Research Article

Evaluation of Total Polar Compounds, Acidity & Peroxide Values Amounts in Oils after Frying Zoolbia & Bamie Sweets

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Abstract

Background: Zoolbia and Bamieh, Iranian traditional sweets, are highly used in Ramadan by a large people. Unfavorable cooking conditions increase total polar compounds (TPC), acidity and peroxide values which have an important role in dangerous disease outbreaks. This study aimed to evaluate the amount of these three values in the oils after cooking these sweets in Behshahr city's pastries in Ramadan.
Methods: This cross-sectional study was conducted on all 11 pastries in Behshahr during a month. In total, 33 samples were taken at the beginning, middle and end of the weeks and at the end of daily cooking. The TPC value was measured by Testo 270 devices, while the acidity and peroxide values were measured according to titration standard methods and the results were analyzed with SPSS.
Results: According to the results, in all cases, the acidity and TPC values were lower than the standard level of waste oils, but peroxide level was high.
Conclusion: Peroxide of sunflower oils for frying rises faster and more than other oils after cooking. According to the comparison of our findings with other studies, the oil samples had higher health status.

Introduction

Frequent use of frying oil is associated with oil hydrolysis and oxidation in the presence of heat and water of the foodstuff. With the occurrence of multiple reactions such as circularization, oxidation, hydrolysis, beta cut, polymerization and isomerization, several new compounds are formed, leading to the analysis of the oil molecule structure. The important features of suitable frying oil are high oxidative stability, high smoke point, low melting and boiling points, good smell and taste, and high nutritional value [1]. Determining this quality is possible by doing some experiments such as the determination of free fatty acids, peroxide value and total polar compounds (TPC) [2]. Since traditional sweets of Zoolbia and Bamieh are used by a large public in Ramadan, in the case of correct, safety and healthy oil for cook, the ingredients of these sweets can be useful and supply some of the food needs of people, especially fasting ones. But unfavorable cooking conditions through producing large amounts of toxic compounds and incidence of various diseases will endanger public health. Therefore, due to the high importance of health and safety of oils in maintaining public health, it is necessary to assess the quality of the used oil after cooking the sweets.

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In many factories and restaurants, oil is used for a long time, and it is changed only after experimental observation and diagnosis. During the frying process, a wide range of chemical reactions leads to the formation of compounds with high molecular weight and high polarity. Therefore, the quantification of TPC is considered as one of the most reliable methods of assessing the quality of oil during frying, and the oil waste point can be determined based on it [3]. Studies have shown that the polarized components separated from the oxidized oils have toxic effects on laboratory animals. In fact, the TPC is formed in fried oil from analyzed products, non-volatile oxidized derivatives, polymerized and cyclized compounds during foods deep frying in oil [4].

Edible animal and vegetable fats as well as oils normally have certain and minor amount of free fatty acids, but these amounts may exceed from threshold limit due to different factors of corruption and an incidence of hydrolysis reaction. Acidity value and acidity are indices that help to recognize the corruption of oils and fats [5].

Peroxide and carbonyl or anisidine are primary and secondary products of lipids' oxidation process, respectively. In general, when the oils' unsaturation degree is greater, oil or oily material will be prepared so much for oxidation. Hydro-peroxides are polar covalent compounds, very strong oxidants and weak reductants which can be easily converted into dangerous polarized secondary compounds [6]. Released free radicals not only are responsible for food corruption, but also cause damage to body tissues and lead to diseases such as cancer, allergical inflammatory diseases, atherosclerosis, premature aging, heart and brain ischemia, respiratory distress syndrome, liver disorders, type II diabetes and so on [7]. According to the standard 4152, Institute of Standards & Industrial Researches of Iran, suitable frying oil for food industry is the fluent oil free of any abnormal smell, taste and pungency with free fatty acids (based on oleic acid weight percentage) with a maximum of 0.07, percentage of linoleic acid and trans fatty acid with a maximum of 2, anisidine number with a maximum of 6 and peroxide with a maximum of 2 mEq gr oxygen per kg of oil. The waste oil is the oil used in food frying process and its physical (color, taste, smell) and physicochemical (smoke point, polar compounds) changes make it impossible for reuse; hence the fresh oil must be replaced. Mireover, the weight percentage of its polar compounds, free fatty acids and oxidized fatty acids must be more than 25, 2, and 1, respectively, as well as the smoke point must be less than 170 °C [8].

