

Oleomargarine Production Using Hazelnut Oil-Carnauba Wax Mixture: Process Optimization and Characterization

Şerife Çevik^{1*}, Erkan Karacabey², Gülcan Özkan²

Abstract: In this study, oleomargarine production was performed by using carnauba wax for the mixture of refined hazelnut oils enriched with virgin olive oil. The response surface methodology was used for the evaluation of the studied responses depending on the production parameters and for their optimization. Hardness and stickiness value (g force), oil binding capacity (%) and crystal formation time (min.) of the oleomargarines were determined. The oleomargarine process was optimized by using the response surface methodology, where the stickiness and crystal formation time (CFT) were minimized and the oil-binding capacity (OBC) (%) was maximized. By the way the optimum production formulation was determined. Acidity, peroxide values, fatty acid composition and DSC melting profiles were analyzed besides of hardness and stickiness value (g, force), oil-binding capacity (OBC, %), crystal formation time (CFT, min). Meanwhile, in oleomargarines, the total phenolic compound and total sterol amounts were spectrophotometrically measured and tocopherol compositions were determined by HPLC. The ratio of oleogelator was found to be significant, since it causes some changes in the hardness and stickiness, CFT (min), and OBC (%) values of oleomargarines as well as physical properties including color values, melting and crystallization temperatures. Oleomargarine samples had higher values of melting and crystallization than the breakfast margarine, which were used as reference food materials. The fatty acid composition (%) of oils and oleomargarine were rich in terms of mono and polyunsaturated fatty acids, whereas saturated ones were at low. When the margarine and oleomargarine samples were compared, the saturated fatty acid content of the oleomargarine samples were found to be significantly lower than the margarine samples. Enrichment with virgin olive oil differed the fatty acid composition, total phenolic content, β - sitosterol and tocopherol composition of oleomargarines depending on its addition ratio in mixture.

Keywords: Edible oils, carnauba wax, oleomargarine, optimization, RSM.

¹**Address:** Isparta University of Applied Sciences, Gelendost Vocational School, Department of Food Processing, Isparta, Türkiye.

²**Address:** Suleyman Demirel University, Faculty of Engineering, Department of Food Engineering, Isparta, Türkiye.

***Corresponding author:** serifecevik@isparta.edu.tr

Citation: Çevik, S., Karacabey, E., Özkan, G. (2022). Oleomargarine Production Using Hazelnut Oil-Carnauba Wax Mixture: Process Optimization and Characterization. Bilge International Journal of Science and Technology Research, 6(2): 118-131.

1. INTRODUCTION

Fats play a crucial role at the processing of various food materials due to their great nutritional properties. The amount and composition of fat have an effect on the basic properties of the food, such as rheological and sensory properties, flavor, shelf life and nutritional value. Edible oils are classified as liquid, semi-solid and solid (hard) oils according to their structural properties at room temperature. These physical states determine not only their basic

properties, but also usage areas (Öğütçü and Yılmaz, 2015, Roller and Jones, 1996). For example, oils that are completely liquid at room temperature are considered as salad oil and/or edible oil. On the other hand, easy spread form solid fats are used as a breakfast spreadable margarine, and oils with higher fat content (margarine and shortening) are used in bakery and patisserie products (cookies, cakes, pastries, etc.) (Öğütçü and Yılmaz, 2015, Pehlivanoglu et al., 2018). In recent years, consumers have led their attention to healthier, natural and functional foods

to meet their nutritional needs in safeway. Bioactive components important for human health vary depending on the raw material used to produce these oils, but the common point valid for all of them is that they constitute essential fatty acids, natural antioxidants such as phenolic substances and tocopherols, and lipophilic components such as sterols (Karasu, 2015).

In addition, the rapid changes in human being-life behavior and the high rate of participation in business life increase the interest in safe and functional food consumption. One of the dietary recommendations made for the protection of human health and accepted all over the world is to reduce the total saturated fat and *trans* fatty acid intake in the diet. Mensink et al. (2003) stated that when fatty acids in the unsaturated *cis* form are consumed instead of *trans* fatty acids and saturated fatty acids, health risks are effectively reduced (Mensink et al., 2003). In addition, *trans* fatty acids cause the high level of bad cholesterol (LDL), whereas they decrease the level of good cholesterol (HDL) (Legault et al., 2004, Brandt et al., 2009). In contrast to *trans* and saturated fatty acids in fat consumption, the World Health Organization (WHO) recommends the consumption of vegetable oils being rich in unsaturated fatty acids. However, it is known that *trans* and saturated fatty acids play a major role in the texture, taste, flavor and aroma of food products, and their direct replacement with unsaturated fats may cause some technical problems in product quality. In order to provide these properties to oil-based products, some technological processes such as hydrogenation, interesterification, fractionated crystallization or a new technology, oleogelation is required to obtain a solid fat with a high melting point. Shorts and hydrogenated oils are formulated to obtain solid fats such as margarine. With the help of these techniques, oils are given functionality such as elasticity, spreadability and plasticity. The mentioned features are important in the formation of the structure that consumers like and prefer on the product (Wassell et al., 2010, Marangoni and Garti, 2011, Pehlivanoglu et al., 2017, Pehlivanoglu et al., 2018).

