

Assessment of the Quality of Heated Oils by Differential Scanning Calorimetry

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Differential scanning calorimetry (DSC) was used to follow changes in the thermal characteristics of commercial frying oils (sunflower seed, colza, and groundnut) during heating at 180 °C for up to 10 h. DSC tracings of oils scanned from 10 to –80 °C were characterized by a single crystallization peak (CP) at –43 to –48 °C. Heating of oils resulted in a progressive shift of the CP to lower temperatures and reduced enthalpies of crystallization (EC). The temperature of the CP decreased as much as 27 °C, and the EC was reduced by almost 90% after heating for 10 h. These changes in thermal characteristics correlated well with the appearance of polar compounds, the increase in viscosity, and color changes of the oil. DSC is a fast method of analysis, requires small samples (15–60 mg) with minimal preparation, and may be implemented directly in fried products.

Keywords: *Differential scanning calorimetry; oil; frying; quality; enthalpy; viscosity; color*

INTRODUCTION

Deep-fat frying is, worldwide, one of the most used cooking methods for foods. The oil plays a critical role as a heat-transfer and impregnation medium, and it is the crucial component of the frying process (Blumenthal and Stier, 1991). Upon repeated use at high temperatures, frying oils undergo several oxidative, polymerization, and thermal degradation reactions leading to changes in their physical, chemical, nutritional, and sensory properties. In particular, health risks including heart disease, diabetes, cancer, and stroke are well established for high-fat diets (Hollingsworth, 1996), and there is some evidence that highly oxidized and abused oils may even have mutagenic properties (Clark and Serbia, 1991).

During frying, triglycerides, which constitute 96–98% of the fresh oil, degrade to form volatile (VDP) and nonvolatile decomposition products (NVDP). VDP are constantly being removed by the steam generated during frying, whereas NVDP are formed mainly by oxidation and/or thermal reactions of unsaturated fatty acids and consist mainly of polymers, dimers, and trimers (Melton et al., 1994). Chemical changes result also in physical alterations of the oil such as increase in viscosity, due to the presence of polymers, and color darkening (Melton et al., 1994).

In their review Stevenson et al. (1984) listed >20 objective methods for measuring oil degradation during frying, none involving its thermal properties. Thermal analysis of frying oils may be of practical importance as a quality control and research tool. Differential scanning calorimetry (DSC) provides information on the excess specific heat over a wide range of temperatures. Any endothermic or exothermic event is registered as

a peak in the chart, and its area is proportional to the enthalpy gained or lost, respectively. We have recently reported the use of DSC to quantify the amount of oil in small portions (e.g., 20–80 mg) of fried potato products and its excellent correlation with other commonly used methods such as Soxtec extraction (Aguilera and Gloria, 1997). Another advantage of DSC, besides the small sample size, is that the oil content may be assessed directly in the fried product, avoiding extraction with solvents. In this paper we report the use of DSC to evaluate the quality of frying oils during use and its comparison to some standard methods used by the industry.

MATERIALS AND METHODS

Samples. Sunflower seed oil (SO), low erucic acid (<0.2%) colza oil (CO), and groundnut oil (GO), purchased in a local supermarket (Migros, Lausanne, Switzerland) and recommended for home frying at 180–190 °C, were used in all experiments.

Determination of Fatty Acid Composition of Fresh Oils. Fatty acid composition was determined by gas chromatographic analysis of the corresponding fatty acid methyl esters (FAMES). Oil (250 μ L) was mixed with 2 mL of hexane and 100 μ L of 2 N methanolic potassium hydroxide (all from E. Merck, Darmstadt, Germany) and centrifuged for 5 min. The Carlo Erba HRGC 5300 chromatograph (CE Instruments, Rodano, Italy) was equipped with a flame ionization detector kept at 280 °C. Injection was cold on-column (injection volume = 0.5 μ L). Separation was achieved on a WCOT fused silica capillary column (50 m \times 0.32 mm i.d.) coated with CP-Sil 88 (0.20 μ m film thickness) type FAMES (Chromapack, Middelburg, The Netherlands). Carrier gas was hydrogen (purity > 99.999 vol %) at 80 kPa. The temperature program was the following: 70 °C, 2 min isothermal, 30 °C/min to 135 °C, 1 min isothermal, 3.5 °C/min to 180 °C, 15 °C/min to 220 °C, 5 min isothermal. Data acquisition and peak integration were done using a Chrom-Card version 1.19 (CE Instruments). Peaks were identified by comparison of retention times with a reference standard GLC 85 supplied by Nu Chek Prep (Elysian, MN) and were calculated as area percent.

