

Quality Assessment of Heated Cooking Oil, Agab, Using a Simple Newly-Developed Spectrophotometric Method

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Abstract Deep fat frying is one of the most widely used cooking practices but heat treatment produces many degradation products, some of which may cause health hazards. A simple, rapid, and inexpensive method for assessment of the quality of cooking oil used for frying was developed using a spectrophotometer. Potato slices were heated in Agab oil (soybean/sunflower:1/1 volume) at 180 ± 5 °C for 8 h per day for 6 consecutive days. Heated samples were collected at 15-min intervals and UV absorbance at $\lambda = 370\text{--}400$ nm was measured; samples were also analyzed for anisidine value (AV), conjugated diene formation (CD), and total polar compounds (TPC). A systematic increase of absorbance in heated oil over frying time was observed. TPC was highest ($R^2 = 0.99$) for the correlation with heating time followed by CD (0.93) and AV (0.89). The spectrophotometric method developed in the present study to assess the quality of heated oils is simple, quick, and reliable because its results were strongly correlated with the results from the TPC.

Keywords Frying oil · Agab oil · Quality assessment of oils · Spectrophotometric method

Introduction

Deep fat frying is popular because it produces desirable flavors, color, and a crispy texture [1]. Deep fat frying is a process of immersing food in hot oil with contact among oil, air, and food at a high temperature of 150–190 °C. Frying oil acts as a heat transfer medium and contributes to the formation of crispy texture and the toasted or roasted flavor of fried foods. During deep fat frying, the simultaneous heat and mass transfer of oil, food, and air produces the various unique qualities of fried foods [2].

A series of degradation reactions occurs in heated frying oils followed by formation of a variety of decomposition compounds. Some of these decomposition products have either positive or negative effects on the quality of the flavor and nutritional value of the fried food [3]. Some of these compounds may be harmful to human health [4]. Therefore, some countries set certain regulations on procedures for discarding overused oils [5].

It is vital that the quality of frying oil is monitored in order to maintain the appropriate quality of both the oil and the fried food product. Some food service operations evaluate oil quality by subjective parameters such as visual and odor characteristics [6]. Traditionally, the quality of heated edible oils was monitored by measuring various values, including total polar compounds (TPC), total free fatty acids (FFA), carbonyl value, and viscosity [7, 8] as well as peroxide value (PV) and anisidine value [9]. However, use of PV to evaluate heated oils may not be adequate because a significant decrease in the PV after reaching maximum value was observed. Therefore, it has been hypothesized that peroxides are unstable and highly susceptible to further changes such as the formation of secondary oxidation products associated with carbonyl compounds (CA) and AV [9]. Among these conventional

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methods, measurement of TPC is the most popular and commonly used [7, 8]. However, the TPC method uses hazardous organic solvents, such as petroleum ether and diethyl ether, and requires 3.5 h per sample [10]. Therefore, this method is more frequently used in basic research studies than by food companies.

In the present study, a spectrophotometric method for the rapid assessment of the quality of a vegetable oil during frying was developed and evaluated in comparison with traditional chemical methods, including AV, CD, and TPC.

Materials and Methods

Materials and Reagents

Soybean oil, sunflower seed oil, and fresh potatoes were bought from a local market in Cairo, Egypt. All chemicals used in this study were purchased from reliable commercial sources.

Sample Preparations of Heat-Treated Oils

Potatoes were peeled and cut into pieces ($7.0 \times 0.5 \times 0.3$ cm) and submerged in water until used. After the water was removed from their surfaces, the potato pieces (20 g) were fried in 2 L frying oil (soybean/sunflower:1/1 volume) at 180 ± 5 °C at 15-min intervals for 8 h per day for 6 consecutive days. Fifty grams of oil were withdrawn after each 4 h of frying (i.e., 2 samples per day). The oil samples were filtered into screw-capped bottles and stored at 4 °C in the dark until analysis. The experiments were conducted in duplicate.

