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Original Article

Designation of a Palm-Free Frying Oil Formulation Based on Sunflower, Canola, Corn and Sesame Oils Using D-Optimal Mixture Design

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ABSTRACT

Background and Objectives: Oils used in frying should include special characteristics such as high oxidative stability, prolonged shelf life, low price, abundance and availability and desirable flavors. Nowadays, consumers are further interested in low saturated frying oils. Recently, manufacturers focus on eliminating palm oil derivatives (as a major vegetable source of saturation) from frying oil formulations. Therefore, achievement of balances between nutritional, technological and economic aspects is a big challenge for the oil industries.

Materials and Methods: The aim of this study was to design and develop a palm-free frying oil formulation based on oils of sunflower (10–30%), canola (10–70%), corn (10–30%) and sesame (10–30%) using D-optimal mixture design. Linolenic acid (Ln) content, trans fatty acids (TFA), saturated fatty acids (SFA), oxidative stability index (OSI) and smoke point (SP) were considered as the response variables. To evaluate performances of these blends during deep frying processes (180 °C for 200 min), total polar compound (TPC) content, peroxide value (PV) and free fatty acid (FFA) content of the blends were assessed.

Results: In summary, the total polar compound content, PV and FFA content of the blends included 15.87–19.41%, 16.41–20.58 meq O_2/kg oil and 0.55–0.77%, respectively; fitted in published recommending ranges. All responses were fitted in the best way ($R^2 > 0.91$) to the linear model used for optimization. The optimal formulation included canola (40.675%), sesame (26.015%), sunflower (23.310%) and corn (10.000%) oils and all experimental values of this formulation were in the confidence interval. This indicated the high accuracy of designation and optimization of the formulas.

Conclusions: In general, the present frying oil formulation can be considered a successful transparent and palm-free formulation in terms of economy, quality and technology considerations, particularly for household uses.

Keywords: Frying oil, Palm-free formulation, Design, Optimization

Introduction

Frying is a complex process; in which, the simultaneous transfer of heat, mass and chemical reactions occurs. In this process, hot oil is the heat transfer agent and the internal moisture of food vaporizes through the surface of food. In fact, frying process is quite similar to drying of foods. The difference is that hot oil replaces the evaporated water. In the frying process, food products undergo dehydration and, at the same time, physical changes while chemical reactions occur in foods as well as frying oils (1, 2). Oils provide important characteristics such as improved texture, special taste, mouthfeel and aftertaste for fried foods. Because of oil chemical reactions and physical changes that occur during the frying process, oils used in frying should include special characteristics such as high oxidative stability, prolonged shelf life, low price, abundance and availability and desirable flavor, taste and after-taste in food products. In industrial fried products, oils used for frying should guarantee prolonged shelf life, high oxidative stability, high smoke point (SP), low foaming, low melting point and mild flavor and taste. The cost of frying oil is highly important for industries. Most of the fried snacks contain 20–40%

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of oils. Therefore, price of frying oils should be as low as possible. Furthermore, the nutritional value of frying oils is particularly important. Nowadays, consumers expect especially nutritional requirements from frying oils. The most important requirements include low saturation, high oxidative stability, very low trans fatty acids (TFA) and desirable taste and aroma (3). Therefore, manufacturer should establish a balance within economic aspects (e.g. final price of the product) and technological aspects (e.g. oxidative stability during processing) as well as nutritional and quality aspects (4–6). No specific guidelines or regulatory standards are available for frying oils in most of the countries. However, recommendations and regulatory guidelines for frying oils are available. For example, European Union (EU) has issued regulations on frying oil safety and regularly monitors oil quality using total polar compound test (7). In Iran, the Iranian National Standards Organization (INSO) has published a comprehensive and relatively strict regulation on quality and safety of frying oils (8).

Palm oil and its products, including palm olein, double-fractionated palm olein, palm stearin and red palm oil, are widely used in industrial frying because of their relatively low price, availability, high oxidative stability and prolong shelf life of the final products. However, palm oil and its derivatives produce a waxy or greasy taste in food products due to high saturation, especially in cold weather. Furthermore, palm oil based frying oils are opaque and become two-phased over time, which is not pleasant to consumers (5). It is noteworthy that countries have started to increase import tariffs and limit palm oil imports. For example, Iran increases tax on palm oil to 40%, while other vegetable oils are taxed up to 24% (9). Designation and formulation of frying oils with good quality and nutritional characteristics such as minimum saturation and high transparency should be on the agenda of food industries. Trying to decrease or remove palm oil and its derivatives from frying oils, especially in frying oils for household uses, is one of these efforts. Sunflower, canola, corn and sesame oils are most widely used edible oils worldwide due to their appropriate price, abundance, low saturated fatty acids or SFA (below 15%), high essential fatty acids (EFA) and natural antioxidants such as tocopherols, squalene (in corn oil), sesamol (in sesame oil) and phytosterols. These oils are popular for cooking, which are widely used in food industries. Moreover, corn and sesame oils can tolerate gentle frying conditions to large extents since they include relatively high contents of antioxidants (1). Canola oil contains high quantities of oleic acid (oleic acid is a desired fatty acid (FA) in frying processes). However this oil is sensitive to oxidation due to high levels of polyunsaturated fatty acids or PUFA (especially linolenic acid or Ln). Canola oil stability can be increased through blending with other vegetable oils (5). Due to various frying oil formulations and standard limitations, achieving a balance between nutritional, technological and economic aspects is a challenge for the oil industries. Moreover, no studies have designed efficient and optimal palm-free frying oil formulations through experimental designation techniques. Designation of such an optimal formulation can meet the oil industry requirement to produce palm-free frying oils. Hence, the present study focused on designation and formulation of palm-free transparent frying oils using sunflower, canola, corn and sesame oils. The study also used D-optimal mixture design and Design-Expert Software v.7.0.0. For this purpose, Ln content, TFA, SFA, oxidative stability index (OSI) and SP were considered as response parameters.

