

Evaluation of the Oxidative Stability of Frying Oil, Mixed with Purslane and Corn Seed Oil

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Abstract

One of the procedures for the stabilizing of frying oil, in order to preserve the synthetic antioxidants, is adding oils containing antioxidant and high oxidative stability compounds. The objective of this research was the quality evaluation of three frying oils mixture (Sunflower, Ladan and Iran) due to the addition of purslane and corn seed oils and frying over 12 h at 170 ± 2 °C for this reason, the mixed frying oil, containing corn and purslane seed oil in the proportion of (70:15:15 w/w) called mixture 1, mixed frying oil containing corn and purslane seed oil in the proportion of (75:15:10 w/w) called mixture 2, corn seed oil, purslane seed oil and mixture of three frying oils in terms of qualitative indexes (peroxide, *p*-anisidine, totox, total polar compounds, oxidative stability and conjugate-DNs), were evaluated. At first the antioxidant activity rate of purslane seed oil was assessed and the value of 52.9 ± 0.19 percent was measured. The comparison of two types of frying oil mixtures indicated that the values of peroxide, *p*-anisidine, totox and conjugate-DNs, indicators of mixture 1 and 2 were (25.83 meq/kg, 80.63, 132.29 and $15.01 \mu\text{mol/g}$) and (28.13 meq/kg, 85.73, 141.99 and $17.17 \mu\text{mol/g}$) respectively which had significant difference with frying and other oils ($P<0.05$). The higher ratio of purslane oil in the frying oil, mixture 1, increased its oxidative stability in contrast to oil mixture 2 and purslane preserved it against early degradation at high temperature.

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Keywords

Corn Seed Oil
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Introduction

Purslane (*Portulaca oleracea*) is the 8th abundant plant in the world (Coquillat, 1951). According to the report of the world health organization (WHO, 1990) it mainly contains unsaturated fatty acids and it is also considered as a botanical source, full of omega-3 fatty acid (Alam *et al.*, 2014; Dweck, 2001). Due to the abundant quantity of

unsaturated fatty acids, purslane is utilized to decrease cholesterol, prevent the growth of cancerous cells and treat psychological depression. Recently it has been recognized that purslane seed oil is a suitable source for omega-3 fatty acids, β -carotene, vitamin, essential amino acids, alkaloids, coumarin, flavonoids and polysaccharides (de Lorgeril *et al.*, 2001; Keyvani &

Bolandi, 2015; Mazza *et al.*, 2007). According to the report of Delfan-Hosseini *et al.* (2017), this oil has indexes of peroxide (meq oxygen/kg), iodine (Iodine g/100 g), acidic (Potassium g/oil g), saponification (Potassium g/g), refractive index and extraction efficiency (%) in values of 0.8, 135.9, 1.93, 181.05, 1.04805 and 59.37 respectively. Phenolic compounds (Gallic acid mg/oil k), antioxidant activity (%) and oxidative stability (h) are 66.51, 53.9 and 9.67 respectively. Furthermore, the values of saturated and unsaturated fatty acid are 21.95 and 78.39 respectively and its mono and poly unsaturated fatty acid are 21.08 and 57.31% respectively (Ren *et al.*, 2015; Uquiche *et al.*, 2008; Yoshida *et al.*, 2005).

The observation of Fangfang *et al.* (2013) indicated that purslane seed oil contains α -linolenic acid 40.25%, linoleic acid 29.43% and oleic acid 15.61%. They also reported that saturated fatty acids included 13.94% of total oil content while mono unsaturated fatty acid and poly unsaturated fatty acid were 16.28 and 69.68%. Furthermore the content of linolenic acid (40.2570%) in purslane seed oil in comparison with camellia seed (0.27%) is too much (Houhoula *et al.*, 2003; Yang *et al.*, 2013). The content of linoleic acid (29.43%) in comparison with to other vegetable oils such as flax seed (15.45%), camellia seed (7.26%), grape seed (11.4%) and olive oil (0.56%), is too much (Fangfang *et al.*, 2013). Linolenic and linoleic acids are omega-3 and omega-6 fatty acids respectively and both are essential fatty acids which have an important role in growth and development of human as well as preserving against various diseases (Dunbar *et al.*, 2014). Furthermore the oils full of omega-3 are very useful for human health (Andrade *et al.*, 2009). It is expected that purslane oil due to high quantity of omega-3 fatty acid, would influence on antioxidant and anticancer functions. Vegetable oils are

rich resources for volatile Terpenoid and Phenolic compounds (Ebrahimzadeh *et al.*, 2009). Corn is an herbal plant that among agricultural crops in terms of cultivated areas has third rank in the world. Among all vegetable oils, corn oil has tenth rank in terms of annual production and shares 2% of produced oil throughout the world.

According to Codex standard (1981), the iodine index of corn oil is 103-128, and its saponification number is 187-195. Five major fatty acids of corn oil in terms of quantity are respectively, linoleic, oleic, palmitic, stearic and linolenic. Despite of higher amount of unsaturated fatty acids, corn oil is very stable, and therefore it is suitable for different consumptions such as frying. The results obtained from evaluation of corn oil fatty acids distribution, indicated that 98% position 2 (β -position) in corn oil triglycerides, are unsaturated and only 2% are saturated (Malek, 2010). During frying, oils hydrolyzed and converted into free fatty acids, mono and diglycerides and by continuous application of oil concentrated in it. Furthermore, oxidized oil, hydroperoxide, conjugated dienoic acids, epoxides, hydroxide and ketones are formed. Increase in the quantity of volatile compounds results in an increase in the index of peroxide, and free fatty acids in oil (Kress-Rogers *et al.*, 1990). Hydroperoxides are first product of oil oxidization and they are also the most important flavor precursors, but their importance depends upon the relative stability and construction of compounds that are produced from them under various situation. In the primary stages of oxidation process, the quantity of these compounds are low, but later in the dispersion stage, the quantity of hydroperoxides intensively increased. In this stage the determination of peroxide number is a suitable index for recognition of oil oxidation condition. In