Treatment of Samples. Oils were subjected to thermoxidative conditions in the absence of food. Samples of 200 g were

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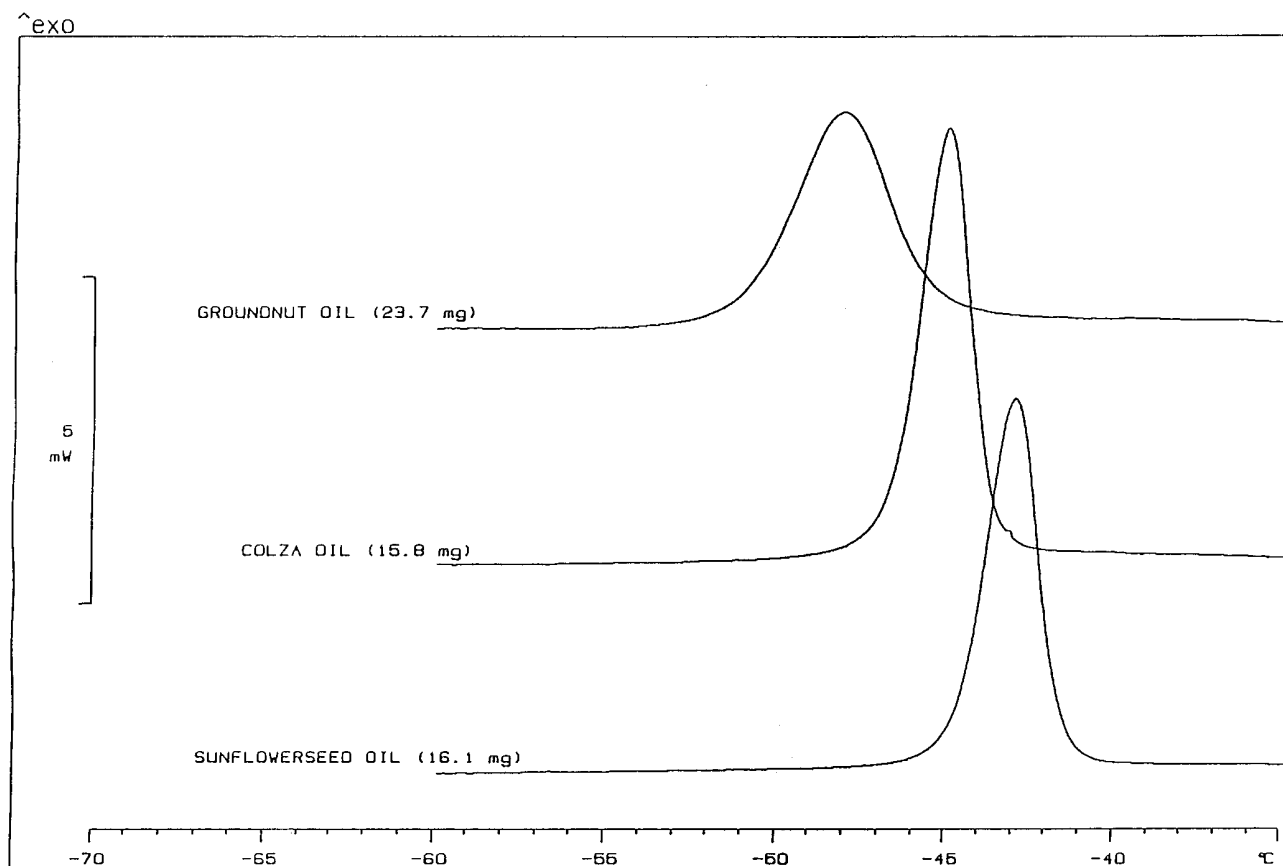


Figure 1. DSC tracings during a DSC cooling experiment of unused commercial SO, CO, and GO.

placed in open glass beakers (250 mL) and heated at 180 ± 2 °C over an electrically heated plate equipped with a contact thermometer programmed at 180 °C. Samples of 20 mL were taken at 2, 4, 6, 8, and 10 h of heating and stored at -25 °C until analysis in the DSC (<1 week).