Materials and Methods

Materials: Refined, bleached, deodorized (RBD) and winterized oils of sunflower, canola, corn and sesame with special specifications (Table 1) were purchased from Kourosh Food Industry Co., Iran. Specifications of the oils were in the standard range of INSO No. 4152 (moisture content $< 0.1\%$, free fatty acids (FFA) $< 0.07\%$, soap content < 5 ppm, peroxide value (PV) < 0.5 meq/kg and anisidine value (AV) < 6). All chemicals were purchased in laboratory grades from Merck, Germany.

Determination of free fatty acids, peroxide value, soap content, anisidine value, wax content and moisture content: The FFA, PV, soap content, AV, wax content and moisture content of sunflower, canola, corn and sesame oils were assessed based on the AOCS methods of Cd 8-53, Cd 8-23, Cc 17-95, Cd 18-90 and Ca 2c-25, respectively (10–12).

Table 1. Chemical characteristics of sunflower, rapeseed, corn and sesame oils

Oil type	Chemical properties						
	FFA (%)	SC (ppm)	PV (meq/kg)	IV	AV	WC (ppm)	MC (%)
SFO	0.061±0.021	0±0.000	0.1>	127.300±0.300	5.160±0.110	18.010±0.154	0.051±0.002
CNO	0.051±0.043	0±0.000	0.1>	120.700±0.500	3.870±0.300	38.231±0.162	0.032±0.005
CO	0.048±0.042	0±0.000	0.1>	128.600±0.200	2.352±0.324	32.160±0.200	0.024±0.001
SMO	0.062±0.014	0±0.000	0.1>	130.600±0.400	3.181±0.225	26.453±0.312	0.056±0.001
	Composition of fatty acids (%)						
	P	S	O	L	Ln	TFA	SFA
SFO	7.350±0.060	4.200±0.040	32.520±0.090	54.670±0.040	0.260±0.030	0.110±0.020	11.550±0.080
CNO	6.680±0.060	3.880±0.070	61.620±0.050	20.160±0.080	6.380±0.060	0.080±0.010	10.560±0.040
CO	12.910±0.020	2.620±0.050	29.850±0.040	51.690±0.090	0.990±0.070	0.110±0.020	15.530±0.050
SMO	12.25±0.080	3.470±0.060	36.730±0.040	43.620±0.050	1.140±0.050	0.080±0.040	15.720±0.070

SFO, sunflower oil; CNO, canola oil; CO, corn oil; SMO, sesame oil; FFA, free fatty acids; SC, soap content; PV, peroxide value; IV, iodine value; AV, anisidine value; WC, wax content; MC, moisture content

Table 2. Composition of mixtures in frying oil formulated with sunflower, canola, corn and sesame oils in a four-component D-optimal mixture design

Formulation code	Component of ingredients			
	% SFO (X_1)	% CNO (X_2)	% CO (X_3)	% SMO (X_4)
1	30	30	10	30
2	10	40	20	30
3	10	50	30	10
4	30	30	20	20
5	30	10	30	30
6	20	30	30	20
7	10	50	10	30
8	30	10	30	30
9	20	30	30	20
10	30	20	20	30
11	10	60	10	20
12	30	50	10	10
13	30	40	10	20
14	10	30	30	30
15	20	60	10	10
16	10	60	10	20
17	20	50	20	10
18	30	30	30	10
19	30	30	30	10
20	10	50	30	10

SFO, sunflower oil; CNO, canola oil; CO, corn oil; SMO, sesame oil

Experiment design: Design-Expert Software v.7.0.0 was used to optimize the qualitative and nutritional properties of frying oil formulations. Due to the economic issues, it was decided that contributions of sunflower, canola, corn and sesame oils respectively included 10–30, 10–70, 10–30 and 10–30% in formulations. The D-optimal mixture design was suggested by the software based on the contribution value assigned for each oil in formulations. The experiment design suggested by the software (consisted of 20 combinations of four components) is presented in Table 2.

Statistical analysis, data processing and formulation optimization: The parameters of Ln content, TFA, SFA, OSI and SP were considered as response parameters for designation and optimization of the frying oil formulations. The linear, quadratic and cubic models (Equations 1–3) were used to fit with experimental values of responses. The statistical significance of each equation was checked at 1% levels using analysis of variance (ANOVA):

Equation (1)

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4$$

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Equation (2)

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_1b_2X_1X_2 + b_1b_3X_1X_3 + b_1b_4X_1X_4 + b_2b_3X_2X_3 + b_2b_4X_2X_4 + b_3b_4X_3X_4$$

Equation (3)

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_1b_2X_1X_2 + b_1b_3X_1X_3 + b_1b_4X_1X_4 + b_2b_3X_2X_3 + b_2b_4X_2X_4 + b_3b_4X_3X_4 + b_1b_2b_3X_1X_2X_3 + b_1b_2b_4X_1X_2X_4 + b_2b_3b_4X_2X_3X_4 + b_1b_2b_3b_4X_1X_2X_3X_4$$

Where, Y was the dependent variables (Ln content, TFA, SFA, OSI and SP), X was the independent variables (sunflower, canola, corn and sesame oils) and *b* was regression coefficient of the equations. To optimize the formulation, range of the five response parameters was calculated according to INSO No. 4152. According to INSO (8), contents of Ln and TFA must be less than 3 and 2%, respectively. The OSI (at 110 °C) and SP must be more than 15 h and 220 °C, respectively. Furthermore, the minimum SFA content was set in this study.