the final oxidation stage, hydroperoxides were disintegrated to secondary oxidation products and their quantity reduced and even could become zero (Chatzilazarou *et al.*, 2006). Totally, the peroxide number is not capable of indicating the real oil destruction during frying and it is not recommended as an index for this objective. Anisidine index is used in order to recognize secondary compounds including low volatile aldehydes in particular 2,4-dienal and 2-alkanols (Tooranigholsalar *et al.*, 2011). Hydroperoxides are instable chemical compounds and do not always have direct relation to oxidation during frying. Furthermore, the quantity of *p*-anisidine, which depends on the product resulted from secondary oxidation, is strictly an experimental evaluation method. Therefore, relying only upon the results of these tests is not adequate and consequently several methods together must be applied in order to find out the critical signs of frying oil destruction to replace or throw it out. Totox index is a proper indicator to the description of oils oxidation since it originated from combination of aldehydes and peroxides (Casal *et al.*, 2010). Application of natural materials for prevention of frying oils destruction was recommended, which includes the addition of materials that are converted into non-saponification products, and resulted from olive, corn and wheat sprout. These materials can protect the frying oil against oxidation destruction during heating. The objective of this research is enhancing the stability and nutritional values of frying oil by

mixing them with purslane and corn seed oils.

Material and methods

Devices and materials used in this research

Laboratory grinder house fryer (Euro max, Switzerland), chromatography gas, gas-liquid (Hewlett-pockard, model HP-5890, France), frying oil (Sunflower and Corn, Ladan and Iran) and purslane seed from Yazd. All chemical materials and solutions purchased from Germany.

Preparation of the sample and oil extraction

Purslane seeds collected from different regions of Yazd province and then dried out in room temperature. The seeds were packed in plastic bags and kept in the refrigerator until extraction process. Purslane oil extraction carried out by mechanical pressing method. The hydraulic cold pressing machine pressed the samples, dried by oven (105 °C) and ground (Moulinex, France) to obtain particles of 0.8±0.15 mm, at 10 MPa pressure for 10 min according to the method of Uquiche *et al.* (2008). Then the extracted oil was filtered and kept at -18 °C to perform experiments and operations (The samples were prepared according to table 1). The moisture content of utilized purslane seeds were 6% on wet basis. The efficiency value based on the seed dry weight and calculated by the Eq. (1) was 18.2%.

(1)

$$\text{Efficiency Extraction (\%)} = (\text{Extracted oil weight} / \text{Dry weight of oil seed}) \times 100$$

Table 1. Treatments of experiment

Treatment	Compounds
1	Purslane seed oil
2	Corn oil
3	Frying oil (Sunflower, Ladan, Iran)
4	70% Frying oil + 15% Corn + 15% Purslane
5	75% Frying oil + 15% Corn + 10% Purslane

The preparation of oils mixture

In order to conduct efficiency evaluation of the mixed purslane and corn oils, mixed with frying oils (Sunflower, Ladan, Iran), two types of the mixture were prepared from 3 kinds of frying oils, with the ratio of (w/w), which include, corn (Ladan, Iran) and purslane. Mixture 1 and 2 were in the proportion of (70:15:15) and (75:15:10) respectively. All the proportions for oils combinations obtained from test, error and normalization of proportions. The weight of all oils, in order to perform process and pour in to the fryer container, were considered 1 kg. 12 h prior to the preparation of the mixtures, all above-mentioned oils were taken into the laboratory and after mixing them, the mixtures were prepared.

Determination of the frequency distribution of fatty acids

Based on the AOCS (1989) method, first the methyl ester of fatty acids was prepared.

The determination of the fatty acids compounds done by gas chromatography with capillary glass column (column length 30 m, inner diameter of column 0.22 mm), and with flame photometer. To carry out this operation, about 0.3 g oil was dissolved at 7 mm *n*-hexane and 2 mm potassium hydroxide solution in methanol, normality 2, was added and properly mixed at 50 °C. 0.4 mm at 150 °C was injected with split/splitless. After 10 min the initial temperature of the oven was 190 °C and at the rate of 4 °C per min its temperature was increased to 210 °C and then kept steady for 5 min at this temperature. Then at the rate of 1 °C per min increased up to 215 °C and was steadily kept 18 min at this temperature. The gas current containing nitrogen, was regulated at 1 mL per min. Eventually the obtained curve level from the device compared to the standard curve and the type and amount of each fatty acid in

the structure of the oil was determined in terms of percentage over 95 min.

Frying operation

The frying operation was carried out in the house fryer (Euro max, Switzerland). The precise regulation of the temperature done via situating a thermal probe inside of the fryer container as well as controlling of import electrical current. The heating operation performed continuously at 170 °C for 12 h. Thermal stability evaluation of the discussed oils and their reactions assessment, carried out at time intervals of 0, 1, 2, 4, 6, 8, 10 and 12 h. From the oil in the container of the fryer some samples were taken in order to perform the chemical tests (peroxide, anisidine, conjugate-DN and totox). For every sample, 15 mL oil taken from the fryer container and put into the glass tubes with screw cap and after cooling down and coding the samples, they were transferred into a freezer for the future tests.

