

Evaluating the Performance of Peroxide and Conjugated Diene Values in Monitoring Quality of Used Frying Oils

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ABSTRACT

Frying oils showed an increase in Peroxide Value (PV) at the initial stages of the frying process followed by a decrease, and there was no correlation between PV and Total Polar Compounds (TPC) in the same set of frying oils. All the frying oils had PVs lower than 4.42 meq O₂ kg⁻¹ oil during the frying process and, consequently, none of them was above the limit of 10 meq O₂ kg⁻¹ oil for edible oils. The variations of Conjugated Diene Value (CDV) presented a pattern different from that of PV. CDV had a good linear relationship with TPC during initial stages of the frying process and then reached a plateau ($R^2=0.9838$). The plateau occurred beyond the TPC of 24-27% for the frying oils, and there was an obvious increasing trend before the range mentioned. The contents found for conjugated dienes of the frying oils during the frying process ranged from 5 to 42 mmol L⁻¹. Assuming that the limit of acceptance for TPC is 24%, this roughly corresponded to 29 mmol L⁻¹ for CDV.

Keywords: Carbonyl value, Conjugated diene value, Deterioration, Frying oil, Peroxide value, Total polar compounds.

INTRODUCTION

Frying of foods is one of the most common and popular practices in their preparation and manufacture [1]. It is a fast, convenient, and energy-efficient cooking method and increases palatability due to fat absorption, crust formation, and pleasant flavors and odors [2]. However, it is well known that frying oils used continuously at high temperatures in the presence of oxygen and water from the food being fried, are subject to thermal oxidation, polymerization, and hydrolysis, and the resultant decomposition products adversely affect flavor and color [3-5]. In addition, undesirable constituents produced from degraded frying oils may even be harmful to health [6].

Peroxide Value (PV) is one of the most frequently determined quality parameters

during oil production, storage and marketing. PV shows the degree of oxidation in the substance and measures the amount of total peroxides as a product of primary oil oxidation [7]. Che Man *et al.* [8] reported a decrease in the PV of oil samples after an initial increase. A significant decrease of PVs after reaching maximum values confirms that peroxides, which are formed in the early stages of oxidation, are unstable components and are highly susceptible to further changes that result in the formation of secondary products of oxidation [9]. Therefore, Fritsch [10] has stated that the determination of PV is not suitable for the assessment of used frying oils. Nevertheless, Susheelamma *et al.* [11] reported a continuous increase of PV during three successive fryings of a model dough in all samples of oils and blends investigated. Innawong *et al.* [6] also observed an increasing trend of PV for peanut oil

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samples during a three-day cycle of poultry product frying.

Conjugated dienes are formed as intermediates through a shift of a double bond of Polyunsaturated Acids (PUFA) [12]. These compounds can be measured by ultraviolet absorption at 232-234 nm [4, 13]. The method is simple, does not depend on a chemical reaction or color development, and requires a small sample size [14]. Maskan and Bagci [14] demonstrated that the variations of Conjugated Diene Value (CDV) of a sunflower oil sample during frying present a pattern different from that of PV. They stated that the CDVs obtained were not related to PVs due to decomposition of peroxides at the frying temperature. Houhoula *et al.* [12] showed that CDV is a representative oxidation index that can be used during frying to characterize the status of oxidation of cottonseed oil. However, it has been reported that the conjugated compounds increase initially and then reach a plateau during frying. This has been related to the establishment of an equilibrium between the rate of formation of conjugated dienes and the rate of formation of polymers formed by a Diels-Alder reaction involving conjugated dienes [4].

During the frying process, a wide variety of chemical reactions result in the formation of compounds with high molecular weight and polarity. For surveying frying oil or fat quality the determination of total polar compounds is considered to be one of the most reliable methods for continuous monitoring of the changes in fats and oils during the frying process. Total Polar Compounds (TPC) is accepted worldwide for the control of frying oils and fats and must be used as reference for the evaluation of other testing procedures [10, 15-17].

The goals of this study were (i) to investigate the changes in the analytical quantities mentioned above in a range of commonly used frying oils during the frying process, and (ii) to evaluate the performance of PV and CDV compared to TPC as a reference method in monitoring the quality of used frying oils.

MATERIALS AND METHODS

Materials

A set of frying oil samples of different compositional properties but passed qualitative and quantitative standards, which were from various vegetable oil sources (individually or as blends), were obtained from seven of big oil factories in Iran. Seven frying oil samples were purchased from local shops and had PVs of less than 2.5 meq O₂ kg⁻¹ oil before frying. They were used for frying potato. All chemicals and solvents were of analytical reagent grade and purchased from Sigma-Aldrich (St. Louis, MO) and Merck (Darmstadt, Germany).