Frying oil production: Refined, bleached, deodorized (RBD) and winterized oils of sunflower, canola, corn and sesame (Table 2) were blended at 300 rpm for 10 min at 40 °C under vacuum. Then, 75 ppm of TBHQ antioxidant were added to the oil blends. Moreover, 100 ppm of citric acid and 10 ppm of polydimethylsiloxane were added to frying oils as antioxidant resonator and anti-foam, respectively.

Fatty acid assessment: Fatty acid methyl esters (FAMEs) were prepared from the oil samples according to AOCS Ce 2-66 (10). Briefly, 6 ml of 0.5 N NaOH in methanol were added to a conical flask containing the oil sample (ca. 0.35 g) and heated under reflux for 10 min. Then, 7 ml of boron trifluoride in methanol (125 g of BF3 in 1 l of methanol) were added to the samples and heated for an additional 2 min. After 2 min, heating was stopped, condenser was separated and 15 ml of a saturated salt solution were added to the mixture to separate the organic phase. Then, 1 ml of the organic phase was removed and a little amount of sodium sulfate was added. This was stirred and filtered using filter papers. Furthermore, 1 ml of normal heptane was added to the solution and then 1 µl of the solution was injected into the gas chromatography (GC) instrument (Agilent 6100, USA), according to AOCS 1Ce-91. The GC instrument was equipped with a split injector and a flame ionization detector. The capillary column included CP Sil 88 (100 m × 0.25 mm × 0.25 µm). The split ratio was 40, the carrier gas was nitrogen and detector and injector temperatures were 280 and 240 °C, respectively.

Oxidative stability assessment: The induction period of oxidation (IP_{OX}) was assessed using Rancimat Metrohm 743, Switzerland, according to AOCS Cd 12b-92. This was repeated three times at 110 °C with 2.5 g of the sample and air flow of 2.5 mL/min (10).

Smoke point assessment: The SP of oil samples was assessed according to AOCS No. Ca 9a-48 (10).

Deep frying: To evaluate performances of the oil blends during frying, a deep frying process was used for 20 consecutive times (each frying period included 10 min). In every period, a 100-g raw potato slice was fried in 500 g of the oil at 180 °C using stainless steel pan (with area of 110 cm^2 × 10 cm). The TPC content was assessed at the end of the process.

Total polar compound (TPC) content: A solid-phase extraction method was used to assess TPC of the frying oil formulations based on the method described by Ng et al. (13). Briefly, a silica SPE cartridge was conditioned with 10 ml of elution solvent (petroleum/diethyl ethers 90:10). The sample solution was prepared by dissolving 0.5 g of the oil sample in 5 ml of the elution solvent. Sample solution was transferred to the cartridge and eluted with 50 mL of the elution solvent, The eluent was collected in a tared 125-ml round-bottom flask using vacuum manifold. Then, solvent was evaporated from the eluent under vacuum condition at 8 °C. To remove the remaining solvent, a vacuum oven was used at 60 °C for 60 min. Then, flask containing the nonpolar fraction eluted from the cartridge was weighed. The TPC content was calculated using the following equation:

Equation (4)

$$\text{Total polar compounds (\%)} = \left[\frac{(m - m_1)}{m}\right] \times 100$$

Where, m_1 was mass of the nonpolar fraction (g) and m was mass of the sample (g).

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Results

Fitness to choose the best model: Table 3 shows the experimental results of Ln content, TFA, SFA, OSI and SP of 20 various frying oil formulations. All independent and dependent variables were fitted to linear, quadratic, special cubic and cubic models and goodness of fit of the models was checked (Table 4). The best model is a model that is statistically significant (*P* < 0.05) with the lowest standard deviation (SD) and highest predicted R^2, which is larger than 0.7 (14). As shown in Table 4, the best fitted model for all responses was a linear model selected to optimize the formulation. The cubic model was aliased for all responses. Linear regression coefficients of the five responses are shown in Table 5.

Table 3. Experimental results for linolenic content, trans fatty acids, saturated fatty acids, oxidative stability index and smoke point at various formulations using D-optimal design

Formulation code	Response				
	Ln content (%)	TFA (%)	SFA (%)	OSI (h)	Smoke point (°C)
1	2.401±0.022	0.097±0.001	12.870±0.120	15.100±0.260	236.600±0.200
2	3.094±0.034	0.092±0.000	13.169±0.211	15.250±0.220	236.200±0.500
3	3.622±0.061	0.096±0.003	12.623±0.342	15.082±0.350	236.800±0.100
4	2.385±0.023	0.099±0.002	12.857±0.234	15.070±0.420	236.900±0.300
5	1.398 ±0.043	0.097 ±0.002	13.564±0.325	15.339±0.220	236.200±0.400
6	2.421±0.020	0.096±0.004	13.240±0.113	15.300±0.260	236.700±0.300
7	3.631±0.052	0.091±0.005	12.66±0.146	15.130±0.410	236.400±0.200
8	1.332±0.074	0.099±0.001	13.888±0.325	15.340±0.110	236.200±0.600
9	2.461±0.059	0.097±0.003	13.261±0.330	15.210±0.430	236.600±0.300
10	1.868±0.030	0.098±0.004	13.379±0.442	15.220±0.120	236.400±0.400
11	4.150±0.050	0.093±0.006	12.146±0.148	14.890±0.140	236.800±0.600
12	3.448±0.061	0.099±0.006	11.826±0.168	14.800±0.510	237.600±0.300
13	2.926±0.043	0.098±0.005	12.348±0.225	14.950±0.470	237.100±0.100
14	2.565±0.047	0.093±0.002	13.678±0.436	15.370±0.210	236.000±0.400
15	4.062±0.079	0.096±0.004	11.721±0.428	14.820±0.520	237.500±0.600
16	4.154±0.058	0.092±0.003	12.138±0.335	14.980±0.660	236.900±0.400
17	3.526±0.038	0.097±0.003	12.23±0.621	14.940±0.110	237.300±0.300
18	2.332±0.083	0.105±0.002	12.862±0.262	15.085±0.140	237.300±0.700
19	2.378±0.045	0.101±0.003	12.844±0.552	15.040±0.220	237.200±0.500
20	3.602±0.051	0.095±0.005	12.634±0.147	15.070±0.300	237.000±0.300

