Food Chemistry 218 (2017) 496–504

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Chemometric approach to develop frying stable sunflower oil blends stabilized with oleoresin rosemary and ascorbyl palmitate

Rohit Upadhyay *, Sneha Sehwag, Hari Niwas Mishra

Agricultural & Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur 721302, West Bengal, India

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form 28 August 2016
Accepted 16 September 2016
Available online 17 September 2016

Keywords:
Rosemary (*Rosmarinus officinalis* L.)
Sunflower oil
Total polar compounds
Triglyceride polymers
Response surface methodology
Principal component analysis

ABSTRACT

The frying performance of sunflower oil blends (SOBs) stabilized with oleoresin rosemary (*Rosmarinus officinalis* L.) (ROSM) (200–1500 mg/kg) and ascorbyl palmitate (AP) (100–300 mg/kg) were tested for 18 h open pan-frying. Sunflower oil with TBHQ (SO_{TBHQ}) (200 mg/kg) and without additives ($SO_{control}$) served as positive and negative controls, respectively. The frying stability was monitored over time by estimating the levels of conjugated dienes, total polar compounds, polymeric compounds *viz.*, triglyceride polymers, dimers, oxidized triglyceride monomers, diglycerides and free fatty acids, and induction period based on Rancimat. Chemometric tools were used to classify the oil samples based on frying stability. Thermo-oxidative changes were reduced significantly for blends stabilized with ROSM and AP ($p < 0.05$). Principal component analysis (PCA) and hierarchical cluster analysis (HCA) distinguished SOBs from positive controls. A formulation consisting of 1309.62 and 129.29 mg/kg of ROSM and AP, respectively, was optimized using a hybrid PCA–RSM approach.

1. Introduction

Among methods of cooking, deep-frying is highly popular and improves the palatability of food (Kalogeropoulos, Chiou, Mylona, Ioannou, & Andrikopoulos, 2007; Matthaus, 2007). During frying, oxidative and hydrolytic deterioration of the oil takes place. This results in the generation and accumulation of non-volatile decomposition products collectively known as total polar compound (TPC) (Arslan et al., 2013; Farhoosh & Tavassoli-Kafrani, 2011). TPC can be categorized into dimerized, polymerized and oxidized forms of triglyceride, namely triglyceride polymer (TGP), triglyceride dimer (TGD) and oxidized triglyceride monomer (oxTGM), respectively. These compounds are formed due to thermo-oxidative and polymerization reactions. Diglyceride (DG) and free fatty acid (FFA) are formed because of the hydrolytic cleavage of triglyceride molecules. TGPs are toxic metabolites that tend to accumulate in the oil and are absorbed by fried products, which decreases their nutritional quality and shelf life (Barbosa-Canovas, 1999). Adsorption chromatography is routinely performed to quantify the content of TPCs in frying oil. In addition, high-performance size exclusion chromatography (HPSEC) can be used quantitatively characterize the TPCs into TGPs, TGDs, oxTGMs, DGs and FFAs (Houhoula, Oreopoulou, & Tzia, 2003). The quantification of polar and polymeric compounds is one of the most reliable methods to determine the point at which fats and oils should be discarded. The frying oil must meet the rejection or critical discard limits of TPC and other polymeric compounds, such as TGDP (TGD + TGP) between 23–27% and 10–16%, respectively (Firestone, 1996; Marquez-Ruiz & Dobarganes, 1996).

The use of sunflower oil (SO) for frying can be considered a healthy choice due to balanced amounts of saturated fatty acids (SFA, ca. 6%) and monounsaturated fatty acids (MUFA, ca. 20%), and a high content of polyunsaturated fatty acids (PUFA), which constitute 68–72% of total fatty acids (Gordon, 1991). However, the relatively high PUFA content makes SO vulnerable to thermo-oxidative degradation leading to rancidity, off-flavors and discoloration, which limits its application as frying oil (Gordon, 1991).

Abbreviations: ANOVA, analysis of variance; AOCS, American oil chemist's society; AP, ascorbyl palmitate; CCRD, central composite rotatable design; CDV, conjugated diene value; DG, diglyceride; FFA, free fatty acid; HCA, hierarchical cluster analysis; HPSEC, high performance size exclusion chromatography; IP, induction period; oxTGM, oxidized triglyceride monomer; PC, principal component; PCA, principal component analysis; SFA, saturated fatty acid; MUFA, mono unsaturated fatty acid; PUFA, poly unsaturated fatty acid; *r*, correlation coefficient; R^2, regression coefficient; ROSM, oleoresin rosemary; RSM, response surface methodology; SO, sunflower oil; SOB, sunflower oil blend; $SO_{control}$, control sunflower oil; SO_{TBHQ}, sunflower oil–TBHQ blend; TBHQ, tertiary butylated hydroquinone; THF, tetrahydrofuran; TGD, triglyceride dimer; TGDP, triglyceride dimer polymer; TGP, triglyceride polymer; TPC, total polar compound.