Measuring antioxidant activities

The antioxidant activity of samples investigated via 2,2 diphenyl-1-picrylhydrazyl (DPPH) in order to perform this test, 0.1 mL purslane oil added into 3.9 mL DPPH solution of 0.1 mmol in methanol and kept at room temperature for about 60 min in the dark. The samples absorbance recorded at the wavelength of 517 nm. For control the DPPH solution, containing distilled water was used (Firestone, 1993). The percentage of free radicals were calculated according to the Eq. (2):

$$\text{DPPH (\%)} = \frac{[(\text{Control absorbance} - \text{Sample absorbance}) / \text{Control absorbance}] \times 100}{(2)}$$

Determination of oxidative stability time

For determination of oil stability against oxidation the rancimat machine (Metrohm 743, Switzerland) was used. In brief 2.5 g of oil sample were put

into the reaction chamber and heated up to 110 °C. The volatile compounds which had been released into the distilled water during oxidation reaction, increased the electrical conductivity of water. The inlet air current velocity regulated at 20 L/h. After sometimes the oil samples oxidized entirely and the diagram slope drawn by the machine was suddenly increasing and the mentioned time was recorded by machine. In this case the machine automatically closed the air current and presented the final result. The diagrams, in terms of time (h) and electrical conductivity (μS), were separately drawn for each air channel (Houhoula *et al.*, 2003).

Measuring total polar compounds (TPC)

The measurement of the total polar compounds was carried out via the column chromatography. That was silicagel dried out at 160 °C, over 24 h and in the proportion of (0.5 silicagel: 9.5 water) mixed with water and then transferred into the determined column. The applied solvent system was isohexane and diisopropyl in the proportion of 85 isohexane and 15 diisopropyl. The oil sample mixed with toluene in the ratio of 1 to 9 and then 1 mL of it was transferred into the column. After termination of chromatography operation, the bottom of column was washed up with toluene and by the method of gravimetric the quantity of polar compounds were measured (AOCS, 1989).

Measuring peroxide index

Considering the quantity of oil peroxide, 0.5 up to 5 g of each sample weighted and mixed with 30 mL acetic acid chloroform in the ratio of 2 to 3. Then 0.5 mL of the saturated potassium iodide solution was added into the solution. After passing 1 min it was titrated with sodium thiosulfate, normality 0.1, in the presence of Starch

glue and, the value of peroxide number was calculated with Eq. (3) (AOAC, 2005).

$$PV = V \times N \times \frac{1000}{W} \quad (3)$$

PV: the amount of peroxide (meq/kg)

V: sodium thiosulfate volume (mL)

N: normality of, sodium thiosulfate

W: sample weight

Measuring *p*-anisidine

The oil sample, depending on the oxidation intensity, was weighed 0.01 to 0.5 g. The selected sample (2.5 g), was weighed inside of the 25 mL volumetric flask and then it was diluted with glacial acetic acid. Then this solution was poured into each of two tubes and mixed properly and then to form the complex (*p*-anisidine, aldehyde and appearance of yellow color), 10 min was given. Eventually the absorbance at 350 nm of sample in comparison with the control (the absorbance difference with the oil sample without solvent) was measured and the index of *p*-anisidine was calculated with the following equation (Shahidi & Wanasundara, 2002).

$$p\text{-AV} = 25(1/2A_s - A_b)/W \quad (4)$$

As: sample absorbance

Ab: control absorbance

W: sample weight

Measuring totox index

Totox index is exclusively used to measure the oxidative stability of refined oils. So that by applying two indexes of peroxide and *p*-anisidine in the Eq. (5), this index can be calculated and evaluated (Foglia *et al.*, 1993).

$$TV = 2PV + p\text{-AV} \quad (5)$$

TV: totox index value

PY: peroxide index value

AV: *p*-anisidine index

Measuring conjugate-DN

The oil sample was diluted in the ratio

of 1:60 with isooctane (w/v), then the absorbance difference of diluted sample was measured in comparison with the control (isooctane without oil) at the wavelength of 233 nm and the quantity of conjugate-DN compounds were calculated with Eq. (6) (Ronald, 2001).

$$C_{cd} = A_{233} / (\Sigma \times l) \quad (6)$$

C_{cd} : conjugate-DN concentration, mmol/L, A: absorbance difference of the sample and control, Σ : constant coefficient (linoleic acid hydroperoxide), the value is 2.525×10^4 and L: Measuring of cuvette length in cm (1 cm). Compounds were calculated with Eq. (7) (Ronald, 2001).

$$CD \text{ value} = (C_{cd} \times (2.5 \times 10^4)) \div w \quad (7)$$

C_{cd} : concentration mmol/mL, W: Sample weight in g and 2.5×10^4 : since the length of applied cuvettes are 1 cm, this factor equals to isooctane from μmol to mmol, exist at 25 mL of the sample volume.

Statistical analysis

All the tests in this experiment were

carried out at three replications. The analysis of obtained data done in the completely randomized design and the comparison of means based on the compare means Duncan test performed by SPSS software (Version 16.0) at the 5% level of probability and the diagrams were drawn by Microsoft Excel software (Version 2013).

Result and discussion

Identifying and determining the frequency distribution of fatty acids, producing oils

The combination of fatty acids in every oil, determined the attributes and application of that oil (Tooranigholsalar *et al.*, 2011). According to Table (2), considering the higher content of unsaturated fatty acids in purslane seed oil ($79.69 \pm 0.22\%$), lower thermal stability was expected for this oil, but based on the measured tests and slower disintegration trend of oil mixture 1, which contains higher amount of purslane oil, was proved the reverse of this reality. The reason is probably the presence of antioxidant compounds in purslane seed oil (Ahn *et al.*, 2012).