Ln content, linolenic acid content; TFA, trans fatty acids; SFA, saturated fatty acids; OSI, oxidative stability index using Rancimat (at 110 °C)

Table 4. Analysis of variance (ANOVA) of the modelled responses

Response	Model	*P*-value	Std. Dev.	R^2	Predicted R^2
Ln content	Linear	< 0.0001*	0.0220	0.9994	0.9991
	Quadratic	< 0.0001*	0.0230	0.9996	0.9988
	Special Cubic	< 0.0001*	0.0270	0.9997	-
	Cubic	Aliased	Aliased	Aliased	Aliased
TFA	Linear	< 0.0001*	0.0010	0.9114	0.8587
	Quadratic	< 0.0001*	0.0011	0.9380	0.7755
	Special Cubic	0.0088*	0.0013	0.9458	-
	Cubic	Aliased	Aliased	Aliased	Aliased
SFA	Linear	< 0.0001*	0.0710	0.9884	0.9808
	Quadratic	< 0.0001*	0.0770	0.9915	0.9717
	Special Cubic	< 0.0001*	0.0940	0.9924	-
	Cubic	Aliased	Aliased	Aliased	Aliased
OSI	Linear	< 0.0001*	0.0300	0.9736	0.9618
	Quadratic	< 0.0001*	0.0320	0.9816	0.9386
	Special Cubic	0.0003*	0.0400	0.9832	-
	Cubic	Aliased	Aliased	Aliased	Aliased
Smoke point	Linear	< 0.0001*	0.0690	0.9804	0.9679
	Quadratic	< 0.0001*	0.0750	0.9854	0.9509
	Special Cubic	0.0002*	0.0960	0.9858	-
	Cubic	Aliased	Aliased	Aliased	Aliased

*Significant model at 0.01 level; Ln content, linolenic acid; TFA, trans fatty acids; SFA, saturated fatty acids; OSI, oxidative stability index using Rancimat (at 110 °C)

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Table 5. Regression coefficients of the fitted models to experimental data in mixture design

Coefficient	Response				
	Ln content (%)	TFA (%)	SFA (%)	OSI (h)	Smoke point (°C)
b_1	1.580	0.085	14.250	15.700	234.460
b_2	4.670	0.094	11.660	14.8200	237.320
b_3	1.450	0.100	14.600	15.6200	236.230
b_4	0.980	0.110	12.200	14.7700	238.140

Ln content, linolenic acid; TFA, trans fatty acids; SFA, saturated fatty acids; OSI, oxidative stability index using Rancimat (at 110 °C)

Fatty acid composition: Table 5 shows the FA composition of 20 various frying oil formulations. Palmitic acid and stearic acid in ranges of 7.972–10.408 and 3.412–3.788% were dominant SFAs in the formulations. The oleic acid and linoleic acid with 35.770–50.571 and 31.426–46.966% were dominant unsaturated fatty acids (USFA) in the formulations. As seen in Table 5, Ln content ranged 1.332–4.154% and TFA content of the formulations ranged 0.091–0.105%.

Oxidative stability index: According to INSO (8), the minimum OSI (at 110 °C) for frying oils is 15 h. The OSI of the formulations was higher than 14.80 h (Table 3). As shown in Table 5, the sunflower oil included the highest effect on OSI, followed by corn, canola and sesame oils, respectively. Figure 1 demonstrates the mixtures plot of OSI as a function of oils. As seen in the figure, increased proportions of the sunflower and corn oils in formulations resulted in increased OSI. In contrast, increased contributions of canola and sesame oils decreased the OSI. This occurred due to the higher saturation rate of sunflower and corn oils, compared to that of sesame and canola oils.

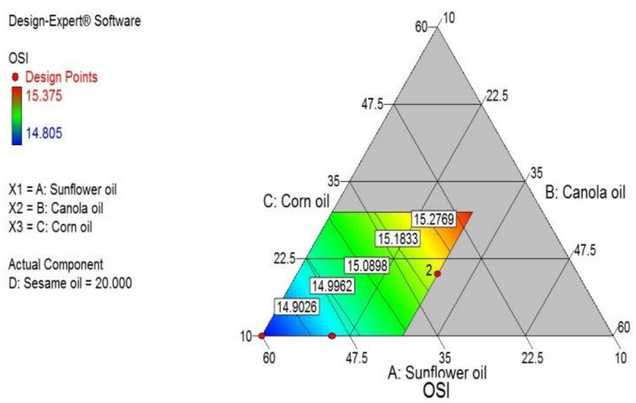

Fig 1. Mixtures plot of oxidative stability index of the frying oil formulations as functions of sunflower, canola, corn and sesame oils

Smoke point: According to the INSO (8), SP should be at least 220 °C. As shown in Table 3, SP of the formulations was reported between 236.200 and 237.600 °C; similar to standard ranges of all the formulations (Table 3).

The total polar compound content of the samples after deep-frying process: According to the INSO (8), if TPC content of the frying oils is higher than 25%, the oils must be discard. The TPC content of the frying oil formulations after 200 min of deep frying are presented in Table 6. The TPC content of the blends was lower than 19.419 %, which indicated a good oxidative stability after 200 min of deep frying. These values were similar to the recommended values.

