Cd 20-91 with slight modifications. Modifications employed were a drying step (103 °C, 30 min) after evaporation of solvent and weighing of the flask after cooling for 15 min in a desiccator. Briefly, 2.5 g of oil was diluted in petroleum ether/diethyl ether (87:13, v/v) and made up to 50 mL with the same solvent mixture. Twenty milliliters of the solution was applied to a silica gel (Merck grade 60, 70–230 mesh, water content standardized to 5%) column. The nonpolar fraction was eluted with 150 mL of petroleum ether/diethyl ether (87:13, v/v) while the polar fraction was eluted with 150 mL of diethyl ether. The fractions were weighed following evaporation of the solvent and drying.

Determination of Iodine Value. Determination of iodine value was conducted according to AOCS official method Cd 1d-92. About 300 milligrams of oil was weighed and dissolved in 15 mL of cyclohexane/acetic acid (1:1). Wijs solution (25 mL) was added, and the reaction was carried out in the dark for 1 h. The reaction was stopped by adding sodium iodide solution. The remaining iodine was titrated using 0.1 N sodium thiosulfate solution.

Determination of Polymerized Triglycerides. The level of polymerized triglycerides was determined according to AOCS official method Cd 22-91, revised 1993. The frozen sample was melted at room temperature or reheated in an oven at 65 °C if needed. A weighed sample of 0.2 ± 0.01 g of melted oil was dissolved in 15 mL of tetrahydrofuran (THF).

Fifty milligrams sodium sulfate was added to the mixture, and after 2 min of magnetic stirring, 2 mL of the sample solution was filtered through a 0.5 μ m disposable filter unit. The high-performance size-exclusion chromatography (HPSEC) system consisted of a Hewlett-Packard (HP) 1050 quaternary pump equipped with an HP 1047A refractive index detector. Manual injection (Model 7125, Rheodyne, Cotati, CA) was performed using a 20 μ L loop (injection volume was 50 μ L). The Phenogel (Phenomenex, Torrance, CA; styrene-divinylbenzene copolymer, particle size 5 μ m, pore size 100 Å) guard column (50 × 7.8 mm i.d.) and column (300 × 7.8 mm i.d.) were operated at ambient temperature (about 24 °C). Mobile phase was unstabilized HPLC grade THF (Omnisolv, EM Science, Gibbstown, NJ; continuously sparged with helium for degassing and to prevent peroxide formation) with a flow rate of 0.7 mL/min.

Determination of Fatty Acid Composition. Fatty acid composition was determined by GC according to AOAC official method 969.33. Glycerides and phospholipids were saponified, and liberated fatty acids were esterified in the presence of BF₃-methanol for analysis by GC. Analyses of fatty acid methyl esters were performed on an HP 6890 gas chromato-graph equipped with a flame ionization detector (FID). A DB-23 fused silica capillary column (30 m × 0.25 mm i.d., $d_f = 0.25 \ \mu m$, (50% cyanopropyl)-methylpolysiloxane; J&W Scientific, Folsom, CA) was employed. Instrument control and data processing were performed with an HP GC ChemStation (Rev. A.04.02).

Determination of Color Index. The photometric color index was determined in duplicate according to AOCS official method Cc 13c-50, reapproved 1993. The absorbance of melted oil samples was recorded at 460, 550, 620, and 670 nm using a Turner Model 690 spectrophotometer (Biomolecular, Inc., Reno, NV).