DSC. DSC of oils was performed using a Mettler DSC 820 (Mettler Instrument AG, Volkestwil, Switzerland). Oil samples (15–60 mg) were weighed directly in 100 mL aluminum crucibles. DSC runs were performed at a cooling rate of 1 K/min within the temperature range of 10 to -80 °C for oils heated for 0, 2, and 4 h and from 10 to -100 °C for those heated for 6, 8, and 10 h. An empty pan was used as reference. Results are the average of duplicate samples.

Total Polar Compounds (TPC). TPC were determined in duplicate by silica column chromatography, according to AOCS official method Cd 20-91 (1993). The polar and nonpolar fractions of heated oils were separated by elution from the column with ethyl ether and light petroleum/ethyl ether (87:13), respectively, desolventized and run in the DSC apparatus under the same condition as the oils.

Viscosity Measurements. A Carri-Med Rheometer CLS2 100 (TA Instruments, Inc., New Castle, DE) was used to study the viscosity of the oils after heat treatment. Measurements were performed in triplicate at 25 °C with a steel cone-plate geometry (6 cm, $1^\circ 58'$ degrees) under a constant shear rate of 100 s^{-1} .

Color. A Macbeth Color-Eye 7000 colorimeter (Macbeth Instruments, New York), equipped with a CIE (Commission International d'Eclairage, Vienna, Austria) standard daylight illumination source D65 was employed to measure transmittance spectra in the range from 360 to 730 nm (in steps of 10 nm). Color changes during heating were expressed as the difference in color (ΔE) with the unused oil, where $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$.

Table 1. Fatty Acid Composition (Percent) of Unused Commercial Oils

fatty acid	SO	CO	GO
miristic acid, C14:0			
palmitic acid, C16:0	4.70	4.70	9.80
palmitoleic acid, C16:1	0.10	0.30	0.10
stearic acid, C18:0	4.00	1.80	3.20
oleic acid, C18:1	54.00	57.00	47.00
linoleic acid, C18:2	35.10	24.50	31.70
linolenic acid, C18:3	0.20	8.20	0.50
arachidic acid, C20:0	0.20	0.60	1.40
eicosenoic acid, C20:1	0.30	1.30	1.20
behenic acid, C22:0	0.80	0.40	2.90
erucic acid, C22:1		0.20	0.10
lignocenic acid, C24:0	0.30	0.20	1.50

RESULTS AND DISCUSSION

DSC of Oils. The total contents of unsaturated fatty acids of SO, CO, and GO were higher than 89, 90, and 80%, respectively (Table 1). Frying oils exhibited a simple thermogram after cooling in the DSC with a well-defined single crystallization peak and significant supercooling (Aguilera and Gloria, 1997). Fresh SO, CO, and GO presented crystallization peaks at -43 , -45 , and -48 °C and enthalpies of 46.8, 49.0, and 29.0 J/g, respectively (Figure 1). According to Roos (1995) the typical cooling curve of the fat shows a single exotherm, which occurs due to crystallization to the least stable α -form.

The effect of heating time at 180 °C on the thermal characteristics of SO is shown in Figure 2 (other oils not shown, but a similar trend was observed) and Table 2. As the time of heating increased, the peak of crystallization shifted to lower temperatures and became broader and the enthalpy decreased dramatically.