In this study, it was aimed to develop a new product composition for oleomargarine that does not contain *trans* fat and is low in saturated fatty acid and rich in mono- or polyunsaturated fatty acids. To achieve this purpose, hazelnut oil was used as a main oil and enriched with virgin olive oil and final mixture were gellated with carnauba wax. The procedure was also optimized. It is thought that these basic results will contribute significantly to oleomargarine production and to the related food industry.

2. MATERIAL AND METHODS

2.1. Material

In the study, refined hazelnut oil used in oleomargarine production was purchased from Çotanak A.Ş. To enrich hazelnut oil, natural extra virgin olive oil was purchased from Tariş A.Ş. As an oleogelator, Kahlwax brand refined carnauba wax was obtained from Ejder Kimya A.Ş.

2.2. Experimental Design

Oleomargarines (oleogel) were prepared by mixing the hazelnut oil-olive oil mixture and gellated with carnauba wax. Table 2 presents the all trials and corresponding mixture ratios for oleomargarine production.

The textural properties, oil-binding capacity, crystal formation time and color values of oleomargarine samples were statistically evaluated using the Response Surface Method (RSM), and optimum conditions were determined for the production of oleomargarine with the desired properties. Crystal formation time, oil-binding capacity, textural properties, color values, peroxide value, acidity value and fatty acid composition of the samples were analyzed as dependent variables.

Central Composite Design was chosen as the experimental design. The independent variables are the precious oil addition ratio (X1) and wax ratio (X2) added to the base oil for enrichment. The coded and uncoded values of the independent variables are given in Table 1 and the central composite design is given in Table 2.

Table 1. The coded and uncoded values of the independent variables in the trial design used in the Production of Oleomargarine

Independent variables	Factor Levels				
	lowest (-1.41)	low (-1)	Centre (0)	High (1)	Highest (1.41)
X1:Oil Addition Ratio (g/100g)	0.00	4.39	15.00	25.61	30.00
X2:Wax Ratio (%)	5.00	5.73	7.50	9.27	10.00

Table 2. Central mixed design applied in the samples used in Oleomargarine Production

Ru n ^a	Encoded Variables		Independent variables	
	X1	X2	Oil Addition Ratio (g/g)	Wax Ratio (%)
1	1	-1	15.00	7.50
2	0	0	15.00	7.50
3	0	0	0.00	7.50
4	-1	1	15.00	5.00
5	0	0	25.61	9.27
6	-1.41	0	15.00	7.50
7	0	0	4.39	9.27
8	1.41	0	15.00	10.00
9	0	-1.41	15.00	7.50
10	0	-1	30.00	7.50
11	1	1	25.61	5.73
12	0	0	4.39	5.73
13	0	1.41	15.00	7.50

^a, randomized

2.3. Preparation of Oleomargarine (Oleogel)

In the study, hazelnut oil was the base oil for the production of oleomargarine (oleogel). It was enriched with natural extra virgin olive oil at different ratios (Table 2). Oleomargarine was obtained by adding carnauba wax to hazelnut oil/extra virgin olive oil mixture at the specified ratio in Table 2. In oleomargarine production, the mixing temperature was adjusted according to the wax melting temperature (90 °C). After the wax completely melted in the mixture, it was kept at this temperature for a certain time (5 minutes). The sample required for the oil-binding capacity and crystal formation time was taken as a liquid phase immediately after formulation was ready and the remaining part was left for the crystallization at room temperature.

2.4. Determination of oil-binding capacity

The method adapted by Da Pieve et al. (2010) was used for the analysis of oil-binding capacity (Da Pieve et al., 2010). First, the tare (a) of the empty eppendorf tube was determined. Afterwards, approximately 1 mL of oleomargarine samples from the completely melted mixture was taken into empty eppendorf and kept in the refrigerator for 1 hour for oleomargarine formation. When the oleomargarine was completely formed in the refrigerator, the tube was weighed (b). In the final step, the eppendorf tube was centrifuged at 1000 rpm for 15 minutes at 20 °C, then turned down and kept that position for 3 minutes to drain excess oil and weighed again (c). Leakage oil (%) and oil-binding capacity were calculated as percent (%) for each sample according to Equations 1 and 2.

$$\% \text{ Leaked oil} = \frac{\{(b-a)-(c-a)\}}{(b-a)} \cdot 100 \quad \text{Eq. 1}$$

$$\% \text{ Oil Binding Capacity} = 100 - \text{Leaked oil} \quad \text{Eq. 2}$$

2.5. Crystal formation time

Approximately 10 ml of oleomargarine sample was taken from the completely melted mixture into a glass tube and kept in a water bath at 90 °C for 2 hours. The tube was then allowed to cool down to room temperature to form a gel. Gelation time was accepted as the cooling time until the flow was not observed when the tube was turned down (Dassanayake et al., 2009).