RESULTS AND DISCUSSION

Fatty Acid Composition of Fresh (Unused) Oils. The fatty acid compositions of canola salad oil, canola liquid frying shortening, corn oil, soybean salad oil, soybean liquid frying shortening, and cottonseed oil are reported in Table 1. The compositions appeared to be typical for these types of oils and fats (Bailey's, 1996; Love, 1996). The sums of the fatty acid percentages ranged from 98.09 to 99.50% with the exception of beef tallow which was only 91.96%. The chromatogram of beef tallow revealed a variety of unknown constituents. It is known that tallow contains hundreds of fatty acids ranging from methyl-branched saturated constituents to geometric and positional isomers of unsaturated fatty acids (Love, 1996) which probably account for the remaining constituents. Canola and soybean liquid frying shortenings contained TBHQ and citric acid as additives to inhibit oxidation due to storage and heat as well as dimethylpolysiloxane as an antifoaming agent. There is some evidence that antioxidants such as BHA, BHT, and TBHQ do provide protection to oils during heating (Fritsch et al., 1979; Chu, 1991) but that they do not significantly prevent deterioration of oils during frying since they lost by steam distillation (Peled et al., 1975; Hawrysh et al., 1990; Tyagi and Vasishtha, 1996).

Total Polar Material (TPM). As a basis for the assessment of the end point of a frying oil we chose 25% TPM which is the regulatory limit in many European countries. Of oils heated at 190 °C corn oil had the fastest rate of deterioration reaching the limit after seven days of heating (Figure 1, bottom). Corn oil had the highest amount of linoleic acid (57.39%) of the oils tested. Canola oil which had about one-third the level of linoleic acid (21.19%) of corn oil and the highest amount of linolenic acid (10.12%) of all oils tested reached 25% TPM after nine days of heating. It was

Table 1. Fatty Acid Composition (%) of Various Fresh (Unused) Commercial Oils and Fats

fatty acid	soybean salad oil	corn oil	soybean liquid frying shortening	canola salad oil	cottonseed oil	canola liquid frying shortening	beef tallow
8:0	_	_	-	_	0.01	-	_
12:0	-	-	-	0.02	0.02	0.12	-
14:0	0.09	0.05	0.08	0.06	0.94	0.12	3.68
16:0	10.75	10.99	10.68	4.20	20.96	5.99	25.01
16:1	0.09	0.10	0.08	0.23	0.63	0.22	2.38
18:0	4.16	2.02	6.17	1.70	2.47	5.21	20.46
18:1	21.48	27.03	29.71	58.51	18.34	60.82	38.34
18:2	52.87	57.39	43.99	21.19	54.19	18.34	1.91
18:3	8.01	0.96	6.58	10.12	0.54	4.96	0.18
20:0	0.31	0.42	0.32	0.59	0.30	0.55	-
20:1	0.18	0.25	0.16	1.40	0.10	1.14	-
22:0	0.34	0.13	0.34	0.32	0.18	0.29	-
22:1	_	_	-	0.50	0.09	0.33	_
24:0	0.10	0.16	0.09	-	0.19	-	-

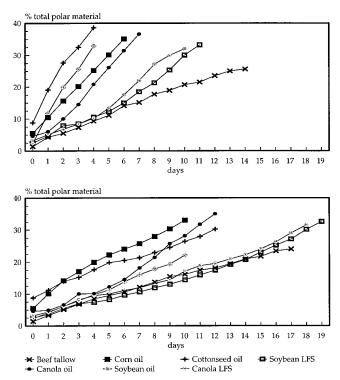


Figure 1. Percentage of total polar material in various commercial oils and fats heated for 8 h/day at 190 $^{\circ}$ C (bottom) and 204 $^{\circ}$ C (top).

followed by cottonseed oil which had the second highest level of of linoleic acid (54.19%). Despite its high level of both linoleic acid (52.87%) and linolenic acid (8.01%), soybean salad oil had only the fourth fastest rate of formation of polar material. Since both corn oil and cottonseed oil contain only trace amounts of linolenic acid, its level may not be the most critical factor in determining an oil's stability during frying (Sebedio et al., 1990). Decreasing the level of unsaturation significantly increased the oil stability as both partially hydrogenated soybean and canola oil took 16 days to exceed 25% TPM. These partially hydrogenated oils had iodine values of about 10 units less than their corresponding non-hydrogenated counterparts (Figure 2, bottom). Heating the oils at 204 °C produced some different results (Figure 1, top). Cottonseed oil reached the limit in only two days while soybean salad oil, corn oil, and canola salad oil took three, four, and five days, respectively, to surpass the limit. The partially hydrogenated oils were more stable taking eight and nine days for canola liquid frying shortening and soybean frying shortening, respectively, to reach 25% TPM. The