Spectrophotometric Measurement of Heated Oils

Color changes of the oil samples were monitored with a U-2000 double-beam UV/Vis spectrophotometer (Hitachi Instruments, Inc., Tokyo, Japan). The samples were placed in a standard quartz cuvette (1-cm optical path) and warmed in a 60 °C thermostatic oven for 15 min before measuring the spectrophotometric absorbance. The spectrophotometric absorbance was zeroed against air without using a cuvette. The oil samples were scanned from 350 to 650 nm wavelength.

Determination of AV, CD, and TPC

TPC, AV, and CD content were measured to assess the quality of oil. The anisidine value of the samples was measured according to the AOCS official method, Cd 3a-63, by alkaline titration. The anisidine value was reported in millimoles per kilogram of sample [11]. The CD content

was measured in absorbance units as described in the AOCS Official Method Ti 1a-64 [12]. The sample was dissolved in isooctane and the absorbance of the solution was measured with a UV-Vis double-beam U-2000 spectrophotometer (Hitachi Instruments, Inc., Tokyo, Japan) at 233 nm.

The TPC of the samples was determined according to the AOCS official method, Cd 20-91, by column chromatography [11].

Statistical Analysis

The data were statistically analyzed using correlation and regression. The curves and the equations of the curves were fitted using Microsoft excel.

Results and Discussion

The color of the oil changed from light yellow to reddish yellow gradually during heating. The oil became more and more viscous over the course of the heating time. The viscosity of the oil increased due to polymerization of degradation products [13]. Table 1 shows the spectral changes that occurred during the frying process monitored with spectrophotometric scanning from 350 to 650 nm. The absorbance—which ranged from 371 nm (sample heated for 0–16 h) to 393 nm (sample heated for 48 h)—increased systematically as the heating time increased, which corresponds to the color changes described above. The maximum absorbance shifted toward higher wavelength ranges over the duration of the heating time. Comparable results were reported previously [14]. There were systematic changes in spectrophotometric absorbance when three canola oils and sunflower oil were heated for 80 h at 190 °C. These changes occurred clearly in the wavelength ranging from 470 to 500 nm. In the present study, the changes occurred in wavelengths ranging from 371 to 399 nm. These differences in the absorbance ranges may be due to the use of different oils, in particular, oils with

Table 1 Spectral changes that occurred during the frying process

| Heating time (h) | Wavelength (nm) | Absorbance |
|------------------|-----------------|------------|
| 0 | 371 | 0 |
| 16 | 371 | 0.398 |
| 20 | 377 | 0.979 |
| 24 | 381 | 1.365 |
| 28 | 385 | 2.108 |
| 32 | 388 | 2.307 |
| 36 | 388 | 2.602 |
| 40 | 391 | 2.624 |
| 48 | 393 | 2.783 |

Table 2 Fatty acid composition of oils used in the previous work and the present study

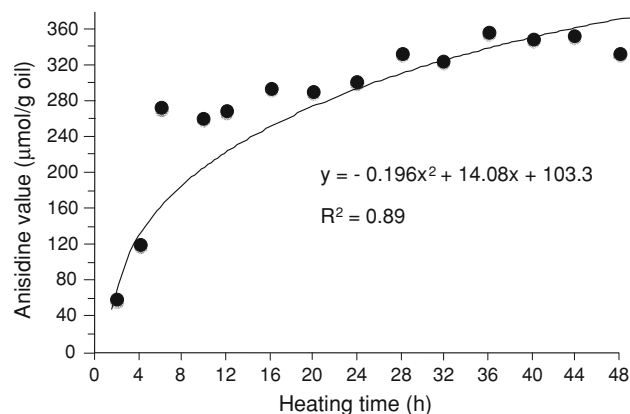
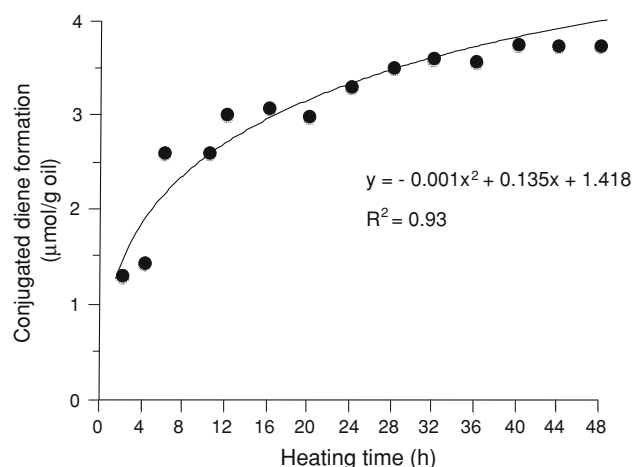
| Oil | Unsaturated/ saturated | Saturated fatty acid | | | | | Mono unsaturated | Poly unsaturated | |
|-----------|---------------------------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|------------------------------|---------------------|----------------------------------|--|
| | | Capric C _{10:0} | Lauric C _{12:0} | Myristic C _{14:0} | Palmitic C _{16:0} | Stearic C _{18:0} | | Oleic (w-6) C _{18:1} | α -Linolenic (w-3) C _{18:3} |
| Canola | 15.7 | – | – | – | 4 | 2 | 62 | 22 | 10 |
| Palm | 1.3 | – | – | 1 | 37 | 4 | 46 | 11 | – |
| Soybean | 5.7 | – | – | – | 11 | 4 | 24 | 54 | 7 |
| Sunflower | 7.3 | – | – | – | 7 | 5 | 19 | 68 | 1 |