2.6. Determination of the textural properties of oleomargarine samples

To determine the textural properties of oleomargarine samples, the produced oleomargarine samples were kept at refrigerator temperature (+4 °C) for overnight, immediately after production. At the end of the period, the hardness and stickiness values of the oleomargarine samples were determined with Texture Analyzer (model/marka) using a stainless ball probe (P/0.75S). The speed of the probe was determined as 1 mm/s during the test and 2 mm/s after the test (Moskowitz, 1987).

2.7. Determination of free acidity value

Free fatty acidity value was determined using the AOCS Ca 5a-40 standard method (AOCS, 1998) and the results were calculated as % oleic acid.

$$\text{Acidity}(\% \text{ Oleic acid}) = \frac{v}{m} * 2.8 \quad \text{Eq. 3}$$

v= amount of spent KOH (ml)

m= sample amount (g)

2.8. Determination of peroxide value

The peroxide value was determined according to the AOCS Cd 8-53 standard method (AOCS, 1998) and the results were calculated as meq O₂/kg oil.

$$\text{Peroxide Value} \left(\text{meq} \frac{\text{O}_2}{\text{kg yağ}} \right) = \frac{(a-b) \times N \times 1000}{m} \quad \text{Eq. 4}$$

a= the amount of sodium thiosulfate consumed for the sample in the titration, ml

b= Sodium thiosulfate amount spent on the blank in the titration, mL

N= Sodium thiosulfate normality, N

m= amount of sample, g

2.9. Determination of specific absorbance values (K232, K270) in UV light

The method defined by Codex Alimentarius (2001) was used to determine the specific absorbance values (K232, K270) in UV light (Alimentarius, 2001).

2.10. Determination of total carotenoid and chlorophyll amount

Minguez-Mosquera et al. (1991), chlorophyll and carotenoid pigments of oils were calculated by measuring absorbances at 470nm, 630 nm, 670 nm and 710 nm wavelengths (Isabel Minguez Mosquera et al., 1991).

$$\text{Carotenoid amount (mg carotenoid/kg oil)} = \frac{(A_{470} \times 10^6)}{(2000 \times 100 \times L)} \quad \text{Eq. 5}$$

$$\text{Chlorophyll amount (mg chlorophyll/kg oil)} = \frac{(A_{670} \times 106)}{(613 \times 100 \times L)} \quad \text{Eq. 6}$$

Eq, A, absorbance; L represents the beam path (cell thickness, mm).

2.11. Determination of fatty acid composition

The IUPAC 2.301 method was used for the preparation of fatty acid methyl esters (Paquot and Hautfenne, 1987). 0.1 g sample was first mixed with 2 mL of heptane and shaken, then 0.2 mL of 2N methanolic potassium hydroxide derivative solution was added. Then the mixture was kept at 70 °C for 30 minutes to complete derivatization. The upper phase fatty acid methyl esters with clarified heptane was injected into the Gas Chromatography system (GC) for determination. Fatty acid components of the oils were determined using the AOCS Official Method Ce 1-62 (AOCS, 1997). The characteristics and operating conditions of the GC device are presented in Table 3.

Table 3. Properties of Gas Chromatography (GC) and working conditions

Gas Chromatography	Agilent
Injector temperature	250 °C
Detector temperature	250 °C
Flow Rate(psi)	15
Detector	FID
Used Gas	Helium
Used Column	Cp WAX 52 CB 50 m * 0.32 mm, 1.2 µm
Temperature Program	After 4 minutes at 60 °C, it reaches 175 °C with an increase of 4 °C per minute. It waits for 27 minutes at 175°C. Reaches 215°C with 4°C increments per minute and waits for 5 minutes. It reaches 240 °C in increments of 4 °C per minute.

In the determination of fatty acids, a mixture of methyl esters of fatty acids, including trans fatty acids, starting from butyric acid to nervonic acid, was used. The fatty acid composition of the samples was calculated as % area with the help of HP Chemstation computer program.

2.12. Determination of the total amount of phenolic substances

The total amount of phenolic compounds extracted from oils by methanol was measured using the Folin-Ciocalteu spectrophotometric method at a wavelength of 765 nm, and the result was calculated as mg gallic acid equivalent (GAE)/kg oil (Singleton and Rossi, 1965).