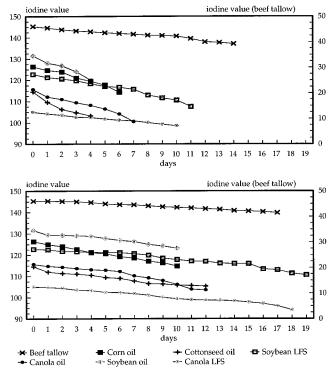


Figure 2. Iodine values (IV) of various commercial oils and fats heated for 8 h/day at 190 $^\circ$ C (bottom) and 204 $^\circ$ C (top).

most saturated fat, beef tallow, reached the limit after 13 days of heating. The oils deteriorated faster at higher temperatures though the rate of formation of polar compounds was different for each oil at different temperatures. In general, oils with a higher level of unsaturated fatty acids produced more polar compounds compared to the more saturated ones. However, the absolute degree of unsaturation as determined by the iodine value was not directly proportional to the amount of polar compounds formed. Soybean salad oil was clearly the most unsaturated of the oils followed by corn oil, partially hydrogenated soybean oil, canola salad oil, cottonseed oil, partially hydrogenated canola oil, and beef tallow (Figure 2, bottom). When heated at 190 °C soybean salad oil did not form the highest amount of polar compounds but was surpassed by corn oil, canola salad oil, and cottonseed oil.

Iodine Value (IV). During heat treatment, a progressive decrease in unsaturation was observed in all oils by measurement of IV. This decrease can be attributed to the destruction of double bonds by oxidation, scission, and polymerization (Cowan, 1954; Cuesta et al., 1991). There was generally a drop of about 5-11

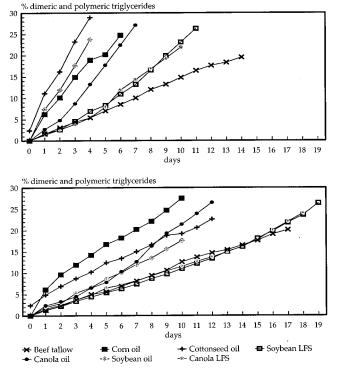


Figure 3. Polymerized triglycerides content of various commercial oils and fats heated for 8 h/day at 190 $^{\circ}$ C (bottom) and 204 $^{\circ}$ C (top).

units before reaching the critical point of 25% TPM. Similar to the production of TPM, corn oil had the fastest loss of unsaturation of oils heated at 190 °C (after 10 days of heating; Figure 2, bottom). It was followed by canola salad oil, cottonseed oil, soybean salad oil, partially hydrogenated canola oil, partially hydrogenated soybean oil, and beef tallow. This was the same order observed for the production of polar material at 190 °C. When heated at 204 °C, different results were found (Figure 2, top). Soybean salad oil had the fastest loss of unsaturation (after four days of heating) followed by cottonseed oil and canola salad oil. Corn oil which had the fastest loss of unsaturation at 190 °C had only the fourth fastest loss when heated at 204 °C. The most saturated oils, partially hydrogenated canola oil, partially hydrogenated soybean oil and beef tallow, had slower changes in unsaturation than the other oils.