Frying Process

Potatoes were peeled and cut into pieces (7.0×0.5×0.3 cm) and submerged in water until needed; potato pieces were fried in the frying oils. The oil (2.0 L) was placed in a 2 L capacity bench-top deep-fat fryer (Kenwood DF280) and heated to 170°C. Potato pieces were fried in 20 g batches at a constant frying temperature. The batches were fried at 15 minutes intervals for 8 hours per day for seven consecutive days. At the end of each day, 30 g of the frying oil was filtered into a screw-cap vial and stored in the dark at 4°C until analyzed. The volume of oil was not replenished during the frying process. The frying experiments were conducted in duplicate on each frying medium [5].

Determination of PV

PV was determined according to the thiocyanate method. The sample (0.01-0.30 g, depending on the extent of peroxidation) was mixed in a disposable glass tube with 9.8 mL chloroform-methanol (7:3 v/v) in a vortex mixer for 2-4 seconds. Ammonium thiocyanate solution (50 µL, 30% w/v) was

added and the sample was then mixed in a vortex mixer for 2-4 seconds. Then, 50 μL of iron (II) chloride solution ([0.4 g barium chloride dihydrate dissolved in 50 mL H_2O] + [0.5 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 50 mL H_2O] + 2 mL 10M HCl, with the precipitate, barium sulfate, filtered off to produce a clear solution]) was added, and the sample was mixed in a vortex mixer for 2-4 seconds. After a 5 minutes incubation at room temperature, the absorbance of the sample was read at 500 nm against a blank that contained all the reagents except the sample using a spectrophotometer (Jenway 6105 UV-VIS). The entire procedure was conducted in subdued light and completed within 10 minutes. All PV analysis results were expressed as $\text{meq O}_2 \text{ kg}^{-1}$ oil [18].

Determination of CDV

This index was measured spectrophotometrically at 234 nm and read against HPLC grade hexane as blank. The oil samples were diluted to 1:600 with hexane [19]. An extinction coefficient of $29,000 \text{ mol L}^{-1}$ was utilized to quantify the concentration of conjugated dienes formed during the frying process [19, 20].

Determination of TPC

TPC was determined according to an economical micromethod developed by Schulte [21]. One gram prepared silica gel 60 was compressionally filled between two cotton wool balls into a 5 mL pipette tip (15 cm long). The oil sample (500 mg) was pipetted into a 5 mL volumetric flask. It was dissolved in 4 mL toluene, and then filled up with the toluene. Under a well ventilated fume hood, 1 mL of the solution was pipetted on top of the pipette tip fixed over a tared aluminium tray, so that it ended 1 mm above the bottom of the tray. After the solution was soaked in, the pipette tip was washed with 1 mL eluent and, after soaking in, 7 mL ($2 \times 3.5 \text{ mL}$) eluent were added. Af-

ter elution ($\sim 15 \text{ min}$), the end of the tip was washed with 500 μL of toluene. The solvent was removed from the eluate with dry compressed air; the evaporation was speeded up by placing the tray on a hot plate of 50°C . After weighing, TPC, in per cent (w/w), was calculated using the formula $100(w-w_1)/w$, in which w and w_1 are the sample weight and the weight of nonpolar components in mg, respectively.

RESULTS AND DISCUSSION

Changes in the PV, CDV and TPC of the frying oils during the frying process are shown in Figure 1. The frying oils showed an increase at the initial stages of the frying process followed by a decrease in PV (Figure 1a). This was in accordance with Fritsch [10] who stated that the determination of PV is not suitable for the assessment of used frying oils. In their study on heating and frying of palm olein, Augustin and Berry [22] indicated that the use of PV for following the oxidative deterioration of fats and oils during deep-frying is problematical because, during the frying process, peroxides are destroyed by high temperature and during cooling new peroxides are formed. In the present study, the average of the PVs for the frying oils was $4.42 \text{ meq O}_2 \text{ kg}^{-1}$ oil during the frying process and, consequently, none of the oil samples were above the limit of $10 \text{ meq O}_2 \text{ kg}^{-1}$ oil for edible oils and the limits of 5 and $7 \text{ meq O}_2 \text{ kg}^{-1}$ oil in accordance with AOCS and ISIRI, respectively, for used frying oils [23]. In addition, there was no correlation between PV and TPC in the same set of frying oils (data not shown). Accordingly, PV may not indicate the actual extent of oil deterioration and is not recommended for measuring oil deterioration during the frying process.