Table 2. Recognition and determination of fatty acids frequency, produced by different oils (%)

Fatty acid	Purslane	Corn	Frying oil	Mixture 1	Mixture 2
C12:0	-	-	0.27±0.05	0.19±0.01	0.2±0.01
C14:0	0.04±0.0	0.63±0.02	0.5±0.05	0.45±0.01	0.48±0.03
C16:0	16.86±0.04	13.23±0.01	33.93±0.14	28.27±0.07	29.72±0.07
C16:1	0.14±0.04	0.42±0.01	0.3±0.01	0.29±0.01	0.3±0.01
C17:0	0.12±0.0	-	-	0.02±0.03	0.01±0.0
C17:1	0.04±0.0	-	-	0.01±0.0	0.004±0.0
C18:0	4.12±0.02	0.79±0.03	4.05±0.04	3.57±0.02	3.57±0.01
C18:1	21.03±0.02	30.06±0.09	32.13±0.12	30.16±0.13	30.71±0.13
C18:2	35.29±0.02	54.23±0.13	26.38±0.14	31.89±0.09	31.45±0.09
C18:3	23.19±0.02	0.65±0.01	2.44±0.11	5.28±0.05	4.25±0.02
C20:0	0.33±0.0	-	-	0.05±0.01	0.03±0.01
C22:0	0.36±0.0	-	-	0.06±0.01	0.04±0.0
Saturated fatty acid	21.83±0.05	14.65±0.02	38.75±0.21	32.58±0.13	34.05±0.14
Unsaturated fatty acid	79.69±0.22	30.47±0.1	32.43±0.11	67.63±0.05	66.7±0.1
Polyunsaturated fatty acid	58.48 ± 0.03	54.88±0.12	28.82±0.25	37.17±0.09	35.7±0.12
Mono unsaturated fatty acid	21.21±0.25	85.35±0.02	61.25±0.21	30.46±0.07	31.014±0.06

* The minor values represented as dash.

Purslane seed oil in comparison to corn oil contains higher amount of saturated fatty acids (21.83 ± 0.05 and $14.65 \pm 0.02\%$ respectively), but also contains higher percentage of unsaturated fatty acid, therefore it can be said with adding frying oil, containing maximum amount of saturated fatty acids ($38.75 \pm 0.21\%$) and minimum amount of poly unsaturated fatty acids ($32.43 \pm 0.11\%$), to corn and purslane oil, containing minimum amount of saturated fatty acids which has minimum thermal stability, it is possible to increase the thermal stability of the final oil mixture.

Determining total antioxidant activity, oxidative stability and polar compounds of purslane seed oil

Antioxidant characteristics of purslane seed oil has a great effect on its oxidative stability. There are various antioxidant compounds such as phenolic compounds, α -Tocopherol, β -carotene, ascorbic acid, glutathione in purslane seed oil (Keyvani & Bolandi, 2015; Mazza *et al.*, 2007).

In this research the according to Table (3), the antioxidant activity of purslane seed oil was $52.9 \pm 0.19\%$ which indicates the abundant presence of percentages of free radical absorbing

compounds in this oil. Antioxidants can prevent the chain reactions by absorbing free radicals and therefore inhibit lipid oxidation (Samaram *et al.*, 2015). There is direct relationship between the content of phenolic compounds and antioxidant activity of oils (Delfan-Hosseini *et al.*, 2017). The most important factor to identify the quality of oil is the measurement of its oxidative stability which in purslane seed oil is 4.51 ± 0.14 h. The oxidative stability also has a direct relationship with total polar compounds and antioxidant activity. Samaram *et al.* (2015), extracted more polar compounds in comparison with this research with treatment of purslane seed oil in microwave, which this phenomenon can be attributed to the partial destruction of cell membrane caused by microwave and the optimization of phenolic compounds release (Simopoulos *et al.*, 1992). Also Yang *et al.* (2013) found out a direct relationship between induction period and total polar compounds of canola oil with different moisture content. The lower oxidative stability of purslane seed oil can be attributed to higher percentage of mono and poly unsaturated fatty acids in the structure of this oil.

Table 3. Antioxidant activity, oxidative stability and polar compounds in total purslane seed oil

Oil type	Studied indexes		
	Antioxidant activity (%)	Total polar compounds (%)	Oxidative stability (h)
Purslane seed oil	52.9 ± 0.19	64.13 ± 4.94	4.51 ± 0.14

Table data reported in mean \pm standard deviation

Evaluating total polar compounds of different oils during frying

In the Figure (1), the quantity of polar compound production during the thermal process has been illustrated. The total amount of polar compounds of studied oils has linearly increased over 12 h of frying operation. The oils oxidation behavior during the thermal process has been illustrated by using the

oils linear equation and the correlation coefficient between heating time and the polar compounds growth rate. 4 h after thermal process, the production rate of these compounds in corn oil has reached 25% that this range (25%) is as oil unusable limit for frying (Brand-Williams *et al.*, 1995). The polar compounds production of oil mixture number 1 did not catch critical

point 8 h after thermal process and still it was useable. The total polar compounds have a direct relationship with oxidative stability and antioxidant activity. The total amount of polar compounds increased during frying process and heating, but this quantity has differently been reported due to the presence of various factors such as the concentration of antioxidants, which in this experiment we encountered with higher antioxidant activity (51%) which

certainly resulted from the presence of its tocopherols and polyphenolic compounds. This effect is more obvious in the oil mixture number 1. As it was said, the amount of various polar compounds increased accordingly with increase in the frying duration (figure 1), and the quantity of compounds resulted from hydrolysis which increases during frying, but decreases during heating process without water (Houhoula *et al.*, 2003).