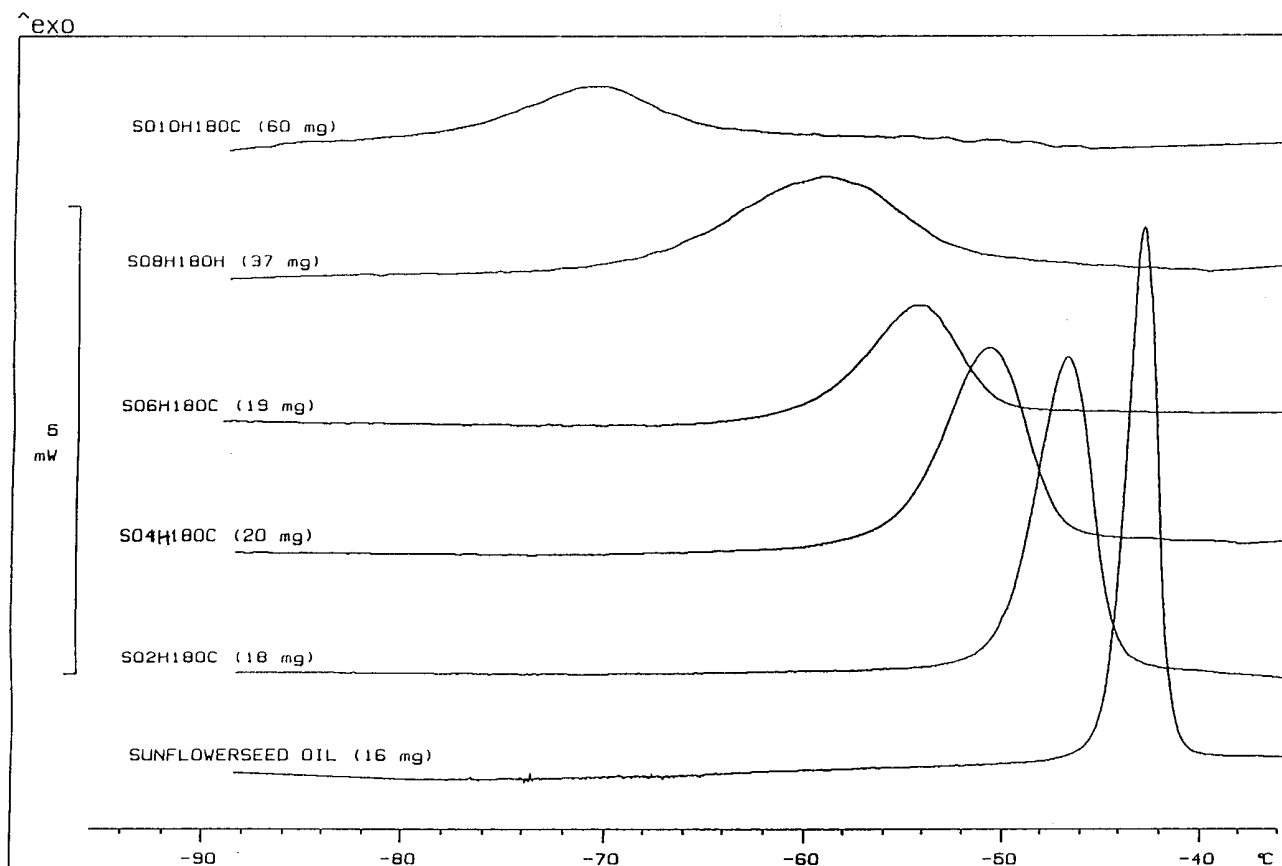


Figure 2. DSC tracings of the effect of heating time (2, 4, 6, 8, and 10 h) at 180 °C on the crystallization peak of SO. The weight of sample is shown in parentheses.

Table 2. Changes in Quality Parameters during Heating of Oils at 180 °C

oil sample	heating time (h)	enthalpy (J/g)	temp peak (°C)	polar comps (%)	viscosity (mPa·s)	color (ΔE)
SO	0	46.8 ± 0.11	-43.0 ± 0.10	4.5 ± 0.30	107.0 ± 0.14	0.0
	2	40.0 ± 0.21	-47.0 ± 0.10	11.9 ± 0.70	122.3 ± 1.41	2.85
	4	33.6 ± 0.92	-51.0 ± 0.14	18.7 ± 0.60	138.3 ± 1.34	2.80
	6	27.2 ± 0.20	-55.0 ± 0.14	26.2 ± 1.00	163.9 ± 3.25	4.90
	8	15.0 ± 0.35	-60.0 ± 0.00	33.2 ± 0.30	190.3 ± 4.31	7.45
	10	4.5 ± 0.01	-70.4 ± 0.21	42.5 ± 0.70	256.2 ± 8.56	14.00
CO	0	49.0 ± 0.00	-44.6 ± 0.02	2.8 ± 0.11	105.7 ± 0.64	0.0
	2	38.8 ± 0.28	-48.0 ± 0.07	10.0 ± 0.23	122.4 ± 0.36	4.70
	4	34.9 ± 0.26	-50.8 ± 0.07	14.5 ± 0.95	130.7 ± 0.92	7.90
	6	30.2 ± 1.06	-54.4 ± 0.28	20.9 ± 0.83	149.0 ± 2.69	13.10
	8	18.8 ± 0.00	-60.3 ± 0.00	28.4 ± 1.92	166.8 ± 8.56	18.90
	10	5.7 ± 0.31	-70.5 ± 0.28	35.9 ± 0.28	225.2 ± 1.34	28.90
GO	0	29.0 ± 0.50	-48.0 ± 0.00	6.2 ± 0.19	118.6 ± 0.07	0.0
	2	25.1 ± 0.03	-50.9 ± 0.00	12.0 ± 0.64	130.8 ± 0.07	1.80
	4	19.5 ± 0.16	-55.0 ± 0.07	17.7 ± 1.36	145.0 ± 0.00	2.50
	6	15.7 ± 0.03	-59.0 ± 0.00	23.9 ± 0.49	164.4 ± 0.07	5.60
	8	5.3 ± 0.19	-68.2 ± 0.21	30.7 ± 0.29	195.8 ± 1.06	9.10
	10	2.3 ± 0.16	-72.1 ± 0.14	37.8 ± 0.15	238.2 ± 0.49	15.80