2.13. Tocopherol Profile Analysis by HPLC

Analysis of the tocopherol components of the oils was carried out by modifying the AOCS Official Method Ce 8-89 (De Greyt et al., 1998). 250 µL of oil samples was dissolved in the mobile phase Heptane/THF (95:5, vol/vol) solvent and the volume was completed to 1 mL and 100 µL of the sample was taken and injected into the HPLC device.

Table 4. Features of the HPLC and operating conditions

Detector	DAD Detector
Auto sampler system controller	SIL-20AC prominence
Pump	LC- 20AT prominence
Degasser	DCU-14A
Column furnace	CTO-10ACvp
Column	Luna Silika (250*4,6 mm, 5 µm)
Mobile Phase	Heptane/THF (95:5)
Flow Rate	1.2 mL/min.
Column Temperature	25° C
Injection Volume	20 µl

In the analysis of tocopherol components, α -(alpha) tocopherol, β -(beta) tocopherol, γ -(gamma) tocopherol and

δ -(delta) tocopherol (Cabliocem, Germany) were used as standards. Analyzes were made in three parallels. The sample chromatograms showing the separations of the standards were presented in Figure 1

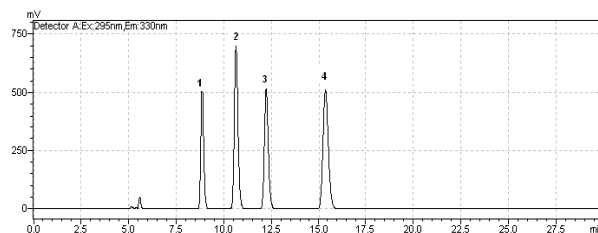


Figure 1. Chromatogram of the standards: 1: α -(alpha) tocopherol, 2: β -(beta) tocopherol, 3: γ -(gamma) tocopherol, and 4: δ -(delta) tocopherol

In the analysis of tocopherol components, α -(alpha) tocopherol, β -(beta) tocopherol, γ -(gamma) tocopherol and δ -(delta) tocopherol (Cabliocem, Germany) were used as standards. Analyzes were made in three parallels. The sample chromatograms showing the separations of the standards were presented in Figure 1.

2.14. Spectrometric sterol determination

The cholesterol method by Rudel and Morris (1973) was modified and sterol extraction was performed from the oil samples and the total sterol (β -sitosterol) amounts were determined by the FeCl₃ method. In this method, sterol substances were first extracted from the oil samples by saponification. The extracted samples were treated with FeCl₃ solution to determine the amount of sterol. Then, 1 ml of H₂SO₄ is added on it and the pink color formed after waiting for an average of 45 minutes were read at 560 nm in the spectrophotometer. Results were calculated from the sterol calibration chart (Rudel and Morris, 1973).

2. 15. DSC analysis

DSC analyzes of oleomargarine and margarine samples were carried out at Burdur Mehmet Akif Ersoy University Scientific and Technology Application and Research Center with AOCS Official Method Cj 1-94 as a service purchase. The operating conditions used in the analysis were given below (Society, 1998).

Brand : Perkin Elmer

Model: DSC 4000

Amount of sample: 3-10 mg

Working Principle: After being heated from 25 °C to 100 °C in 10 degree increments per minute in a nitrogen environment and kept for 10 minutes, it was cooled from 100 °C to -50 °C for 30 minutes and kept from -50 °C to 100 °C. It has been heated to.

2.16. Statistical Analyzes

In the study, the response surface methodology (Response Surface Method, RSM) was used to plan the production of oleomargarine (central mixed design), evaluate the

responses, and find the optimum points. Minitab Statistics Package Program (17) was used in the implementation of the method. Model adequacy was evaluated by considering R^2 value. Model was determined according to bivariate quadratic equality (Eq.7).

$$Z = \beta_0 + \sum_{i=1}^2 \beta_i X_i + \sum_{i=1}^2 \beta_{ii} X_i^2 + \sum_{i=1}^1 \sum_{j=i+1}^2 \beta_{ij} X_i X_j$$

Eq. 7

In the equation, Z dependent variable, X independent variable, β_0 constant coefficient, β_i first-order (linear) equation coefficient, β_{ii} quadratic equation coefficient and β_{ij} is the two-factor cross-interaction coefficient.