Dimeric and Polymeric Triglycerides (DPTG). When the rate of formation of DPTG was evaluated, the data look similar to those obtained for the production of TPM. Previous studies indicated that oil was no longer acceptable for frying if it contained $\geq 20\%$ high molecular weight species (Husain et al., 1991). Several European countries (e.g. Netherlands) use this method for evaluating frying oil quality and the critical value for an oil to be regarded as deteriorated is 16% DPTG (Dutch Food & Commodity Act, 1992). Of oils heated at 190 °C (Figure 3, bottom) corn oil had the fastest rate of formation of polymeric triglycerides (to the 16% limit). Although cottonseed oil had a consistently higher level of polymeric material than canola salad oil early in the heating operation (day 0 through 8), both oils reached the limit after eight days of heating. After the eighth day of heating, canola salad oil had a consistently higher level of polymeric material than cottonseed oil. Soybean salad oil exceeded the 16% limit after ten days while partially hydrogenated canola oil, partially hydrogenated soybean oil, and beef tallow all reached the limit after 14 days of heating. It is noteworthy that

beef tallow had higher levels of polymeric triglycerides than partially hydrogenated canola oil and partially hydrogenated soybean oil on days 8 through 14. After day 14 of heating (days 15 through 17) there was again a reversal in order as beef tallow had a lower level than both partially hydrogenated canola oil and partially hydrogenated soybean oil. With treatment at 204 °C, the results were identical to that produced with TPM (Figure 3, top). Cottonseed oil had the fastest production of polymeric triglycerides, exceeding the limit in two days of heating. Soybean salad oil, corn oil, and canola salad oil passed the limit in three, four, and five days, respectively. Partially hydrogenated soybean oil had a greater percentage of polymeric triglycerides than partially hydrogenated canola oil during the first five days of heating though the order was reversed on the sixth, seventh, and eighth days. Both oils exceeded the limit at the eighth day of heating while beef tallow took eleven days. Lumley (1988) had reported that plotting TPM versus DPTG for unused and corresponding used oils resulted in lines whose slopes tended to decrease with increasing saturation; the more unsaturated the oil the greater the tendency to form polymeric rather than polar products. The frying temperature and types of food fried were not mentioned. In our study we observed contradictory results. Oils heated at 190 °C had a similar tendency to form both polar and polymeric material. Surpringly, beef tallow, the most saturated fat, had a higher level of polymerized triglycerides than partially hydrogenated canola oil and partially hydrogenated soybean oil on days eight through fourteen. Of oils heated at 204 °C formation of polar and polymeric material followed the same order. After five days of heating, beef tallow had a lower level of polymerized triglycerides (which it maintained throughout the heating operation) than both partially hydrogenated canola oil and partially hydrogenated soybean oil.

Color Index. Color has been widely used as an index of oil quality. Oil color darkens as heating or frying proceeds and can be monitored using single or multiple wavelengths with a spectrophotometer, using color standards, or using a Lovibond Tintometer (red, yellow, and blue; AOCS Official Method Cc 13e-92, reapproved 1993). Oil color is influenced by a number of factors including the type and amount of food being fried. Food components can interact with oils and oil degradation products to form colored constituents such as Maillard browning products. Since oil color can result from more than one chemical process, the use of oil color to monitor quality is not valid when evaluating a wide range of frying operations. Figure 4 (bottom) shows the color index for oils heated at 190 °C. Corn oil and canola salad oil had the fastest rates of color formation in an order that followed the production of polymerized triglycerides and total polar material. Despite its high resistance to degradation (as measured by a low rate of production of polymerized triglycerides and total polar material), beef tallow developed color at the third fastest rate. Cottonseed oil and soybean salad oil formed the lowest amounts of color though these oils were clearly less stable to heating than the partially hydrogenated oils. Of oils heated at 204 °C corn oil and canola salad oil again had the fastest rates of color formation (Figure 4, top). Soybean salad oil which had the slowest rate of color production at 190 °C now developed color at the third fastest rate. The more saturated oils had the slowest rate of color formation at the higher temperature with beef tallow falling in between the partially

 Table 2. Pearson Product Moment Correlations between Total Polar Material (TPM) and Three Other Oil Quality

 Indices: Dimeric and Polymeric Triglycerides (DPTG), Color Index (CI), and Iodine Value (IV)^a