It has been reported that the presence of free fatty acids, partial glycerides, and oxidation products shifts the melting range to lower temperatures (Che Man and Swe, 1995). Consequently, it is expected that the same products are responsible for the shift in the crystallization peak. The reduction in the enthalpy of crystallization with frying time may be attributed to the disappearance of triglycerides and the formation of degradation products that do not crystallize in the scanning temperature range (see below).

TPC. TPC are defined as all materials in the oil that are not triglycerides, and they are believed to be one of

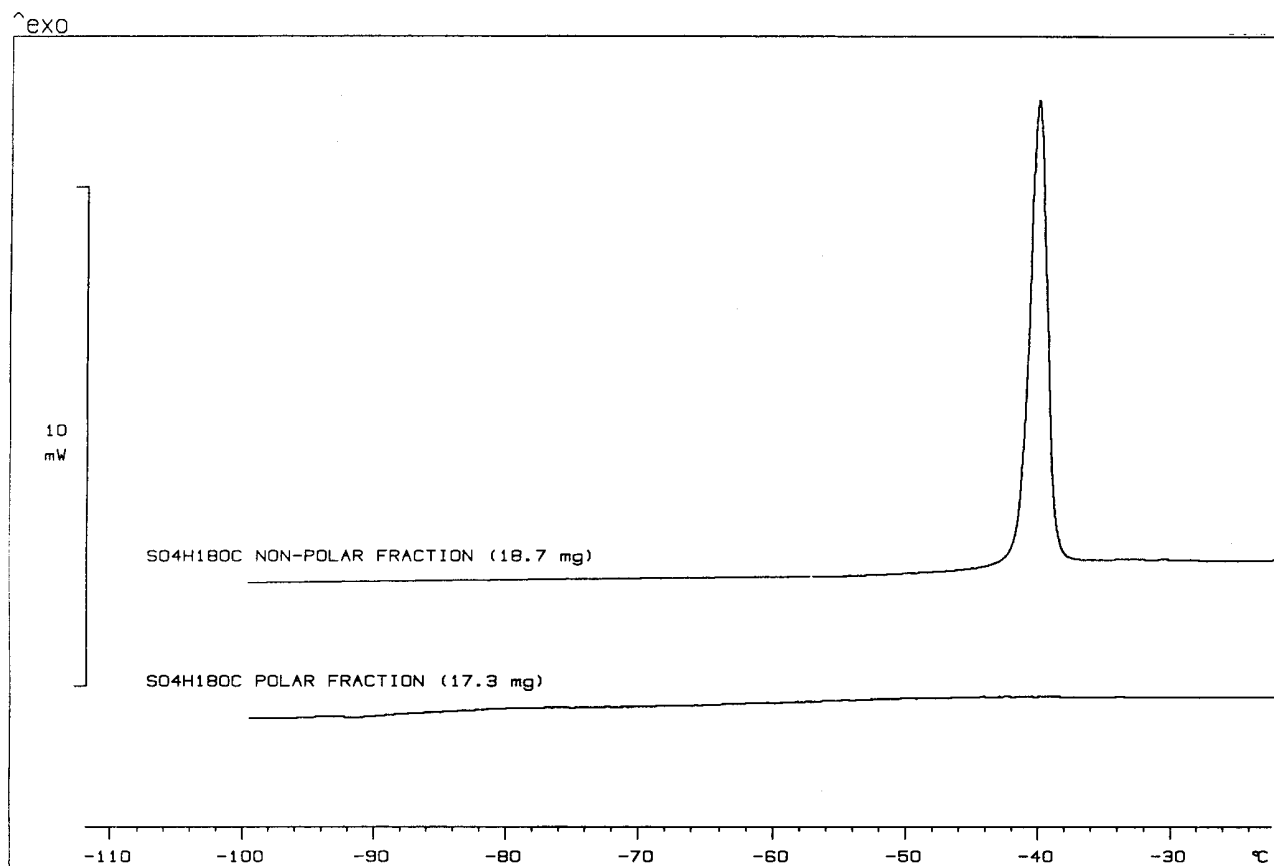
the best indicators of frying oil quality (Melton et al., 1994). TPC in fresh frying oil include sterols, mono- and diglycerides, free fatty acids, and their oil soluble compounds, which are more polar than the triglycerides. TPC in heated oils include all of the breakdown products from the frying process, including oxidized triglycerides. When they reach a level of 25%, the oil should be discarded (Melton et al., 1994).