Methods

In this cross-sectional study, the samples were taken from used oils after cooking Zoolbia and Bamieh in all 11 pastries of Behshahr, at the end of each working day and on three occasions of beginning, middle and end of the week, in small dark glass containers with lids, filled completely. For TPC measurement, the Portable German Testo 270 Device was used to measure the health of cooking oils. In laboratory, the TPC percentage was measured by reaching samples' temperatures into 40 C° in beaker and immersing the device's sensor located at the tip of device's rod, up to the rod's indication line in oil for 20 seconds [9].

After oil sampling, the test was done by titrimetric method according to the standard 4178, Institute of Standards and Industrial Researches of Iran. For sample preparation, it was mixed well. It was leached by a paper filter if it was not clear. The solid oil sample was melted in a lab's oven at 50°C (or maximum 10°C above the melting point of the sample) and was mixed thoroughly. First, 50 ml of ethyl alcohol 96% and 5 ml of phenolphthalein were added to a 250 ml Erlenmeyer flask. Erlenmeyer flask containing alcohol was put on the stirrer heater so that it started consistent boiling by achieving 70°C. To neutralize the probable acids in ethanol and prevent the error potential in determining the sample acidity, the alcohol (pH) was neutralized by adding a few drops of 0.1 normal sodium hydroxide solution until obtaining stable pink color (like union skin) appeared in solution. Then, 20 gr of the oil sample was added to another 250 ml Erlenmeyer flask and the neutralized alcohol was poured into the Erlenmeyer flask containing the sample as well as a clean stirrer magnet was put in the Erlenmeyer flask. Next, we put it on the stirrer heater to heat while rotating magnet and stirring the solution. After that, a few drops of phenolphthalein solution were added to the boiling contents. Titration was continued via adding drops of the 0.1 normal sodium hydroxide solution by hundredths ml pipette until the stable light pink color (like onion skin) be observed for at least 30 seconds. The volume of consumed sodium hydroxide solution was placed in the formula 1, and then, the AV (Acid Value) calculated based on the highest fatty acid and weight percentage (molecular weight of oleic acid 282) in 100 gr of sample

$$\frac{V \times 282 \times N \times 100}{w \times 1000}$$

Formula 1: The formula for calculating the number of acidity.

The basis was that the oil sample was solved in a solution of acetic acid and chloroform as well as the potassium iodide was added, and the released iodine by peroxides was measured using iodometric method in the presence of starch and sodium thiosulfate solution (Formula 2). First, the sampling was taken based on the mentioned procedures in the laboratory and according to the standard 4179, Standards Institute of Iran for conventional fats and oils, 5 gr of sample was weighted in a 250 ml Erlenmeyer flask, and the sample precise weight was noted with thousandth precision. The 30 ml of peroxide solvent (a mixture of acetic acid and chloroform at a ratio of 3:2) was added to the Erlenmeyer flask containing the sample with graduated cylinder and it was stirred well until the sample was dissolved. Then, 0.5 ml of saturated potassium iodide solution made by distilled water was added by a pipette. This Erlenmeyer flask was kept in a dark place for a minute and it must be stirred well during this period. Then, 30 ml of newly boiled and cooled distilled water was added and stirred again. A few indicator drops of 1% starch solution were added and shaken well. Finally, the titration method was continued through the help of hundredth ml pipette and with 0.1 normal sodium thiosulfate solution until the blue color solution (resulting from starch solution indicator and iodine) became colorless. The volume of consumed sodium thiosulfate solution was noted and put in the formula (Formula 2) as well as the peroxide value was calculated in terms of mEq active oxygen in 1 kg of fat [10]. In each sampling, the oils' temperature was measured by Testo digital and laser thermometer in the cooking place during frying. Moreover, the total period of heating oil, types of used containers, amount of sweet production and volume of daily consumed oil were evaluated.

$$V \times N \times 1000 \,/\, W$$

Formula 2: The formula for calculating the peroxide value.