The peroxide value of the samples after deep-frying process: After deep frying for 200 min, PV of the samples were 16.41–20.58 meqO2/kg (Table 6). No INSO standard limits have been set for the PV of discard frying oils.

The free fatty acid content of the samples after deep-frying process: The FFA contents of the samples after 200 min of deep frying are presented in Table 6. The FFA contents varied 0.55–0.77 %, which indicated an increase during frying. The INSO (8) indicates that frying oils must be discarded when the FFA level in oils exceeds 1%. in this study, all FFA of the samples were in the standard range.

Discussion

Fatty acid composition: Oxidative stability of the oils primarily depends on their USFA contents, which mainly include linoleic and linolenic acids. In fact, as the number of double bonds in FA increases, the relative oxidation velocity increases at a higher rate than the linear rate. The relative oxidation rate for stearic, oleic, linoleic and linolenic acids includes 1, 10, 100 and 150, respectively. The Ln is further appropriate to oxidize and linoleic acid is less reactive than Ln. Therefore, for maximum oxidative stability in oils, Ln content should be low. As a result, oils such as canola and soybean oils that naturally include 7–8% of Ln are not appropriate for frying and must be hydrogenated or blended with other oils. Although the oxidative stability of linoleic acid is higher than that of Ln, it is much lower than the stability of oleic acid. Therefore, pure regular sunflower oil (on average containing 65% of linoleic acid) is not appropriate for frying. However, this is not a general principle since oils such as sesame, corn and cotton seed oils that contain more than 40% of linoleic acid show a relatively good oxidative stability in frying processes. Hence, these oils can be used even in industries, which is possibly due to the presence of relatively high levels of natural antioxidants such as tocopherols and tocotrienols. Moreover, sesame oil includes the sesamol antioxidant that is considered as one of the strongest natural antioxidants in oils (1).

Table 6. Fatty acid composition of the fresh frying oil formulations and total polar compounds content, peroxide value and free fatty acid content of the oil blends after 200 min of deep frying

Formulation code	Fatty acid composition (%)								Total polar compound (%)	PV (meq/kg)	FFA (%)
	P	S	O	L	Ln	TFA	SFA	Others			
1	9.146±0.025	3.724±0.014	42.237±0.020	40.671±0.025	2.401±0.022	0.097±0.001	12.870±0.120	1.657	17.642±0.211	18.48±0.21	0.75±0.18
2	9.640±0.034	3.529±0.022	44.883±0.018	36.926±0.018	3.094±0.034	0.092±0.000	13.169±0.211	1.766	16.723±0.134	17.25±0.15	0.62±0.15
3	9.162±0.030	3.461±0.015	46.722±0.023	35.363±0.041	3.622±0.061	0.097±0.003	12.623±0.342	1.670	18.340±0.119	19.54±0.20	0.74±0.11
4	9.218±0.026	3.639±0.028	41.562±0.011	41.477±0.029	2.385±0.023	0.099±0.002	12.857±0.234	1.570	18.060±0.221	19.11±0.10	0.55±0.20
5	10.408±0.022	3.511±0.029	35.869±0.026	46.942±0.035	1.398 ±0.043	0.097 ±0.002	13.564±0.325	1.755	16.430±0.204	16.96±0.16	0.77±0.25
6	9.778±0.018	3.483±0.027	41.296±0.023	41.181±0.022	2.421±0.020	0.096±0.004	13.919±0.113	1.872	16.740±0.100	17.44±0.10	0.75±0.14
7	9.014±0.041	3.646±0.016	48.061±0.026	33.773±0.032	3.631±0.052	0.091±0.005	12.66±0.146	1.717	17.387±0.245	18.23±0.26	0.68±0.19
8	10.400±0.036	3.506±0.030	35.772±0.032	46.966±0.035	1.332±0.074	0.099±0.001	13.906±0.325	2.015	16.254±0.322	16.55±0.08	0.71±0.22
9	9.781±0.024	3.356±0.019	41.300±0.016	41.188±0.027	2.461±0.059	0.097±0.003	13.137±0.330	1.817	17.070±0.156	18.00±0.10	0.69±0.20
10	9.772±0.061	3.607±0.025	39.059±0.044	43.824±0.027	1.868±0.030	0.098±0.004	13.379±0.442	1.706	16.961±0.414	17.15±0.08	0.77±0.23
11	8.473±0.043	3.680±0.018	50.571±0.035	31.428±0.026	4.150±0.050	0.093±0.006	12.153±0.148	1.605	19.170±0.183	20.36±0.13	0.58±0.26
12	8.038±0.030	3.788±0.036	47.243±0.045	35.977±0.018	3.448±0.061	0.099±0.006	11.826±0.168	1.385	19.419±0.320	20.58±0.09	0.70±0.17
13	8.592±0.022	3.756±0.041	44.74±0.050	38.324±0.043	2.926±0.043	0.098±0.005	12.348±0.225	1.521	18.914±0.220	20.09±0.12	0.76±0.20
14	10.266±0.037	3.412±0.034	41.705±0.041	40.079±0.016	2.565±0.047	0.093±0.002	13.678±0.436	1.815	15.870±0.114	16.41±0.07	0.72±0.24
15	7.972±0.025	3.749±0.022	50.155±0.022	32.528±0.029	4.062±0.079	0.096±0.004	11.721±0.428	1.415	19.196±0.125	20.70±0.06	0.64±0.17
16	8.46±0.033	3.678±0.019	50.564±0.037	31.426±0.035	4.154±0.058	0.092±0.003	12.138±0.335	1.581	18.779±0.241	19.84±0.11	0.58±0.21
17	8.598±0.017	3.632±0.033	46.977±0.025	35.681±0.058	3.526±0.038	0.097±0.003	12.23±0.621	1.464	18.933±0.279	19.93±0.20	0.74±0.23
18	9.293±0.028	3.549±0.020	40.872±0.045	42.290±0.051	2.332±0.083	0.105±0.002	12.842±0.262	1.559	17.914±0.147	18.80±0.05	0.73±0.22
19	9.290±0.021	3.554±0.025	40.887±0.021	42.283±0.029	2.378±0.045	0.101±0.003	12.844±0.552	1.483	18.770±0.264	19.87±0.06	0.69±0.22
20	9.158±0.029	3.476±0.011	46.711±0.051	35.385±0.022	3.602±0.051	0.095±0.005	12.634±0.147	1.543	18.473±0.328	19.66±0.14	0.70±0.24