different fatty acids compositions. Table 2 shows the fatty acid composition of the oils used in a previous study (canola and palm oil) [14] and in the present study (soybean and sunflower oil) [15]. The fatty acid composition of oils used in the two studies were different. Therefore, difference in fatty acid composition might influence formation of degradation products. However, both studies showed consistent absorbance related to the heated oils.

Changes in degradation of oil during frying must include the formation of various kinds of products, which range from low molecular weight carbonyls ([16] to high molecular weight pigments [17]. The formation of these different products may affect the absorbance of a heated oil [18–20]. However, the changes observed in the present study were correlated to the wave length 370–400 nm, which are sufficiently consistent with the wave length 300–400 nm used to monitor the changes of degradation products in frying oils in a previous study [17], in which the complete spectra of the oils heated for 1, 20, and 40 days with a maximal absorbance at 312 nm were shown.

In addition to the spectrophotometric measurement, chemical analyses for CD, AV, and TPC were conducted to monitor the degradation of the oil and assess quality. Fig. 1 shows the results from the AV determination in heated oil. The values are means \pm SD ($n = 3$). SDs do not appear in the figure because values are too small ranging from 0.14 (from oil heated for 2 h) to 3.67 (from oil heated for 10 h). AV has been commonly and widely used as a conventional method for evaluating the quality of oils oxidized in various ways, including frying [21]; long-term heating [22]; and UV irradiation [23]. In the present study, AV increased over time and reached a maximum after 36 h of heating, after which it leveled off or slightly decreased. The correlation (R^2) between heating time and AV was 0.89. A previous report indicated that the relationship between heating temperature and the increase in AVs showed the closest correlation for rapeseed oil, sunflower oil, goose fat, and pig fat at 180, 165, 160, and 160 °C (R^2 values: 0.95, 0.78, 0.42, and 0.87, respectively) [22].

Figure 2 shows the results of conjugated diene analysis. The values are mean \pm SD ($n = 3$). SDs do not appear in

**Fig. 1** Effect of heating time (0–48 h) on the anisidine value (AV) of Agab oil**Fig. 2** Effect of heating time (0–48 h) on conjugated diene formation (CD) of Agab oil

the figure because values are too small ranging from 0.01 (from oils heated for 12 and 16 h) to 0.20 (from oil heated for 6 min). CD have been known to form at the early stage of lipid peroxidation induced by heat and are widely used to monitor lipid peroxidation [24, 25]. In the present study, CD content increased gradually and plateaued after 36 h heating time. The CD content of heated oil increased

approximately 70% after 24–36 h. The correlation (R^2) between heating time and CD content was 0.93. A previous study on various cooking oils heated under frying conditions (at 180 °C for 25 h) reported that the increasing % of CD content ranged from 75 (high oleic sunflower oil) to 92% (peanut oil), suggesting that the results from this study [26] are consistent with the ones from the present study.