3. RESULTS

Refined hazelnut oil and natural extra virgin olive oils were used for the production of oleomargarine, and carnauba wax was used as a gelling agent. Refined hazelnut oil was enriched with extra virgin olive oil, and carnauba wax was added to the oil mixture at the specified ratio determined in the design, and oleogel production was carried out. Before the production of oleomargarine, the main quality parameters of the oils such as free acidity, peroxide, UV specific absorbance values (K_{232} and K_{270}) and color values such as chlorophyll and carotenoid values, fatty acid composition, total phenolic substance content, tocopherol amount and sterol amount (β -sitosterol) were determined.

The free acidity value, which is defined as the percentage of oleic acid of the total unbound fatty acids in oils, and the peroxide value, which is the indicator of the primary oxidation products in oils, are determined by titration (Nas and Gökalp, 2001). K_{232} conjugated diene compounds (the indicator of the primary oxidation products) and K_{270} conjugated triene components (the indicator of the secondary oxidation products) are determined spectroscopically at a wavelength of 232 nm and 270 nm, respectively, for oil samples (Ayadi et al., 2009). Color substances, which are one of the important quality parameters, are composed of chlorophylls, which are responsible for the green color and stability of the oils and have antioxidant activity in the dark and pro-oxidant activity in the light, and carotenoids responsible for the color from yellow to brown (Ayadi et al., 2009). The values of free acidity (% oleic), peroxide (meq O₂/kg oil), K_{232} and K_{270} , chlorophyll and carotenoid values of the oils used in the study were given in Table 5.

Table 5. Average values of oil quality parameters (n=3)

Sample	^a HO	OO
Acidity (% oleic)	0.13±0.020	0.86±0.020
Peroxide Value (meq O ₂ /kg of oil)	4.70±0.640	6.66±0.600
K_{232}	2.43±0.010	2.06±0.010
K_{270}	0.89±0.000	0.16±0.000
Chlorophyll (ppm)	0.03±0.000	0.04±0.001
Carotenoid (ppm)	0.02±0.001	0.11±0.000

^aHO: Hazelnut oil, OO: Olive oil

Among the quality parameters of the oil samples, acidity values were between 0.13 - 0.86, and peroxide values were between 4.70 and 6.66. These values were examined according to the Turkish Food Codex Communiqué on Oils Called by Plant Name (Communiqué No: 2012/29) and the Turkish Food Codex Olive Oil communiqué and it was determined that they were within the limits determined by the codex. Our data are compatible with the findings obtained in the literature studies. If we examine the studies on various oils, free acidity (% oleic) and peroxide values (meq O₂/kg oil) were found in the range of 0.05 to 0.9 in refined hazelnut oil, respectively (Kesen et al., 2016). It has been reported that it varies between 0.52 - 1.05 and 3.20 - 9.47 in olive oils (Bozdoğan Konuşkan, 2008, Aşık and Özkan, 2011, Cevik et al., 2014). K_{232} and K_{270} values were determined as 0.89 - 2.43 in hazelnut oil and 0.16 - 2.06 in olive oil, respectively. No study has been found in the literature on the K_{232} and K_{270} values of refined hazelnut oil. The K_{232} and K_{270} values of olive oil were determined as 1.4935 and 0.0985 (Aşık and Özkan, 2011). Our data are compatible with the findings obtained in the literature studies. Chlorophyll and carotenoid values affecting the appearance of oils were determined in the range of 0.033 - 0.021 (ppm) and 0.043 - 0.111 (ppm) in refined hazelnut oil and virgin olive oil, respectively. While no study has been found in the literature on the color values of refined hazelnut oil, it has been reported that the chlorophyll and carotenoid values of the virgin olive oil were determined in the range of 0.457 - 2.276 and 0.438 - 1.383 (ppm), respectively (Aşık and Özkan, 2011, Cevik et al., 2014).

Before oleomargarine production, the fatty acid composition of refined hazelnut oil and virgin olive oil were determined and given in Table 6.

Table 6. Average values of fatty acid composition (% area) of oils (n=2)

Fatty Acid	^a HO	OO
Myristic acid (C14)	0.04±0.00	Nd
Palmitic Acid (C16)	5.56±0.06	12.51±0.97
Stearic acid (C18)	2.73±0.02	3.18±0.08
Σ SFA ^b	8.33±0.04	15.68±1.04
Palmitoleic acid (C16.1)	0.17±0.00	0.57±0.00
Oleic Acid (C18.1)	74.52±0.05	71.64±0.89
Gadoleic Acid (C20.1)	nd	0.53±0.03
Σ MUFA	74.69±0.05	72.74±0.86
Linoleic acid (C18.2)	16.80±0.08	10.65±0.14
Gamma Linolenic acid (C18.3)	0.19±0.00	0.58±0.05
Alpha Linolenic acid (C:18:3n3)	nd	0.35±0.01
Σ PUFA	16.99±0.09	11.58±0.18

^aHO: Hazelnut oil, OO: Olive oil

^b Σ SFA: Total Saturated Fatty Acid, Σ MUFA: Total Monounsaturated fatty acid, Σ PUFA: Total Polyunsaturated Fatty acid, ^cnd: below the detectable value.