P, palmitic acid; S, stearic acid; O, oleic acid; L, linoleic acid; Ln, linolenic acid; TFA, trans fatty acids; SFA, saturated fatty acids (sum of P and S); PV, peroxide value; FFA, free fatty acid

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Based on Table 4, which indicates linear regression coefficients between responses and components, the highest effects on Ln content, TFA and SFA were associated to canola, sesame and corn oils, respectively. Figure 2 shows the mixture plot belonging to Ln content, TFA and SFA as functions of sunflower, canola, corn and sesame oils. Based on Figure 2a, increased contribution of sunflower, corn and sesame oils resulted in decreases in Ln content. By increasing the contribution of canola oil, the Ln content increased. This is due to a higher Ln content of canola oil (Table 1). Indeed, TFA included a direct association with corn and sesame oils and an inverse association with contribution of sunflower and sesame oils in formulations (Fig. 2b). Increased proportions of canola and sesame oils in formulations decreased SFA, while increased proportions of sunflower and corn oils increased SFA (Fig. 2c). This is due to a higher saturation of sesame and corn oils as well as higher unsaturation of canola and sesame oils. According to Table 6, almost the major FA content of the formulations belonged to oleic acid. This data was similar to data by Tavakoli et al. (15). who studied 36 Iranian frying oil samples. They documented an average of 9.10% for SFA content of frying oils.

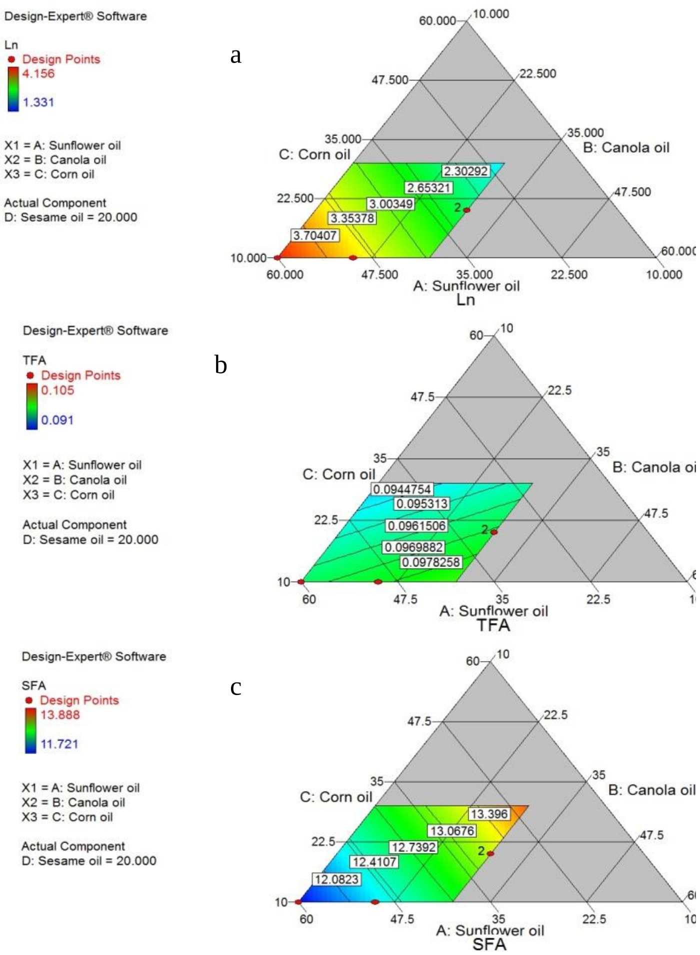

Fig 2. Mixtures plots of linolenic acid content (a), trans fatty acids (b) and saturated fatty acids (c) of the frying oil formulations as functions of sunflower, canola, corn and sesame oils

Oxidative stability index: Major chemical reactions, including hydrolysis, oxidation, oxidative polymerization and thermal polymerization, may occur in oil during frying processes. Auto-oxidation can be the major reaction that occurs in frying processes. Oxidation of FA develops the flavor and taste of the fried foods. Compounds that result in good taste and flavor of the fried foods include lactones and particularly aldehydes; most of which are formed from linoleic acid. Oxidation process of USFA begins by free radicals, which are formed from the exposure of USFA to oxygen and metals such as iron, nickel and copper. In fact, high temperatures worsen this process. Due to high temperature and relatively long heating time in frying processes, oxidative stability of frying oils is highly important (16, 17). Oxidative stability of oils is a function of the USFA contents, oxygen, partial components and process conditions. The USFAs operate as peroxidans. The higher USFA content accelerates oil deterioration and consequently unpleasant tastes and flavors, toxic compound formations and losses of nutritional values. Toxic compounds resulting from oil deterioration can cause health problems such as tumor formations, heart failures, cataracts and brain dysfunctions (18). Similar to current results, Tavakoli et al. (15) recently reported a range of 14.7–17.2 h (15.46 h on average) for the OSI of 36 fresh frying oil samples collected from Iranian retail markets.