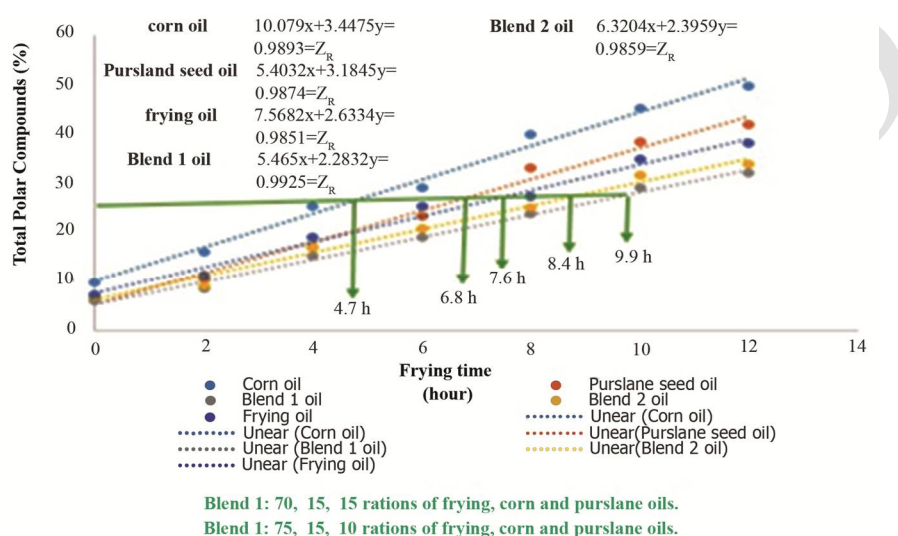


Figure 1. Variation of total polar compounds of different oils during frying at $170 \pm 2^\circ\text{C}$

Corn oil: $10.079x + 3.4475y = 0.9893 = Z_R$; Purslane seed oil: $5.4032x + 3.1845y = 0.9874 = Z_R$; Frying oil: $7.5682x + 2.6334y = 0.9851 = Z_R$; Oil mixture-1: $5.465x + 2.2832y = 0.9925 = Z_R$; Oil mixture-2: $6.3204x + 2.3959y = 0.9859 = Z_R$

Evaluation of oxidative stability of different oils prior to thermal process

The oxidative stability results obtained from rancimat machine has been illustrated in Table (4). Purslane seed oil appeared lower thermal stability in contrast to corn oil, however this difference was not significant, but its reason could be attributed to the presence of fatty acid 18:3. Although purslane oil saturated fatty acid was more than corn oil but the effect of 18:3 fatty acid presence was much more and increased the oxidative stability of corn oil in comparison with purslane oil. The previous researches have demonstrated

that unsaturated fatty acids in comparison with saturated fatty acids are more sensitive to thermal oxidation and oxidase quicker and can produce higher level of polar compounds during the process (Warner & Mounts, 1993). The oil mixture 1 had higher oxidative stability in spite of having more poly unsaturated fatty acids and lower saturated fatty acids than frying oil, that, the reason of which can be attributed to higher amount of purslane oil and the position of fatty acids in the triglyceride structure of both oils.

Table 4. The oxidative stability of different oils prior to the thermal process

Oil type	Studied index
	Oxidative stability (h)
Purslane seed oil	4.51± 0.14 ^a
Corn oil	4.57± 0.08 ^a
Oil mixture 1	6.62± 0.12 ^b
Oil mixture 2	6.51± 0.59 ^b
Frying oil	5.59 ± 0.12 ^c

Table data reported in mean±standard deviation.

Oil mixtures 1 and 2 contain frying oils of corn and purslane in the ratio of (70:15:15) and (75:15:10) respectively.

Changes of peroxide and *p*-anisidine indexes of various oils during frying

2 h after frying, considering the slope of peroxide index diagram (figure 2), the increase rate of peroxide index, decreased, and 6 h after frying this index decreased, since in the eventual stages of oxidation, hydroperoxides disintegrated to the secondary oxidation products (Chatzilazarou *et al.*, 2006). Peroxides indexes in fats and oils during their spontaneous oxidation, generally indicates the prime oxidation rate of fats and oils.

p-Anisidine evaluation method in comparison with peroxide is more acceptable, since it measures the oxidation secondary products which are stable during thermal process (Ghazali *et al.*, 2009). Among the methods that confirm disintegration of oil, many of them are not suitable for frying. For instance in order to measure peroxide index which is the characteristics of oil hydroperoxide and oxidation content, is not an appropriate index in the frying process, since at frying temperatures hydroperoxide is unstable. Furthermore hydroperoxide can increase after taking oil out of fryer, but it must be analyzed prior to complete cooling (Blumenthal, 1991). Tooranigholsalar *et al.* (2011) expressed that disintegration tendency rate of this compound in comparison with its production rate is much lower. In the first frying hours the values of this index in the oil mixtures 1 and 2 were more than purslane seed oil which is probably due to oxidative stability and antioxidant compounds of purslane oil,