The fatty acid composition of the refined hazelnut oil consisted of 8.33% saturated fatty acids, 74.69% monounsaturated fatty acids and 16.99% saturated fatty acids. The fatty acid composition of olive oil consisted of 15.68% saturated fatty acids, 72.74% monounsaturated fatty acids and 11.58% polyunsaturated fatty acids. In another study examining the fatty acid composition of crude and refined hazelnut oils, the fatty acid composition of refined hazelnut oil was found as 8.38% of saturated fatty acids, 71.20% of monounsaturated fatty acids and 20.24% of polyunsaturated fatty acids (Kesen et al., 2016). Tüfekci (2018) determined that the fatty acid composition of hazelnuts grown in the black sea region, in his doctoral thesis, the mean of SFA, MUFA, and PUFA 8.12, 83.16 and 8.56, respectively. The fatty acid composition varies depends on the harvested region and the harvest season (Tüfekci, 2018). In studies examining the fatty acid composition of Memecik and Gemlik olive oils, it was determined that the fatty acid composition were as 12.75-24.86% saturated fatty acids, 58.72-76.86% monounsaturated fatty acids and 9.44 - 13.64% polyunsaturated fatty acids (Cevik et al., 2014, Aşık and Özkan, 2011). It has been reported that the fatty acid profile of oils changed depending on maturity (Cevik et al., 2014).

Functional compounds in oils are important for human health, but they vary depending on different factors including the raw material. Thus, it is required to define them for corresponding raw materials. Essential fatty acids were given in Table 6, natural antioxidants such as phenolic substances and tocopherols lipophilic bioactive components such as colorants, sterols were given in Table 7.

Table 7. Average values of functional properties of oils (n=2)

Functional Feature	^a HO	OO
Total Phenolic Substance (mg GAE/kg oil)	61.59±2.20	193.79±2.20
Alpha tocopherol (α)	618.64±0.53	171.13±0.19
Beta tocopherol (β)	27.61±0.20	37.43±0.50
Gamma tocopherol (γ)	85.89±0.45	nd
Total sterol (β -sitosterol)	866.21±4.58	1160.60±8.02

^aHO: Hazelnut oil, OO: Olive oil

nd: not determined

The total amount of phenolic substances of the oils was determined as gallic acid equivalent (GAE). It was determined as 61.59 mg/kg for hazelnut oil and 193.79 mg/kg for olive oil. Yorulmaz (2009) determined the sterol, phenolic and triglyceride structures of Turkish olive oils. They reported the total phenolic content of olive oils obtained from different regions in the range of 48.72-646.30 ppm (Yorulmaz, 2009). Aşık and Özkan (2011) studied the physical, chemical and antioxidant properties of olive oil obtained from the Memecik olive variety, and found the total phenolic content of olive oils as 169.25 mg GAE/kg oil. Cevik et al. (2014) examined the effect of harvest time on the physicochemical quality parameters, oxidation stability and volatile compounds of extra virgin olive oil obtained from Gemlik olive fruits at different maturity stages. The total phenolic content of the oils varied from 86.11 and 227.80 mg GAE /kg oil according to the harvest time. Delil et al. (2022), in their study of optimizing the phenolic composition of extra virgin olive oil, determined the total phenolic content of the olive oils obtained at different kneading temperatures and times in the range of 86.11-338.94 mg/kg oil (Delil et al., 2022).

The amounts of α , β and γ tocopherols for corresponding refined hazelnut oil/olive oil was found to be as 171.13/618.64 mg/kg oil, 27.61/37.43 mg/kg oil and nd/85.89 mg/kg oil, respectively. In the study about the lipid properties and oxidative stability of Turkish Tombul hazelnut (*Corylus avellana* L.), oil sample was extracted from Tombul hazelnuts and the tocopherol composition of hazelnut oil was determined. The amount of α tocopherol was determined as 38.23 mg/100 g oil, the amount of β tocopherol was 1.15 mg/100 g oil and the amount of γ tocopherol was 3.89 mg/100 g oil (Alasalvar et al., 2003). In the study investigating the effect of refining on the bioactive composition and oxidative stability of hazelnut oil, it was stated that the refining process caused a decrease in the amount of tocopherol. At the end of the refining process, the tocopherol composition of hazelnut oil was determined and the amount of α - tocopherol was 459.69 mg/kg oil, β - tocopherol amount was 10.41 mg/kg oil, γ - tocopherol amount was 97.35 mg/kg oil, and δ - tocopherol amount was 4.82 mg/kg oil (Durmaz and Gökmen, 2019).