As observed in Table 2, the initial TPC contents of oils were different (mean values: SO = 4.5%; CO = 2.8%; and GO = 6.2%) but within the expected values and natural differences in the composition of the oils.

Table 3. Correlation Coefficients between Methods^a

	polar compds SO/CO/GO	enthalpy SO/CO/GO	temp peak SO/CO/GO	viscosity SO/CO/GO	color (ΔE) SO/CO/GO
polar compds	1.00				
enthalpy	0.993/0.991/0.990	1.00			
temp peak	0.986/0.978/0.994	0.991/0.992/0.997	1.00		
viscosity	0.970/0.958/0.980	0.981/0.980/0.973	0.996/0.994/0.975	1.00	
color (ΔE)	0.950/0.991/0.961	0.965/0.995/0.948	0.984/0.997/0.954	0.992/0.988/0.995	1.00

^a $n = 6$, significance at 0.001 ($p < 0.001$).

**Figure 3.** DSC tracings of the polar and nonpolar fractions of SO heated for 4 h.

TPC accumulated in oils after 10 h of heating in the following order: SO > GO > CO. The recommended maximum TPC value for discarding an oil (25%) was exceeded after 6 h of heating for SO and after 8 h for CO and GO.

Figure 3 shows individual DSC tracings for the polar and nonpolar fractions of SO heated for 4 h. The nonpolar fraction (triglyceride-like products) exhibits a fairly narrow crystallization peak at -40.7°C , only 2.3°C higher than the peak of the fresh oil (Figure 1), and an enthalpy of crystallization of 48.3 J/g . It can be speculated that the presence of 4.5% polar compounds in the fresh SO (Table 1) is responsible for the drop of the temperature of its crystallization peak to -43°C . The polar fraction, however, did not show any major thermal transition in the selected temperature range (Figure 3).

Viscosity (η). Fresh food oils are Newtonian liquids having high viscosity due to their long chain structure (Muller, 1973). The increase in oil viscosity during frying has been attributed to polymerization and the concomitant formation of high molecular weight compounds via carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges between fatty acids (Stevenson et al.,

1984). The tendency of η to increase during heating of the oil correlates well with formation of polymers (Bracco et al., 1981). From fundamental physics of polymers it is known that η has a power dependence with molecular weight (M) (e.g., $\eta = KM^p$).

Initial values of η around $110\text{ mPa}\cdot\text{s}$ agree well with those in the literature for unused food oils (Barnes et al., 1989). Viscosity increased continuously during heating and more than doubled after 10 h (Table 2). This trend has also been reported by other authors [e.g., Bracco et al. (1981)], but absolute comparisons are difficult since results are not always of dynamic viscosity (SI units, $\text{Pa}\cdot\text{s}$) but from empirical viscosity tests [e.g., Tyagi and Vasishtha (1996)]. Further work is needed to corroborate the assumption that heated oils are still Newtonian liquids, since most polymer solutions tend to be non-Newtonian (e.g., viscosity depends on the shear rate). Some mixtures of low molecular weight triglycerides can be slightly pseudoplastic (Eiteman and Goodrum, 1994). Thus, values reported here are for a constant shear rate of 100 s^{-1} .