Results & Discussion

According to the taken samples, it was observed that the pastries generally used two types of oils: 1- Sunflower unsaturated liquid oil (special for cooking Zoolbia and Bamieh) containing anti-foam 2- Typical sunflower unsaturated liquid oil (special for frying), and also two types of containers including 1-Deep steel containers 2- Flat zinc trays were used. In most pastries, typical small oven was applied to transfer the heat to container centrally and non-steadily. A limited number of the pastries used special oven with stainless steel enclosure and digital thermometers. In all of the pastries, the amounts of produced sweets and consumed oil volume were approximately constant and equal on most days. But during two days at end of the week, the production and consumption of oil were slightly increased. All pastries, at the end of daily cooking, collected the waste oil and used fresh oil every day at the beginning of cooking.

Figure1 shows the TPC, figure 2 illustrates the AV and figure 3 displays the PV amounts of used oils in the pastries, in three sampling stages of beginning, middle and end of the week for Behshahr city's pastries.

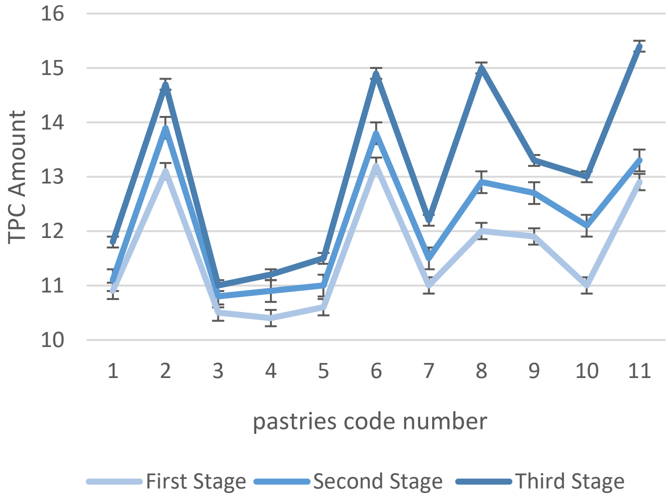

Figure 1: Measured TPC of the three sampling stages in the pasties

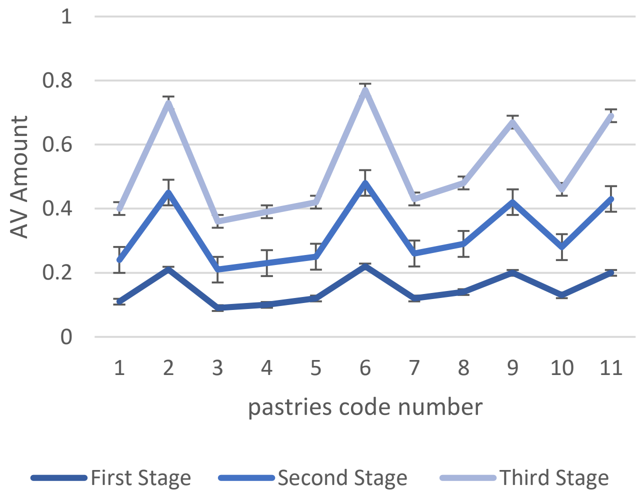

Figure 2: Measured AV of the three sampling stages in the pasties

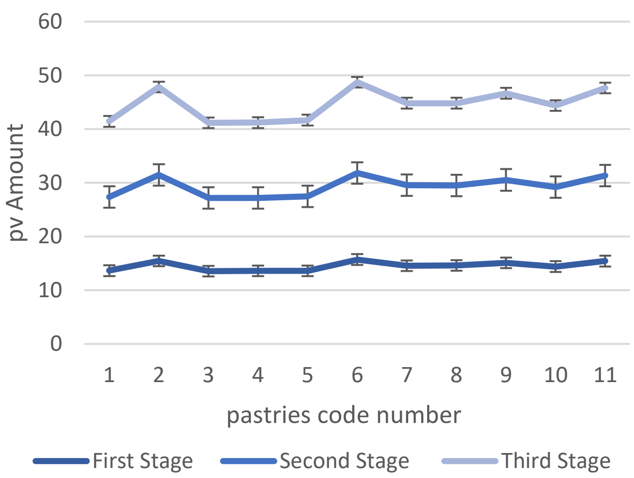

Figure 3: Measured PV of the three sampling stages in the pasties

According to the performed study, the minimum, maximum, average and standard deviation of the measured values for these three indices for each of the 11 units of pastries were described during three sampling stages including in the beginning, middle and end of the week (Table 1). By using Kolmogorov-Smirnov test, the data normality assumption examined that all the obtained possibility amounts confirmed the normality assumption rejection ($p<0.05$). The frequency percentage of using each type of container and oil for cooking Zoolbia and Bamieh in the Behshahr city's pastries was estimated (Table 2).

Table 1: Measured PV of the three sampling Descriptive statistics of measured values for three studied index in the three sampling stages from all pastries