	DPTG 190 °C	DPTG 204 °C	CI 190 °C	CI 204 °C	IV 190 °C	IV 204 °C
soybean LFS	0.999ª	0.997ª	0.995ª	0.995ª	-0.991ª	-0.992ª
corn oil	0.998 ^a	0.990 ^a	0.980^{a}	0.985 ^a	-0.992^{a}	-0.988^{a}
soybean salad oil	0.998 ^a	$0.997^{\rm a}$	0.973 ^a	0.957°	-0.984^{a}	-0.981 ^b
canola LFS	0.998 ^a	$0.997^{\rm a}$	0.995 ^a	0.995 ^a	-0.992^{a}	-0.977^{a}
canola salad oil	0.997 ^a	0.998 ^a	0.973 ^a	0.958 ^a	-0.993^{a}	-0.974^{a}
cottonseed oil	0.996 ^a	0.993 ^a	0.946 ^a	0.966 ^b	-0.977^{a}	-0.992^{a}
beef tallow	0.996 ^a	0.997 ^a	0.974 ^a	0.960 ^a	-0.988^{a}	-0.970^{a}

^a Significant at 0.001 (P < 0.001) (a), 0.01 (P < 0.01) (b), and 0.05 (P < 0.05) (c).

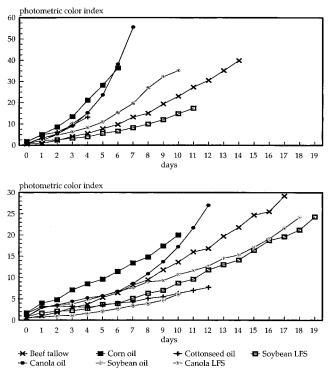


Figure 4. Photometric color index of various commercial oils and fats heated for 8 h/day at 190 °C (bottom) and 204 °C (top).

hydrogenated oils. It is apparent that color is not a reliable indicator of oil quality even when no food is being fried. The results support the assessment of Blumenthal (1996) that "Oil color should not be used as an index for state of degradation, oil quality, or for discard".

Linear Correlations between TPM and Three Other Oil Quality Indices, DPTG, CI, and IV. The Pearson Product Moment correlations for all seven oils and fats are shown in Table 2. For oils heated at 190 °C, TPM exhibited high correlation coefficients (r > 0.97, negative in the case of IV) and very significant correlations (P < 0.001) with DPTG, CI and IV. For oils heated at 204 °C, TPM again showed high (r > 0.99) and significant correlations (P < 0.001) with DPTG. Previous frying studies with sunflower oil showed similar significant correlations between TPM and polymerized triglycerides and also triglyceride dimers (Arroyo et al., 1992; Sánchez-Muniz et al., 1993). Oils heated at 204 °C showed high and significant correlations (P < 0.001) between TPM and color index with the exception of soybean salad oil and cottonseed oil which yielded lower correlation coefficients but still significant correlations. In the case of TPM and IV all oils heated at 204 °C except soybean salad oil (P < 0.01) yielded high negative correlation coefficients which had very significant correlations (*P* < 0.001).

In summary, seven commercial oils and fats were subjected to discontinuous heating at two different temperatures. Oils and fats tended to form polar compounds in a similar order as the production of polymerized triglycerides; corn oil had the fastest rate of production (of both polar compounds and polymerized triglycerides) with heating at 190 °C while cottonseed oil had the fastest rate of oils heated at 204 °C. In general, the more saturated oils and fats were more resistant to degradation. Though color index was significantly correlated to total polar material it was not a reliable indicator of oil quality.

ABBREVIATIONS USED

DPTG, dimeric and polymeric triglycerides; TPM, total polar material; AOCS, American Oil Chemists' Society; TBHQ, *tert*-butylhydroquinone; HPSEC, highperformance size-exclusion chromatography; HPLC, high performance liquid chromatography; FID, flame ionization detector; GC, gas chromatography; IV, iodine value; CI, color index; LFS, liquid frying shortening.

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