Figure 3 shows the effect of heating time on TPC of tested oils. The values are means \pm SD ($n = 3$). SDs do not appear in the figure because values are too small ranging from 0.01 (from oil not heated) to 1.15 (from oil heated for 40 h). The amount of TPC kept increasing over heating time. It reached the critical level of 24% [27] within 10 h. The previous study on quality alterations of oils during long-term heating reported that the amount of TPC increased faster in vegetable oils (rapeseed oil and sunflower oil) than in the animal fats (pig and goose) [22]. Because the correlation between heating time and TPC was the highest among the three methods used in the present study ($R^2 = 0.99$), TPC was chosen to compare with the spectrophotometric method to assess the deterioration of heated oils. TPC is directly correlated with total oxidation products, while anisidine value or conjugated diene value measures only total alkenals or oxidative isomerization, respectively.

Figure 4 shows the correlation between TPC and the spectrophotometric absorbance at 371–399 nm for Agab oil during 48 h frying. Comparing the spectrophotometric absorbance of the heated oil at $\lambda = 371\text{--}399$ nm with the corresponding TPC formed during the 48 h frying time revealed a high correlation ($R^2 = 0.99$) between them with an equation of conversion of the spectrophotometric absorbance to TPC content: $y = 8.079x^2 + 1.082x + 3.141$. The maximal allowed level of TPC in the frying oil is 27%, which must correspond to a spectrophotometric absorbance of about ≤ 1.7 .

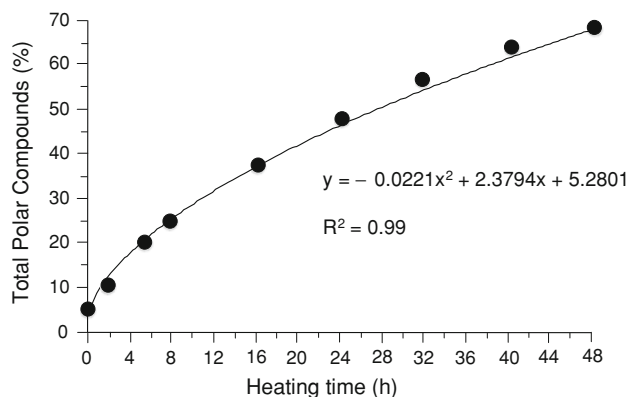


Fig. 3 Effect of heating time (0–48 h) on polar compound formation of Agab oil

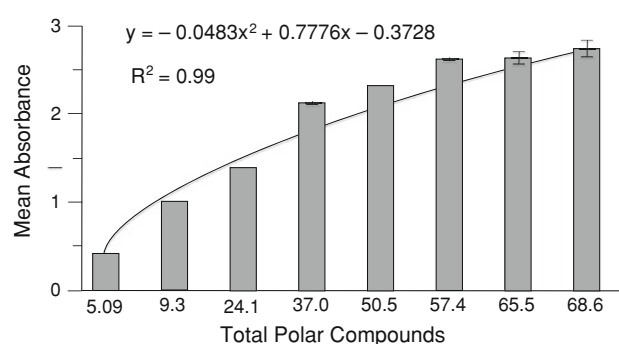


Fig. 4 Correlation of total polar compounds (TPC) determined by the standard method and the spectrophotometric absorbance method at 371–399 nm for Agab oil during 48 h frying time

Conclusions

The significant increase in consumption of edible oils in the deep-fat frying industry entails the need for simple, rapid, accurate, and low cost-effective techniques for the determination of heated-oil quality. Most of the methods used to assess quality of heated oils—including AV, CD, and TPC—are tedious, costly, not amenable to on-line assessment, and usually require reasonable analytical expertise [7, 8]. Use of high-performance size-exclusion chromatography and high-temperature gas chromatography have received much attention recently to evaluate the fat degradation but they are time-consuming and expensive. Therefore, these methods are customarily used in research work rather than in routine work by the food industry [28]. The spectrophotometric method used in the present study, which correlated well with TPC, may be used routinely, reliably, and economically as a method for rapid evaluation of heated-oil quality.

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