All the frying oils showed a nearly similar trend of change in CDV with time during the frying process. As can be seen in Figure 1b, CDV of the frying oils linearly increased during the initial stages of the frying process and then reached a plateau. The variations of

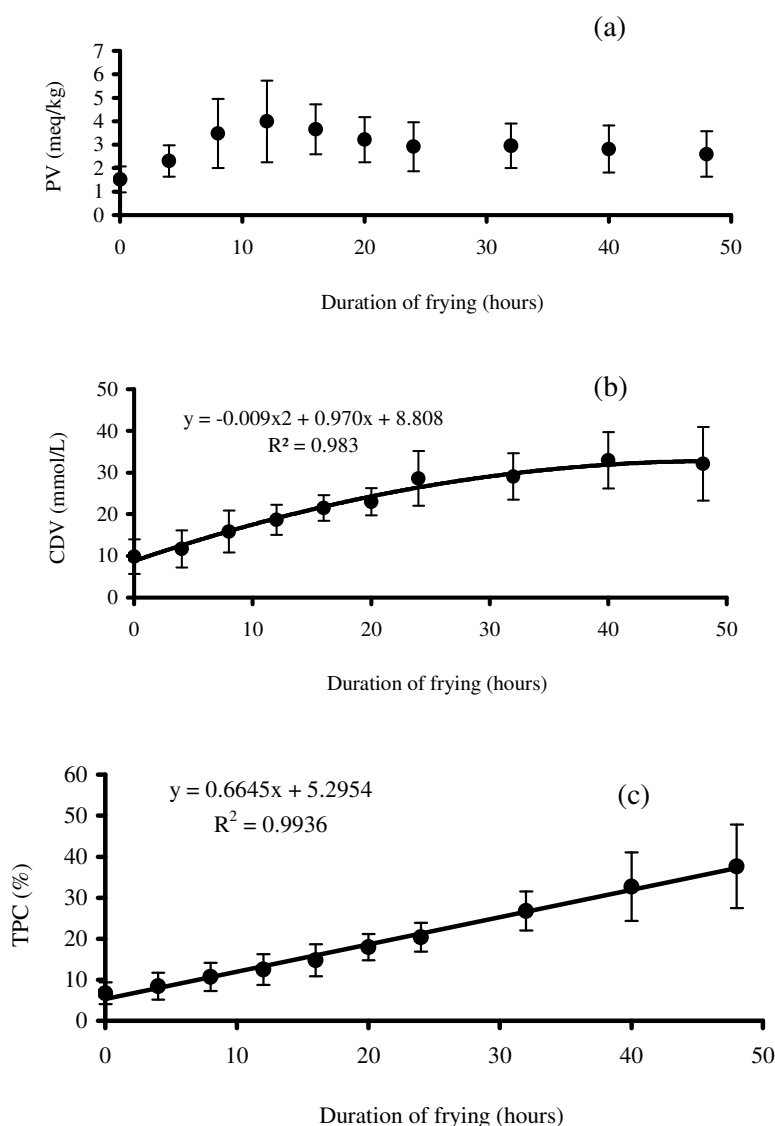


Figure 1. Changes in: (a) Peroxide Values (PV); (b) Conjugated Diene Values (CDV), (c) Total Polar Compounds (TPC) of the frying oils during frying process (each data point in the graphs represents the mean taken from seven frying oil samples \times two replicates \pm standard deviation).

CDV presented a pattern different from that of PV. This means that conjugated dienes formed during frying increased absorbance at 234 nm in addition to peroxides formed even at low concentrations [14]. In this study, CDVs obtained were not related to PVs due to the decomposition of peroxides at the frying conditions.

To examine the relationship between CDV and TPC, we plotted the experimental data obtained from the frying oils (Figure 2). A

high determination coefficient, $R^2 = 0.9838$, was obtained. As can be seen, CDV had a good linear relationship with TPC during the initial stages of the frying process and then reached a plateau. Houhoula *et al.* [12] in their kinetic study on the deterioration of a refined cottonseed oil during the frying process found a significant linear correlation of CDV with TPC ($R^2 = 0.862$), but the frying time in their study was no more than 12 hours. National legislation in several coun-