Smoke point: Smoke, flash and firing points of the frying oils and fats are safety evaluation indicators when oils are heated in presence of air. The SP is defined as a temperature; at which the oil sample begins smoking at specified conditions of the test. The SP includes the highest importance in evaluating the quality of frying oils, since the FFAs produced in frying processes decrease the SP (19). Hydrolysis is another important reaction occurring in oils during the frying process. It is a reaction; in which, triacylglycerol molecules react with water molecules and produce FFAs and diacylglycerols. For this reaction, simultaneous presence of water and oil is essential and surfactants accelerate the reaction. This reaction is majorly responsible for the production of FFAs in frying oils (16, 20, 21). Increases in FFAs during the frying process decrease the SP, because FFAs include lower boiling and evaporation points, compared to those of triacylglycerols (20). The SP of fried fats affects the oil absorption by the fried foods. A significantly negative correlation is reported between the oil absorption by donuts and SP of the frying oils (22–25). In this study, SP of the formulations was higher than 236.20 °C, which was included in the legal limit (Table 3). Moreover, contributions of corn and sunflower oils in formulations included direct effects on SP, while effects of canola and sesame oils were indirect (Figure 3). The highest effects on SP were linked to sesame, canola, corn and sunflower oils, respectively (Table 5).

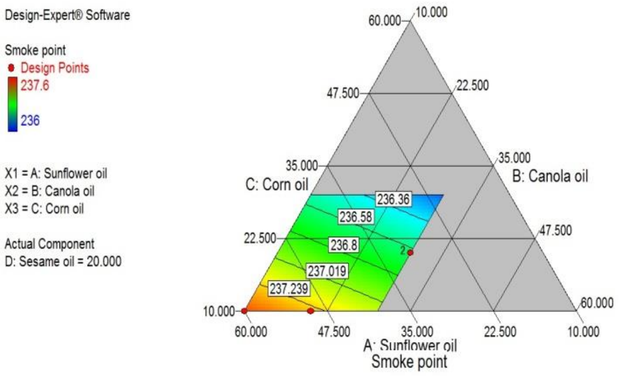

Fig 3. Mixtures plot of smoke point of the frying oil formulations as functions of sunflower, canola, corn and sesame oils

Studying performances of the oil samples after deep-frying processes: The TPC content in frying oils is one of the major indicators of oxidative degradation products. Polar compounds such as FFAs, hydroperoxides, acids, alcohols, aldehydes, ketones and epoxides are indicators of the breakdown rete of oils during food frying (7). Polar compounds have been shown to include toxic effects on laboratory animals; thus, increased polar compounds in oils must be prevented. It is noteworthy that oils are rejected if they include more than 27% of TPC (1). In some European countries such as France, Spain, Switzerland, Austria and Belgium as well as other countries such as Iran, TPC is used to verdict when frying oil must be discarded (7). Sebastianet al. (7) assessed quality and safety of the frying oils used in Canadian restaurants (downtown Toronto). They reported that TPC content of the discarded frying oil samples ranged 6.5–16%, which were lower than that reported by the current study (15.87–19.41%). The PV is an indicator of the initial oxidation products (hydrogen peroxides). Due to high temperatures used in frying processes, PV of the frying oils increases at a relatively higher rate (1). As seen in Table 6, a direct correlation existed between the PV and the TPC of the oil samples. The FFA content is an important quality indicator during each stage of the oil processing (26). High temperature and moisture during the frying processes result in released FA from glycerol molecules (hydrolytic degradation of triacylglycerols), and consequently lost oil aroma quality (27). Hence, the FFA content is considered as a good indicator of the oil discard time. Production of FFA during the frying process is associated to decreased SP. Tseng et al. (28) believed that if FFA of the frying oil exceeded 1%, it would no longer be usable. Quantity of the FFA formed during the deep frying process (0.55–0.77%) was much lower than those described by Sebastianet al. (0.38–4.30%) in another study (7).

Optimization of formulations: Optimization of the frying oil formulations was carried out by solving the previous equations (Table 5) to achieve the mean values of each independent variable. The objective defined for each response was as follows: 1) maximum 3% of Ln content; 2) maximum 2% of TFA; 3) minimum SFA; 4) maximum OSI of 15 h at 110 °C; and 5) maximum SP. In this method, a series of combinations of sunflower, canola, corn and sesame oils were reported (Table 7). Table shows the best combination of oils and predicted values of each response with their confidence interval and experimental values. As seen in formulas suggested by the software, the contribution order of each oil from highest to lowest included canola, sesame, sunflower and corn oils. In this study, desirability plot of the optimization was 0.917 (Figure 4). The desirability function provides a general overview of the multiple responses optimization. The minimum favorable desirability in industrial food optimization is 0.7 (24). Comparison of predicted and experimental values for each response showed that optimization was highly successful in this study. All experimental values of optimal formulation suggested by the software were in the confidence interval, indicating high accuracy of the optimization (Table 7).