Color. Color of oils is often used as a subjective or objective index to determine the quality of used oils. Many different techniques are used to evaluate color of

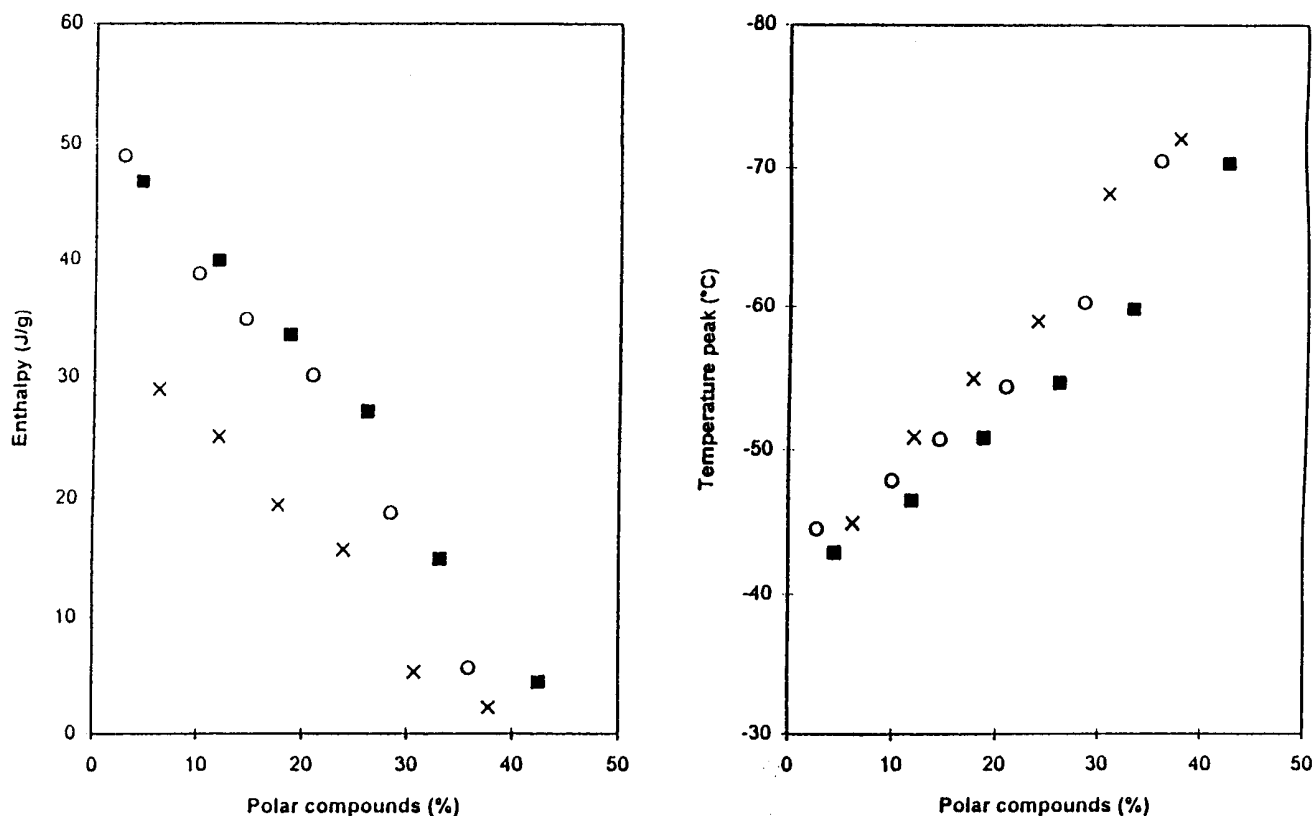


Figure 4. Correlation between polar compounds (percent) and DSC parameters enthalpy and temperature peak: SO (■); CO (○); GO (×).

Table 4. Relationship between TPC (X) and Other Indicators of Oil Quality (n = 6)

oil sample	eq of regression line			
	enthalpy	temp peak	viscosity	color
SO	$Y = 53.461 - 1.124X$	$Y = -38.320 - 0.697X$	$Y = 76.827 + 3.776X$	$Y = -2.280 + 0.334X$
CO	$Y = 52.954 - 1.248X$	$Y = -40.553 - 0.757X$	$Y = 87.280 + 3.341X$	$Y = -3.689 + 0.849X$
GO	$Y = 35.299 - 0.895X$	$Y = -39.728 - 0.870X$	$Y = 85.686 + 3.727X$	$Y = -4.462 + 0.479X$

frying oils objectively including colorimetric kits (Croon et al., 1986) and use of colorimeters such as Lovibond (Al-Kahtani, 1991) and Agtron (Warner et al., 1994). UV absorption, although outside the visible spectrum, has also been related to color changes (Melton et al., 1994; Mazza and Qi, 1992). A steady increase in ΔE (changes in color) was observed with frying time (Table 1).