In the study conducted by Aşık and Özkan (2011) the physical, chemical and antioxidant properties of olive oil obtained from the Memecik olive variety were investigated. The tocopherol composition of olive oils was determined

and the amount of α -tocopherol was 205.45 mg/kg oil, β -tocopherol amount was 1.645 mg/kg oil, γ -tocopherol amount was 6.065 mg/kg oil, δ -tocopherol amount was 0.325 mg/kg oil. Cevik et al. (2014), in their study the tocopherol composition of the oil samples extracted from Gemlik at different maturity stages. It has been determined that the amounts of α -, β -, and γ -tocopherol varied in the ranges of 128.35-154.50 mg/kg oil, 0.90-5.45 mg/kg oil, and 0.80-1.20 mg/kg oil.

The variation range of total sterol content (in terms of β -sitosterol) was determined. The result was in the range of 866.21 – 1160 mg/kg oil. No study has been found in the literature on determining the sterol content of oils by spectroscopic method. However, in literature studies, total sterol amounts of oils were determined by GC method. In one of them, Turkish Chubby Hazelnut (*Corylus avellana* L.) lipid properties and oxidative stability, the sterol composition of plump hazelnut oil were examined. The amount of β -sitosterol was determined as 105.48 mg/100 g oil (Alasalvar et al., 2003). Yorulmaz (2009) studied the sterol, phenolic and triglyceride structures of Turkish olive oils and determined the total sterol amount of olive oils obtained from different olive varieties in the range of 728.75 – 2247.07 mg/kg. In their study, Matthäus and Özcan (2011) determined the total sterol content of olive oils obtained from Turkish olive varieties and reported their range as 1200.80 - 2762 mg/kg oil ((Matthäus and Özcan, 2011). Aydın et al. (2020) studied the effect of kneading temperature and time on the total sterol content of olive oils. They found that total sterol content was in the range of 936.78 - 1574.55 mg / kg oil (Aydın et al., 2020). Our results about total sterol content of oil samples are consistent with the part of the literatures, although there are differences as well. These variations in the results were thought to be due in part to the differences in methodologies used.

3.1. Experimental Design of Oleomargarines in which Refined Hazelnut Oil is Enriched with Extra Virgin Olive Oil

After enrichment of refined hazelnut oil with extra virgin olive oil, oleomargarin was produced using carnauba wax. The textural values of hardness (g force) and stickiness (g force), crystal formation time and oil binding capacity of oleomargarine samples were measured (Table 8). The models defining the variation in these parameters (hardness (g force) and stickiness (g force), OBC (%) and CFT (min)) depending on process variables were developed and the obtained coefficients and model performance values were given in Table 9.

Table 8. Hardness (g, force), stickiness (g, force), OBC (%) and CFT (min.) values of oleomargarine samples

Run ^a	HOC ^b			
	Hardness	Stickiness	OBC	CFT
1	246.34	-58.94	85.18	9.20
2	245.03	-56.43	86.09	9.12
3	258.20	-60.46	85.67	10.00
4	43.84	-10.43	64.30	10.59
5	509.14	-109.82	96.46	9.50
6	247.68	-56.66	86.03	9.25
7	512.60	-108.47	96.52	9.36
8	673.69	-112.25	97.26	9.10
9	245.29	-57.35	87.41	9.20
10	250.52	-61.32	85.36	10.05
11	94.12	-21.23	70.42	10.38
12	89.19	-21.15	71.25	10.48
13	221.20	-54.79	86.18	9.27

^a, randomized, ^b, HOC, Hazelnut oil, olive oil, carnauba wax

The hardness of oleomargarine samples was measured after the samples were kept at +4 °C for one night and the results were found to be varied in the range of 43.84 - 673.69 g.force. It was determined that the stickiness value changed in the range of (-)112.25 – (-)10.43 g.force. The oil binding capacities (%) of the HOC samples were 64.30-97.26, respectively, while the crystal formation times (min) varied from 9.10 to 10.59 min. In the literature, no study was found in which refined hazelnut oil was enriched with extra virgin olive oil and gelled with carnauba wax. However, there are studies on the structuring of these oils and the production of oleomargarine. In the study, where it was aimed to determine the product with the most suitable spreadability for oleomargarine samples prepared by adding carnauba wax oleogelator (at the ratio of 3%, 7% and 10%) to olive oil, the hardness values were found to be in between 6.99 and 728.75 g, the stickiness value was between 10 and 200 g, and the OBC values (%) were found to vary between 40.82 – 93.41 (Yılmaz and Ögütçü, 2014a). In the study where they aimed to determine the product with the most suitable spreadability in oleomargarine samples prepared by adding carnauba wax oleogelator (at the ratio of 3%, 7% and 10%) to olive oil, the hardness values were between 6.99 and 728.75 g, whereas the stickiness values were between 10 and 200 g (Ögütçü and Yılmaz, 2014). In that study the OBC values of oleomargarine samples were determined and the results were found to vary between 40.82 – 93.41. In the study of optimization and characterization of soybean oil carnauba wax oleogel, hardness and OBC value changed between ND – 16.63(N), 75.33 – 99.73 (%), respectively (Thakur et al., 2022).