	Min.	Max.	Mean	±SD
Cooking Temperature	142	178	166.09	9.576
Cooking Time	65	145	110	26.926
TPC Value (First Stage)	10.4	13.2	11.59	1.077
TPC Value (Second Stage)	10.8	13.9	12.18	1.191
TPC Value (Third Stage)	11	15.4	13.09	1.668
Acid Value (First Stage)	0.09	0.14	0.12	0.021
Acid Value (Second Stage)	0.1	0.16	0.135	0.026
Acid Value (Third Stage)	0.11	0.19	0.165	0.036
Peroxide Value (First Stage)	15.55	17.71	16.51	0.831
Peroxide Value (First Stage)	15.61	18.12	16.81	0.985
Peroxide Value (Third Stage)	15.98	18.89	17.25	1.071

Table 2: Frequency percentage of using each type of container and oil

Variable	Frequency	
Container type	Container 1	54.5
	Container 1	45.5
Oil type	Oil 1	36.4
	Oil 2	63.6

In table 3-4, the frequency percentage of using each type of container and oil for cooking Zoolbia and Bamieh in the Behshahr city's pastries were estimated.

Table 3: Comparing the studied index according to the type of cooking container in the pastries

	Oil type 1		oil type 2		Mann- Whitney test result	
	mean ±SD	**mean rank**	**mean ±SD**	**mean rank**	**p**	**z**
TPC Value	12.917 ±1.752	5.67	13.300 ±1.737	6.4	0.715	-0.365
Acid Value	0.202± 0.056	5.67	0.210± 0.055	6.4	0.715	-0.367
Peroxide Value	17.105 ±1.211	5.67	17.434 ±0.980	6.4	0.715	-0.065

Table 4: Comparing the studied indices according to the type of cooking oil in the pastries

	Oil type 1		oil type 2		Mann- Whitney test result	
	mean ±SD	**mean rank**	**mean ±SD**	**mean rank**	**p**	**z**
TPC Value	11.375± 0.350	2.5	14.070 ±1.220	8	0.008	-2.646
Acid Value	0.160± 0.0082	2.63	0.231 ±1.050	7.93	0.01	-2.563
Peroxide Value	16.072± 0.102	2.5	17.930 ±0.667	8	0.008	-2.646

As a result, the non-parametric statistics was used for analysis. The Spearman's non-parametric correlation coefficient was applied to find the correlation between temperatures and cooking time with each one of the studied index (Table 5).

Table 5: Table 5: Results of correlation analysis of three evaluated index

		TPC Value	Acid Value	Peroxide Value
Temperature	Correlation	0.788	0.927	0.943
	Probability	0.004	<0.001	<0.001
Time	Correlation	0.881	0.856	0.822
	Probability	<0.001	<0.001	<0.001