Relationships between Oil Quality Indicators. Relationships between oil quality indicators for SO, CO, and GO are shown in Table 2 and Figure 4. Correlations ($p < 0.001$) between all methods were >0.94 independent of the oil source. In particular, the high correlation found between enthalpy and temperature peak determined in this work with changes in color, viscosity, and TPC suggests application of the DSC method to the study of oil quality during frying. Results in Table 2 confirm the previous findings of Al-Kahtani (1991), who also reported a high correlation between TPC and viscosity in oils sampled from restaurants, and those of Melton et al. (1994), who related TPC with overall color difference measured in a Hunterlab colorimeter.

TPC has been accepted as the most reliable method for determining oil deterioration during frying and is currently the standard method of IUPAC and AOAC (Al-Kahtani, 1981). Table 4 shows linear regression equations between TPC and DSC parameters.

CONCLUDING REMARKS AND FUTURE APPLICATIONS

A shift in peak temperature and changes in enthalpy of crystallization occur during prolonged frying of the studied oils. DSC is a fast method of analysis and requires small samples (15–60 mg) with minimal preparation. As demonstrated by Aguilera and Gloria (1997), DSC analysis of the oil can also be performed directly in fried products (e.g., fried potato products) without interference of solids. Thus, DSC could be a fast and direct way to assess the quality of oils being consumed in prefried commercial products or in ready-to-eat meals, if the nature of the oil is known or determined (a subject that we are currently studying). As reported by Pokorny (1980), some degradation products of heated oils tend to accumulate in the frying substrate.

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LITERATURE CITED

Aguilera, J. M.; Gloria, H. Determination of oil in fried potato products by differential scanning calorimetry. *J. Agric. Food Chem.* **1997**, *45*, 781–785.

- Al-Kahtani, H. A. Survey of quality of used frying oils from restaurants. *J. Am. Oil Chem. Soc.* **1991**, *68*, 857–862.
- AOCS. *Official Methods and Recommended Practices of the American Oil Chemists Society*, 4th ed.; Firestone, D., Ed.; AOCS Press: Champaign, IL, 1993.
- Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*; Elsevier: Amsterdam, 1989; p 11.
- Blumenthal, M. M.; Stier, R. F. Optimization of deep-fat frying operations. *Trends Food Sci. Technol.* **1991**, *2*, 144–148.
- Bracco, U.; Dieffenbacher, A.; Kolarovic, L. Frying performance of palm oil liquid fractions. *J. Am. Oil Chem. Soc.* **1981**, *58*, 6–12.
- Che Man, Y. B.; Swe, P. Z. Thermal analysis of failed-batch palm oil by differential scanning calorimetry. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1529–1532.
- Clark, W. L.; Serbia, G. W. Safety aspects of frying fats and oils. *Food Technol.* **1991**, *45* (10), 84–89, 94.
- Croon, L. B.; Rogstad, A.; Leth, T.; Kiutamo, T. A comparative study of the analytical methods for quality evaluation of frying fat. *Fette, Seifen, Anstrichm.* **1986**, *88*, 87–91.
- Eiteman, M. A.; Goodrum, J. W. Density and viscosity of low-molecular weight triglycerides and their mixtures. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1261–1265.
- Hollingsworth, P. The leaning of the American diet. *Food Technol.* **1996**, *50* (4), 86–90.
- Mazza, G.; Qi, H. Effect of after-cooking darkening inhibitors on stability of frying oil and quality of french fries. *J. Am. Oil Chem. Soc.* **1992**, *69*, 847–853.
- Melton, S. L.; Jafar, S.; Sykes, D.; Trigiano, M. K. Review of stability measurements for frying oils and fried food flavor. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1301–1308.
- Muller, H. G. *An Introduction to Food Rheology*; Heinemann: London, 1973; pp 53–55.
- Pokorny, J. Effect of substrates on changes of fats and oils during frying. *Rev. Ital. Sostanze Grasse* **1980**, *57*, 222–225.
- Roos, Y. H. *Phase Transitions in Foods*; Academic Press: San Diego, CA, 1995; pp 142–148.
- Stevenson, S. G.; Vaisey-Genser, M.; Eskin, N. A. M. Quality control in the use of deep frying oils. *J. Am. Oil Chem. Soc.* **1984**, *61*, 1102–1108.
- Tyagi, V. K.; Vasishta, A. K. Changes in the characteristics and composition of oils during deep-fat frying. *J. Am. Oil Chem. Soc.* **1996**, *73*, 499–506.
- Warner, K.; Orr, P.; Parrot, L.; Glynn, M. Effects of frying oil composition on potato chip stability. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1117–1121.

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