but 6 h after frying this process converted because of more stability of frying oil at higher temperatures. The peroxide index of purslane seed oil reached 40.5±0.65 meq/kg 6 h after frying at the temperature of 170±2 °C, and it changed the orientation in the time space of 6 to 8 h and reached 38.24±0.45 meq/kg. The reaction pattern of purslane oil and oil mixture 1 were different from others, since the range of orientation change in other oils were 4 to 6 h but in these oils the pattern varied and became 6 to 8 h. The results indicate that in the initial frying hours, *p*-anisidine index increases but 5 to 6 h after frying with peroxide disintegration, *p*-anisidine index suddenly and remarkably increases. The maximum registered value of *p*-anisidine was at the end of frying period which was 118.5 mol/g μ and 94.02±0.97 mol/g μ for corn and purslane oils respectively, so that purslane seed oil in comparison with corn oil revealed better thermal stability. Choe & Min (2006) found out that higher amount of linoleic acid causes plenty of changes in the amount of *p*-anisidine during frying period. They also observed with increased frying time, the value of *p*-anisidine index increased, so that the amount of fatty acid (18:2) was very effective in the promotion of this index. The results indicated that prior to the disintegration of hydroperoxides, the variation of these two factors were closely similar to each other and their correlation coefficient was 0.998 in purslane seed oil, and in the

corn oil, oil mixture 1 and 2, and frying oil was calculated 0.976, 0.989, 0.98 and 0.979 respectively, this correlation was significant at the level of 0.05 meq/kg. The increase pattern of *p*-anisidine index for oil mixture 1 was partially linear and ascending 4 h after frying, but other oils did not follow such a pattern. The *p*-anisidine test is a reliable test in order to assess of oxidation secondary products, since it reveals proper instability during thermal process (Al-Kahtani, 1991). Diminution of *p*-anisidine vale in the early frying hours, can be attributed to the escape of aldehydes with higher volatility in the initiation of thermal process. *p*-Anisidine indicator prior to

the disintegration of hydroperoxide anti aldehyde, reacts with non-volatile section of fatty acid. This test has higher sensibility to unsaturated aldehydes in particular 2,4-dienals, but it cannot measure the chiton products of secondary oxidation stage. The oil that has *p*-anisidine index lower than 10, has appropriate quality (Naghshineh *et al.*, 2009). Russell (1983) reported that *p*-anisidine index is an applicable index for the evaluation of oils which have higher quantity of poly unsaturated fatty acids and by descending peroxide index production, the index of *p*-anisidine ascends suddenly and remarkably.

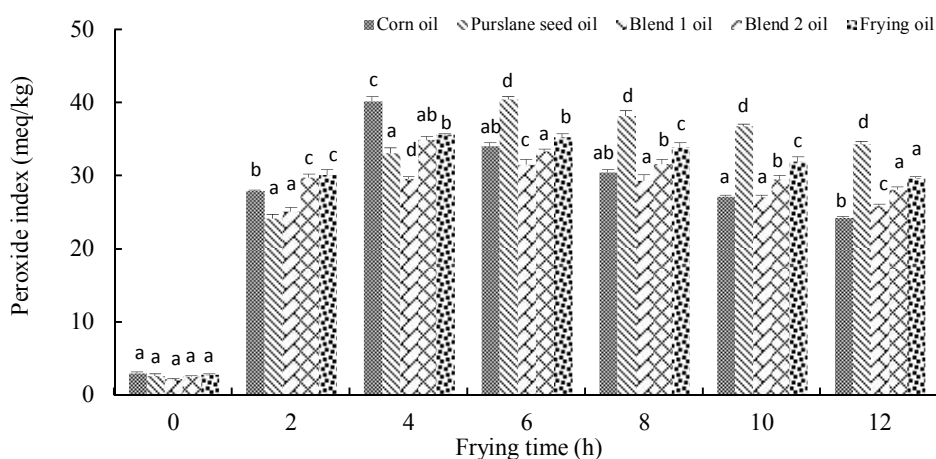


Figure 2. The variation of peroxide values in the different oils during frying at the temperature of 170 ± 2 °C

The changes of different oils totox index during frying

Totox index expresses the oxidative deterioration of oils, since it is originated from the combination of aldehydes and peroxides. Hydroxides are unstable at higher temperatures which are encountered during frying. The disintegration of one peroxide results in the formation of 2 aldehydes, since 2 oxygen molecules participate in the construction of peroxides while 1 oxygen molecule participates in the construction of aldehydes (Patterson, 1989). Abdulkarim *et al.* (2007) reported that at 185 °C after 12 h, the

totox index of soybean oil reached 142.37 which was higher in compare to oil mixture 1 and 2. According Figure (3), totox values increased considerably ($P<0.05$) by increasing frying temperature in all oils. The results demonstrate that the totox index of various oils have different processes, hence peroxide and *p*-anisidine indexes of these oils are different. 12 h after thermal process, the totox index of purslane seed oil reached 162.62 ± 1.02 and corn oil 166.94 ± 0.98 which indicated the thermal stability of purslane oil was better than corn oil.