During the measurements conducted on the TPC index for crude oil samples before using and both types of oils, after several random samplings, it became clear that all crude oils types I and II had 8 and 8.5 TPC percentage. Besides, the TPC percentage and acid values, generated after cooking oil in all samplings even on the last day of the week (the third stage of samplings with the maximum amount of cooked sweets) did not exceed from 15.5 and 0.3, respectively. In accordance with Standard 4152 of Standards Institute of Iran, the TPC and acidity values of the waste oil were x>25 and x>2, respectively. However, the obtained amounts were lower than the standard which could be related to continuous and daily oil changing, adding fresh oil while cooking, low demand and daily production of these sweets in all pastries, causing lower amount and frequency of sweet dough entrance into the cooking oil, leading to shorter heating time in daily consumed oil, and therefore less impact of materials and oxidation agents on the oil. Moreover, in accordance with the standard, it is recommended that the temperature of frying process must not exceed from 180°C, but in most pastries, the temperatures were very close to the maximum limit. On the other hand, since in most cases, the oven with concentrated and small flames, and large and flat containers were used for cooking, these factors resulted in non-steady and more heat transfers to the middle area of the oil container; hence, the sweet dough in the middle area of the container was fried faster than other areas. In addition, for the confectioners wait until all the sweets in the container are fried completely, the oil and dough in the middle area of the container endure higher temperatures and severe burns and oxidation. During the measurements conducted on the AV index for crude oil samples before using and both oil types, after several random samplings, it became clear that all crude oils type I and type II had an acidity percentage of x≤0.07 and peroxide value of x≤1.9, respectively, which are consistent with Standard 4152 defined by Standards Institute of Iran [8]. The results of determining the quality of two formulated oil samples showed that the TPC, acidity and peroxide amounts were enhanced linearly in oils by increasing temperature, time, volume of frying materials, release of heavy metals from the cooking container and oxidizing agents in the frying and heating process, which are consistent with our results. The amount of this quantity was different due to various factors (the amount of fresh oil addition during frying, frying time and temperature, fried material volume, heating method, the initial quality of oil, fryer container type, type and concentration of antioxidants as well as oxygen value [11].

High thermal temperatures not only cause the analysis of fats, sugars and proteins of foodstuff dough, but also combine the derivatives synthesized by them with each other and synthesize too dangerous oxidizing agents such as acrylamide [12].

According to the obtained results about the effect of temperature and time on the hydro-peroxide synthesis and analysis in canola and soybean oils, it was defined that in peroxide synthesis and analysis speed as primary and unstable products of oxidation, the temperature and time were two important external factors and the composition of oils' fatty acids was identified as an important internal factor. It was found that at 70-80°C, the peroxide synthesis increased over time, and through increasing temperature and synthesizing speed, the rate of peroxide analysis was increased, so that the temporary peroxide analysis as well as the temporary and permanent analysis were more at 100-120°C and 140°C, respectively. By rising the temperature, the slow period of peroxide synthesis was also reduced [13].

Conclusion

Investigating the values obtained from the TPC and acidity of this study according to the Standard 4152 of Iran, it was determined that all values were below the standard limit, but they had more peroxide proportions. Hence, in the overall comparison of the values of these three index with those of other studies, these oils had higher health quality because of mentioned reasons; thus, peroxide value was not an appropriate index in assessing this kind of oils. Based on the results of the current study and other researches, it can be concluded that the synthesized peroxide is more in the unsaturated liquid vegetable frying oils than the solid saturated frying oils, and the former oils reach to smoke point faster. Although the saturated solid crude oils have higher peroxide values compared to unsaturated liquid crude oils before using and have higher risk of cardiovascular disease, the former oils do not react with oxygen easily so that the less peroxide synthesizing, the less dangerous free radicals are synthesized; consequently, they have much less carcinogenic power. Though the permitted limit of the initial peroxide for non-frying liquid vegetable oils (cooking and salad) is considered higher compared with the liquid frying oil, the synthesized peroxide in them after cooking is less because they have smaller AV (free fatty acids). This factor makes them to have a greater oxidative resistance against the heat and reach the smoke point at higher temperatures. The free fatty acids of unsaturated liquid vegetable frying oils than saturated solid oils are minimal, so they have high thermal resistance. In an overview, how much unsaturation rate, the polyunsaturated fatty acids (linoleic acid), frying times, volume of fried materials, release of heavy metals from the cooking container, presence of oxygen and water molecules (oxidizing agents), thermal degree, heating time, initial values of the TPC and free fatty acids in oils are higher, and the initial values of oleic acid and TBHQ antioxidant are lower lead to more peroxide synthesizing and the amounts of unsaturated fatty acids and iodine index are reduced in the oil.

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