* Corresponding author.
E-mail addresses: ruv.16jy@gmail.com, rohit.upadhyay@iitkgp.ac.in (R. Upadhyay).

http://dx.doi.org/10.1016/j.foodchem.2016.09.105
0308-8146/

Synthetic antioxidants (*e.g.* TBHQ) are judiciously added to cooking oils to prolong their shelf life and frying stability. However, their application in food is highly regulated and limited due to health concerns (Chen, Shi, & Ho, 1992; Kahl & Kappus, 1993). Among the natural sources of antioxidants, plant extracts containing polyphenols, carotenoids, tocopherols, and ascorbic and citric acid are widely used to reduce oxidative degradation of cooking oils (Hamied, Nassar, & Badry, 2009; Jaswir & Man, 1999; Jaswir, Man, & Kitts, 2000). Frying requires the use of thermally efficient antioxidants that can delay thermodegradation of triglycerides. Our previous investigations demonstrated increased stabilization of SO mixed with individual and combinations of natural antioxidants *viz.*, oleoresin rosemary (ROSM), oleoresin sage and ascorbyl palmitate (AP) (Upadhyay & Mishra, 2015a, 2015b, 2015c, 2015d; Upadhyay & Mishra, 2016). These findings encouraged us to undertake a systematic assessment of frying performance using the synergistic combination of ROSM and AP in SO.

Applications of chemometric tools are increasing in food research because of their ability to demonstrate correlations among different parameters. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) allows easy interpretation of complex relationships frequently encountered in multivariate analysis (Funatsu, Katoh, Kawasaki, Konagaya, & Usui, 2001; Saavedra, Cordova, Galvez, Quezada, & Navarrao, 2013; Upadhyay & Mishra, 2015b, 2016). Use of chemometric approaches in testing the frying performance of SO blends has not been attempted widely. Here, PCA and HCA were used to classify SO blends into different groups, based on the alteration of compositional parameters and formation of polar compound. An attempt was also made to explore the applicability of combined PCA and response surface methodology (RSM) approaches for optimization of synergistic blend composition. The literature reports the usefulness of PCA to mitigate problems associated with the correlation of responses between multi-response optimization studies where RSM-based optimization often leads to unsatisfactory models that are, generally, overlooked (Purkayastha, Dutta, Barthakur, & Mahanta, 2015). These misinterpreted results often lead to model instability, overfitting and errors in prediction. Purkayastha et al. (2015) revealed the superiority of the PCA–RSM approach over RSM-based models, which confirmed the better prediction accuracy of the former. A thorough investigation of the literature indicated different RSM-based optimization methods to formulate frying stable synergistic blends of natural antioxidants (Hras, Hadolin, Knez, & Bauman, 2000; Jaswir & Man, 1999; Jaswir et al., 2000). However, the hybrid PCA and RSM approach has not been tested previously.

Through this study, the impact of ROSM and AP on the frying performance of SO blends was tested. The time-dependent monitoring of the formation of polar and polymeric compounds and changes in physicochemical parameters over time was performed. Optimization of a synergistic blend of ROSM and AP, with greatest frying stability, was achieved using the PCA–RSM approach. This hybrid PCA–RSM method is likely to improve the predictive accuracy of the model by amalgamating the unique characteristics of each approach.

2. Materials and methods

2.1. Materials

Fresh lots of SO (refined, bleached, deodorized, and free from added antioxidants), oleoresin ROSM (Moroccan variety, oil soluble formulation) and AP (> 99%) were supplied by Synthite Industries Limited (Kerala, India). The initial peroxide value (AOCS, 1993) and fatty acid composition (gas chromatography, TSQ 8000, GC–MS, Thermo Fisher Scientific, Austin, TX, USA) of SO were $\leqslant$1.5 milliequivalents O_2/kg oil and 6.3% C16:0, 3.6% C18:0, 21.7% C18:1, 68.4% C18:2, 1.7% C18:3, respectively. The contents of active antioxidant compounds in ROSM *viz.*, carnosic acid and carnosol,