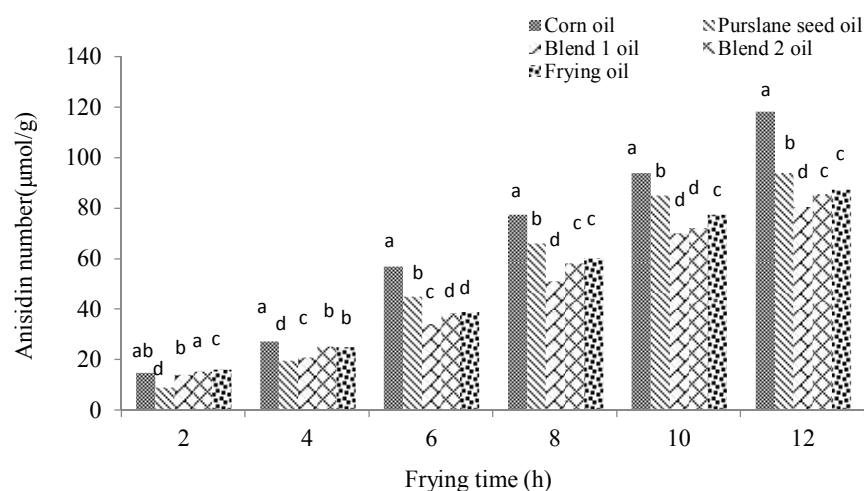


Figure 3. Variation of *p*-anisidine values in different oils during frying at temperature of 170 ± 2 °C

According Figure (4), the totox index of oil mixture 1 with a mean value of 132.29 ± 0.86 was in better condition in comparison with other oils at the end of

frying process. The totox index of frying oil with a mean value of 146.83 ± 1.18 was further than the totox index of mixtures 1 and 2.

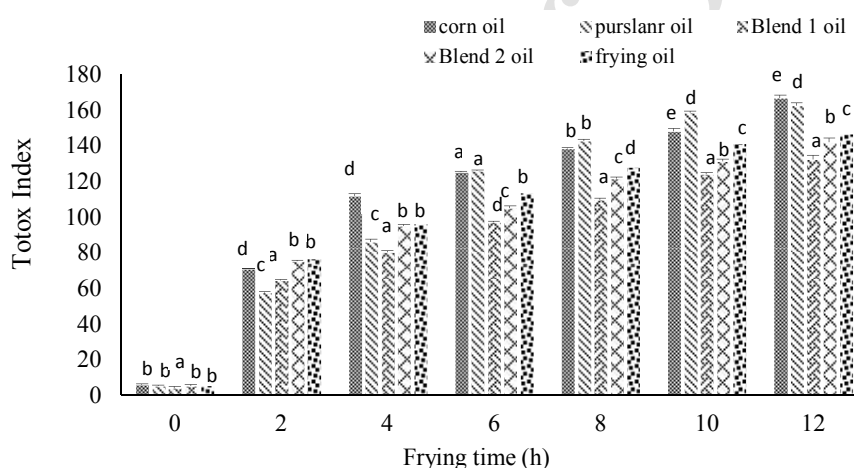


Figure 4. The variation of totox index values in different oils during frying at the temperature of 170 ± 2 °C

Variation of different oils conjugate-DN during frying

Conjugate-DN acids were produced due to the movement of dual bonds during the oxidation of poly unsaturated fatty acids. Along with the increase of absorbtion by the spectrophotometer, the value of conjugate-DN increased which was proportionate to the rate of oxygen absorption by oil during frying and formation of hydroperoxides in the early stages of oxidation (Farmer, 1946). Tooranigholsalar *et al.* (2011) reported that conjugate-DN value of mixed oil (soybean, palm olein and corn) which

had higher thermal and oxidative stability, was 18.52, 8 h after frying at 180 °C, but the values of this index in this research 8 h after frying were lower for all experimental oils except the corn oil. The values of oil conjugate-DN (mmol/mL) had considerable increase in the early hours of frying, but this trend was stable and slow in the final frying hours. The value of this index in the oil mixture 2 reached 15.01, 12 h after frying process that revealed very suitable stability and the reason is that the total amount of saturated fatty acids and mono unsaturated fatty acids was

65.064% which participated very little in the reaction. For the formation of conjugate-DN there must be at least two dual bonds in the oil structure, that due to the higher percentage of purslane oil poly unsaturated fatty acids, it is possible to prevent from the increase of conjugate-DN by increasing the proportion of frying oils (Schulte, 2004). Another effective factor is the presence of phenolic and free radical absorber compounds in purslane oil which prevented the increase of this factor. In another research carried out by Arkanit *et al.* (2006) it is demonstrated that the conjugate-DN values increase by expanding frying time. This issue was even demonstrated by absorbed oil in French fries. They also reported that by increasing the frying temperature, the production rate of conjugate-DN ascends, so that the value of conjugate-DN reached to the maximum in the early stage of frying process at 190 °C. The produced mixture 1 conjugate-DN during the thermal process, at 180 °C and zero time as well as 12 h after heating, were 3.83 ± 0.33 and 15.01 ± 0.2 respectively that these values obtained 4.01 ± 0.12 and 19.34 ± 0.55 for the frying oil. As it has been illustrated in Figure (5), mixture 2 diagram in

comparison with oil mixture 1 situated a little upper, but the behavior of these 2 oils in the production value of this index can be considered the same, since in many points there are no significant differences between the results of these 2 oils. These results revealed the presence of purslane seed oil in the combination of oils mixture which had considerable effect in the oil oxidative stability in particular in the initial frying times. The controversial point about oil mixture 1 is its increase pattern on the production value of conjugate-DN in the range of $15 \mu\text{mol/g}$, which indicates the reduction in the intensity of production process in this range. Purslane seed oil after corn oil showed the highest amount of conjugate-DN production among other oils, so that at the end of the frying process it reached $18.59 \pm 0.39 \mu\text{mol/g}$ and this increase occurred mostly in the terminal hours of frying. The reason of this issue can be attributed to the lower thermal stability of this oil than the frying oil, that due to the presence of antioxidant phenolic compounds in this oil, this stability was more than other oils at the lower temperatures and in the early hours, and also because of higher proportion of unsaturated fatty acids to saturated ones, revealed further thermal stability at higher temperatures.