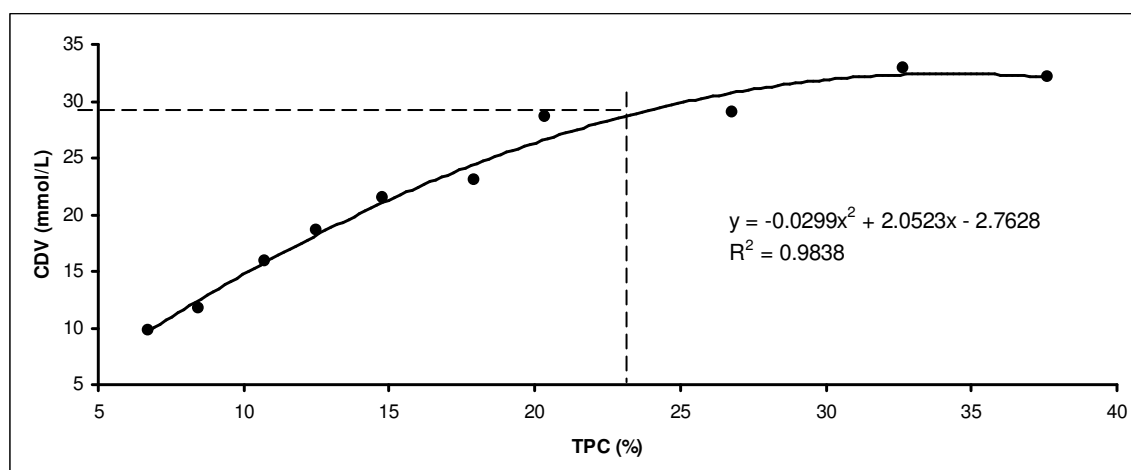


Figure 2. Correlation of Conjugated Diene Value (CDV) with Total Polar Compounds (TPC) in a set of frying oil samples.

tries specifies an acceptable upper limit of TPC of 24-27% for frying oils [24]. It was interesting to find that the plateau occurred beyond the TPC of 24-27% for the frying oils, and there was an obvious increasing trend before the range mentioned. The contents found for conjugated dienes of the frying oils during the frying process ranged from 5 to 42 mmol L⁻¹. Assuming that the limit of acceptance for TPC is 24%, this will roughly correspond to 29 mmol L⁻¹ for CDV (shown in Figure 2). Therefore, the measurement of CDV can be considered to be a suitable method in monitoring of the quality of used frying oils. Furthermore it is cheaper and easier than the TPC method.

CONCLUSION

The results of the present study demonstrated that PV may not indicate the actual extent of oil deterioration and is not recommended for measuring oil deterioration during the frying process. The measurement of CDV can be considered to be a suitable method in monitoring of the quality of used frying oils. It is, moreover, cheaper and easier than the TPC method. Assuming that the

limit of acceptance for TPC is 24%, this will roughly correspond to 29 mmol L⁻¹ for CDV.

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ارزیابی عملکرد اعداد پراکسید و دی ان مزدوج برای سنجش کیفیت روغنهای سرخ کردنی استفاده شده

ر. فرهوش و س.م. ر. موسوی

چکیده

عدد پراکسید روغنهای سرخ کردنی در مراحل ابتدایی فرایند سرخ کردن، افزایش و سپس کاهش پیدا کرد. هیچ گونه همبستگی میان عدد پراکسید و میزان کل ترکیبات قطبی مجموعه روغنهای مورد آزمایش مشاهده نگردید. عدد پراکسید تمام روغنهای سرخ کردنی طی فرایند سرخ کردن کمتر از ۴/۴۲ میلی اکسیژن بر کیلوگرم روغن بود که به این ترتیب عدد پراکسید هیچ یک از آنها از حد ۱۰ در خصوص روغنهای خوراکی فراتر نرفت. الگوی تغییرات متفاوتی را عدد دی ان مزدوج نسبت به عدد پراکسید طی فرایند سرخ کردن از خود نشان داد. طی مراحل ابتدایی فرایند سرخ کردن، عدد دی ان مزدوج به موازات تغییر میزان کل ترکیبات قطبی به صورت خطی افزایش پیدا کرد و سپس به حد ثابتی رسید ($R^2 = 0/9838$). نیل به چنین حد ثابتی از تغییرات عدد دی ان مزدوج زمانی بروز پیدا کرد که میزان کل ترکیبات قطبی به محدوده ۲۴ تا ۲۷ درصد رسیده بود و روند افزایشی مشهودی پیش از رسیدن به محدوده یاد شده مشاهده گردید. عدد دی ان مزدوج روغنهای سرخ کردنی طی فرایند سرخ کردن از ۵ تا ۴۲ میلی مول بر لیتر متغیر بود. با فرض حد قابل قبول ۲۴ درصد برای میزان کل ترکیبات قطبی، این رقم تقریباً معادل ۲۹ میلی مول بر لیتر برای عدد دی ان مزدوج بود.