Table 1
Two factor and five levels central composite rotatable design and concentration levels (mg/kg) of food additives (oleoresin rosemary (X_1) and ascorbyl palmitate (X_2)) in sunflower oil blends (SOB).[≠]

Run No.	Sunflower oil blends	Coded values of independent variables (actual values)		Initial value of compositional parameters							
		X_1	X_2	TPC[a]	TGP[b]	TGD[c]	oxTGM[d]	DG[e]	FFA[f]	IP[g]	CDV[h]
4	SOB1 (Factorial)	1 (1309.62)	1 (270.71)	4.32^{b}	0.31^{a}	6.32^{a}	18.98^{ab}	9.72^{ab}	1.77^{a}	3.89^{e}	10.67^{a}
5	SOB2(Axial)	−1.414 (200)	0 (200)	4.41^{a}	0.31^{a}	6.46^{c}	19.37^{e}	9.92^{d}	1.80^{a}	3.38^{a}	10.84^{c}
9	SOB3(Centre)	0 (850)	0 (200)	4.40^{a}	0.31^{a}	6.44^{bc}	19.33^{e}	9.90^{d}	1.80^{a}	3.64^{c}	10.73^{b}
6	SOB4(Axial)	1.414 (1500)	0 (200)	4.33^{b}	0.31^{a}	6.34^{a}	19.02^{b}	9.74^{b}	1.77^{a}	4.16^{f}	10.68^{a}
1	SOB5(Factorial)	−1 (390.38)	−1 (129.29)	4.36^{a}	0.31^{a}	6.38^{b}	19.15^{c}	9.81^{b}	1.78^{a}	3.70^{d}	10.72^{b}
2	SOB6(Factorial)	1 (1309.62)	−1 (129.29)	4.30^{b}	0.31^{a}	6.30^{a}	18.89^{a}	9.68^{a}	1.76^{a}	4.54^{g}	10.66^{a}
12	SOB7(Centre)	0 (850)	0 (200)	4.38^{a}	0.31^{a}	6.41^{b}	19.24^{d}	9.86^{c}	1.79^{a}	3.62^{c}	10.77^{bc}
8	SOB8(Axial)	0 (850)	1.414 (300)	4.36^{a}	0.31^{a}	6.38^{b}	19.15^{c}	9.81^{b}	1.78^{a}	3.45^{b}	10.72^{b}
10	SOB9(Centre)	0 (850)	0 (200)	4.37^{a}	0.31^{a}	6.40^{b}	19.20^{cd}	9.83^{b}	1.79^{a}	3.60^{c}	10.74^{b}
7	SOB10(Axial)	0 (850)	−1.414 (100)	4.36^{a}	0.31^{a}	6.38^{b}	19.15^{c}	9.81^{b}	1.78^{a}	3.98^{ef}	10.72^{b}
13	SOB11(Centre)	0 (850)	0 (200)	4.33^{b}	0.31^{a}	6.34^{a}	19.02^{b}	9.74^{ab}	1.77^{a}	3.60^{c}	10.73^{b}
11	SOB12(Centre)	0 (850)	0 (200)	4.35^{a}	0.31^{a}	6.37^{b}	19.11^{c}	9.79^{b}	1.78^{a}	3.64^{c}	10.74$_{b}$
3	SOB13(Factorial)	−1 (390.38)	1 (270.71)	4.38^{a}	0.31^{a}	6.41^{b}	19.24^{d}	9.86^{c}	1.79^{a}	3.73^{d}	10.77^{bc}
Experimental domain											
Independent variables			−1.414	−1		0		1		1.414	
X_1: Concentration of oleoresin rosemary (mg/kg)			200	390.38		850		1309.62		1500	
X_2: Concentration of ascorbyl palmitate (mg/kg)			100	129.29		200		270.71		300	

[≠] All the CCRD trials were conducted in duplicates. The response variables were reported as the mean value of two determinations for each set of experimental combination ($n = 4$) with coefficient of variation (=standard deviation/mean) <10%. Mean values with different superscript letters are statistically different ($p < 0.05$).
[a] Total polar content (% *w*/*w*).
[b] Triglyceride polymers (mg/g oil).
[c] Triglyceride dimers (mg/g oil).
[d] Oxidized triglyceride monomers (mg/g oil).
[e] Diglycerides (mg/g oil).
[f] Free fatty acids (mg/g oil).
[g] Induction period (h).
[h] Conjugated diene values (mmol/L).