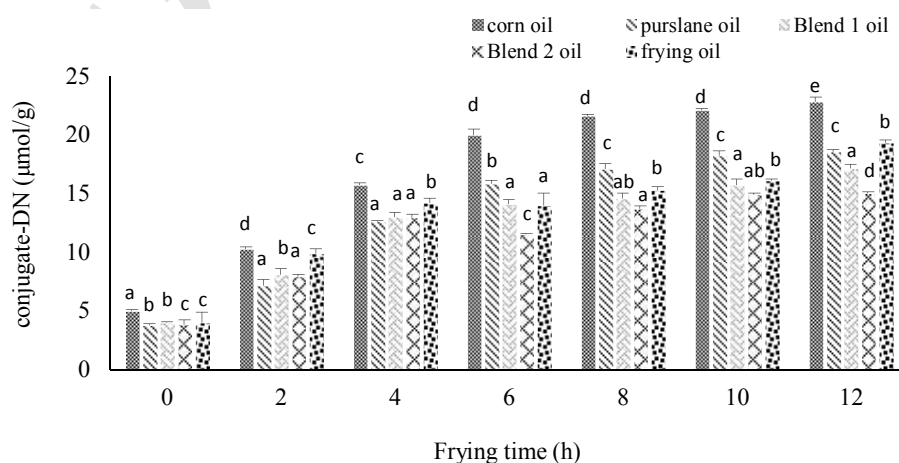


Figure 5. The variation of conjugated-DNs values in different oils during frying at the temperature of 170 ± 2 °C

Conclusion

The objective of this research was the increase of oxidative stability of the frying oils (aimed at the elimination of synthetic antioxidants and adding the oils with natural antioxidative compounds and higher oxidative stability) via mixing with purslane and corn oil. The results revealed that the production value of primary oxidative compounds such as peroxides and conjugate-DN of oil mixture 1 (frying oils, corn and purslane in the proportion of 70:15:15) descended in comparison with the frying oil. The conjugate-DN number of oil mixture 1, reached 15.01 $\mu\text{mol/g}$ whose value was better in comparison to other oils with significant difference at the level of 5%. The results demonstrated that the production of secondary oxidation

compounds such as aldehydes in the frying oils decreased by mixing them with corn and purslane oils. While corn and purslane oil alone, revealed lower oxidative stability at higher frying temperature, however, the purslane seed oil revealed higher stability in comparison with other oils due to the presence of antioxidant phenolic compounds in the early hours of frying, but because of lower oxidative stability than other oils in the final frying hours, this process was converted. Considering the above-mentioned results, it is possible to prepare the special frying oil by mixing with purslane and corn oil which reveals proper stability in comparison with the frying oil and add nutritional properties such as antioxidant phenolic compounds.

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بررسی پایداری اکسیداتیو روغن سرخ کردنی مخلوط شده با روغن دانه خرفه و روغن ذرت

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چکیده

یکی از راه‌های پایداری روغن سرخ کردنی، به منظور حذف آنتی‌اکسیدان‌های سنتزی، افزودن روغن‌های با ترکیبات ضد اکسایشی و پایداری اکسیداتیو بالا می‌باشد. هدف از این پژوهش، ارزیابی کیفی مخلوط سه نوع روغن سرخ کردنی (آفتاب‌گردان، لادن و ایران) در اثر افزودن روغن دانه خرفه و ذرت طی ۱۲ ساعت سرخ کردن در دمای 170 ± 2 سانتی‌گراد بود. برای این منظور روغن سرخ کردنی مخلوط حاوی روغن دانه ذرت و خرفه با نسبت‌های (۱۵:۱۵:۷۰ وزنی/وزنی) تحت عنوان مخلوط ۱ و روغن سرخ کردنی مخلوط حاوی روغن دانه ذرت و خرفه با نسبت‌های (۱۰:۱۵:۷۵) تحت عنوان مخلوط ۲، روغن دانه ذرت، روغن دانه خرفه و مخلوط سه روغن سرخ کردنی از لحاظ شاخص‌های کیفی (پراکسید، پارانیزیدین، توتوکس، ترکیبات قطبی کل، پایداری اکسیداتیو و دی‌ان‌های مزدوج) مورد ارزیابی قرار گرفتند. در ابتدا میزان فعالیت آنتی‌اکسیدانی روغن دانه خرفه مورد بررسی قرار گرفته و $52/9 \pm 0/19$ درصد اندازه‌گیری شد. مقایسه بین دو مخلوط روغن سرخ کردنی نشان داد مقادیر شاخص‌های پراکسید، پارانیزیدین، توتوکس و دی‌ان‌های مزدوج مخلوط ۱ و مخلوط ۲ به ترتیب (۲۵/۸۳ میلی‌اکی‌والان بر کیلوگرم، ۸۰/۶۳، ۱۳۲/۲۹ و ۱۵/۰۱ میکرومول بر گرم) و (۲۸/۱۳ میلی‌اکی‌والان بر کیلوگرم، ۸۵/۷۳، ۱۴۱/۹۹ و ۱۷/۱۷ میکرومول بر گرم) بود که تفاوت قابل معنی‌داری ($P < 0/05$) با روغن سرخ کردنی و سایر روغن‌ها داشت، نسبت بالاتر روغن خرفه در روغن سرخ کردنی مخلوط ۱، پایداری اکسیداتیو این روغن را نسبت به روغن مخلوط ۲ بالا برده و روغن دانه خرفه از تخریب زود هنگام آن در برابر حرارت ممانعت می‌کنند.

واژه‌های کلیدی: پایداری اکسیداسیونی، روغن دانه خرفه، روغن ذرت