Table 7. Optimum mixture proportions, desirability of optimization, predicted and experimental responses and confidence intervals

Component	Proportion (%)		
SFO	23.310		
CNO	40.675		
CO	10.000		
SMO	26.015		
Response	**Predicted value**	**Experimental value**	**Confidence interval**
Ln content	3.000	3.015	2.980-3.020
TFA	0.096	0.096	0.096-0.097
SFA	12.468	12.477	12.410-12.530
OSI	15.000	15.030	15.000-15.130
Smoke point	236.906	236.890	236.850-236.960

SFO, sunflower oil; CNO, canola oil; CO, corn oil; SMO, sesame oil; Ln content, linolenic acid; TFA, trans fatty acids; SFA, saturated fatty acids; OSI, oxidative stability index using Rancimat (at 110 °C)

Conclusion

In general, results from this study showed that the experimental data were fitted in the best way by the linear model; therefore, the model was used for the optimization. In the optimal formulation suggested by the software, the order of contribution of each oil from highest to lowest included canola (40.675%), sesame (26.015%), sunflower (23.310%) and corn (10.000%) oils. All experimental values were in the confidence interval, which indicated accuracy and success of the optimization. Furthermore, the oil blends showed good performances during deep frying processes since contents of TPC, PV and FFA were lower than 19.41%, 20.58 meq/kg and 0.77%, respectively. In conclusion, the frying oil formulation presented in this study was a palm-free transparent formulation, which was especially approved for household uses due to its qualitative and technological characteristics.

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References

1. Shahidi F. Bailey's Industrial Oil and Fat Products, 6 Volume Set: Wiley-Interscience; 2005.
2. Idun-Acquah N, Obeng GY, Mensah E. Repetitive Use of Vegetable Cooking Oil and Effects on Physico-Chemical Properties–Case of Frying with Redfish (Lutjanus fulgens). SCI TECHNOLOGY. 2016;6(1):8-14.
3. O'brien RD. Fats and oils: formulating and processing for applications: CRC press; 2008.
4. Freire PCM, Lobo LCB, Freitas GdS, Ferreira TAPdC. Quality of deep frying oils and fats used in street-fairs in Goiânia, Brazil. FOOD SCI TECH. 2013;33(3):569-76.
5. Matthäus B. Use of palm oil for frying in comparison with other high-stability oils. Eur. J. Lipid Sci. Technol. 2007;109(4):400-9.
6. Rossell J. Frying: improving quality: Woodhead Publishing; 2001.
7. Sebastian A, Ghazani SM, Marangoni AG. Quality and safety of frying oils used in restaurants. FOOD RES INT. 2014;64:420-3.
8. Iranian National Standards Organization (INSO). Frying oil- specifications and test methods. 1st amendment, Standard No. 4152. 1st edn Tehran: INSO press 2014.
9. Saghafi Z, Zargaraan A, Tabibiazar M, Hosseini H. Is Trans Fatty Acid Still an Issue for Policy Makers in Iran? A Technical Report. Nutrition and Food Sciences Research. 2018;5(2):47-51.
10. American Oil Chemists' Society. Official methods and recommended practices of the AOCS. Champaign: AOCS press, 1997.
11. Heshmati A, Khodadadi I. Reduction of cholesterol in beef suet using lecithin. J FOOD COMPOS ANAL. 2009;22.7-8:684-688.
12. Heshmati A. Effects of margarine and butter on lipid profile and serum fatty acid composition in rats. Koomesh. 2016;18.118-188.
13. Ng CL, Wehling RL, Cuppett SL. Method for determining frying oil degradation by near-infrared spectroscopy. J. Agric. Food Chem. 2007;55(3):593-7.
14. Cornell JA. Experiments with mixtures: designs, models, and the analysis of mixture data: John Wiley & Sons; 2011.
15. Tavakoli HR, Naderi M, Jafari SM, Naeli MH.. Postmarketing surveillance of the oxidative stability for cooking oils, frying oils, and vanaspati supplied in the retail market. Food Sci Nutr. 2019;*7*(4):1455-1465.
16. Chang SS, Peterson RJ, Ho CT. Chemical reactions involved in the deep-fat frying of foods1. J. Am. Oil Chem. Soc. 1978;55(10):718-27.
17. Choe E, Min D. Chemistry of deep-fat frying oils. Journal of food science. 2007;72(5):R77-R86.
18. Przybylski R, Zambiazi RC. Predicting oxidative stability of vegetable oils using neural network system and endogenous oil components. J. Am. Oil Chem. Soc. 2000;77(9):925.
19. Gertz C. Chemical and physical parameters as quality indicators of used frying fats. J Lipid Sci Technol. 2000;102(8-9):566-72.
20. Ziaiifar AM, Achir N, Courtois F, Trezzani I, Trystram G. Review of mechanisms, conditions, and factors involved in the oil uptake phenomenon during the deep-fat frying process. Int J Food Sci Technol. 2008;43(8):1410-23.
21. Bracco U, Dieffenbacher A, Kolarovic L. Frying performance of palm oil liquid fractions. J. Am. Oil Chem. Soc. 1981;58(1):6-12.
22. Dobarganes C, Márquez-Ruiz G, Velasco J. Interactions between fat and food during deep-frying. Eur J Lipid Sci Technol. 2000;102(8-9):521-8.
23. Erickson MD. Deep frying: chemistry, nutrition, and practical applications: Elsevier; 2015.
24. Ouchon P, Aguilera J, Pyle D. Structure oil-absorption relationships during deep-fat frying. J. Food Sci. 2003;68(9):2711-6.
25. Granato D, Ares G. Mathematical and statistical methods in food science and technology: John Wiley & Sons; 2014.
26. Naeli MH, Farmani J, Zargaraan A. Rheological and Physicochemical Modification of trans-Free Blends of Palm Stearin and Soybean Oil by Chemical Interesterification. J FOOD PROCESS ENG. 2017;40.2: e12409.
27. Farahmandfar R, Naeli MH, Naderi M, Asnaashari M. Stabilizing corn oil using the lemon balm (Melissa officinalis) antioxidants extracted by subcritical water. J Food Sci Technol. 2019;*56*(2):695-704.
28. Tseng YC, Moreira R, Sun X. Total frying-use time effects on soybean-oil deterioration and on tortilla chip quality. INT J Food Sci Tech. 1996);31(3);287-294.