Table 9. Models of the changes in the hardness (g force), stickiness (g force), OBC (%) and CFT (min.) values of oleomargarines produced using carnauba wax after enrichment of refined hazelnut oil with natural extra virgin olive oil, depending on the production conditions. coefficients and evaluation parameters

Model Coef. ^a	HOC			
	Hardness	Stickiness	OBC	CFT
β ₀	358.8***	46.5***	-	18.25**
β ₁	-0.69ns	0.91ns	-0.04ns	-0.13ns
β ₂	-	-6.69***	19.10***	-
β ₁₁	0.047ns	-0.027ns	-0.002ns	0.004**
β ₂₂	18.40***	-1.05ns	-0.82***	0.102**
β ₁₂	-0.11ns	-0.02ns	0.01ns	0.003*
Model	***	***	***	***
R ²	99.60	97.78	99.20	99.32

^a. β₀ constant coefficient. β_i Coefficient of first order (linear) equation. β_{ii} quadratic equation coefficient and β_{ij} is the two-factor cross-interaction coefficient. ns. nonsignificant statically ($p \geq 0.05$); *. Statistically significant at the 95% level ($p \leq 0.05$); **. Statistically significant at the 99% level ($p \leq 0.01$); ***. Statistically significant at the 99% level ($p \leq 0.001$).

The developed expression for each response was evaluated in terms of model performance. All obtained equations explain more than 97% of the changes in the hardness and stickiness values of oleomargarine samples (HOC) depending on the processing conditions ($R^2 > 0.97$) (Table 9). In the models the oil addition ratio was found to be statistically insignificant in the models of hardness, stickiness and OBC (%) values of the HOC samples ($p > 0.05$). While the first-order term of oil addition ratio was statistically insignificant for the expression developed for the CFT (min.) value, its second-order term and interaction with wax ratios were found to be significant ($p \leq 0.05$). Another independent variable, the wax ratio, was significant for first order terms of all developed models and second order terms of the models for the hardness, OBC and CFT values of HOC samples ($p \leq 0.001$) (Table 9). The change of hardness and stickiness of oleomargarines as a function of oil addition and wax ratios were shown in Figure 2.

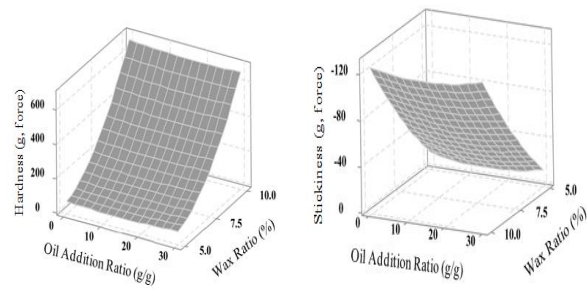


Figure 2. The effect of oil addition ratio (%) and wax ratio (%) variables of HOC oleomargarine samples on hardness (g force) and stickiness (g force) values of oleomargarines

As can be seen from Figure 2, there was no significant effect of oil addition ratio on the hardness value of the HOC sample. From the same figure, the strong effect of wax ratio can be seen, where the hardness increased with an increase in wax ratio (Figure 2). Similar effects of oil addition and wax ratios were determined on the stickiness value (Figure 2). With the increase of oil addition and wax ratios, an increase is observed in the adhesiveness value (Figure 2). Being consistent with our results, in other studies, an increase in the hardness and stickiness values of oleomargarines was detected with increasing ratio of gelling agents used (Yılmaz and Ögütçü, 2014a, Ögütçü and Yılmaz, 2014, Yılmaz and Ögütçü, 2014b).

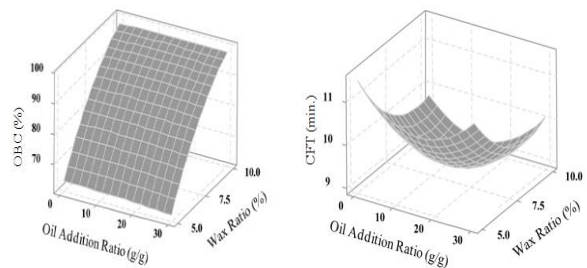


Figure 3. The effect of oil addition ratio (%) and wax ratio (%) variables on HOC oleomargarines OBC (%) and CFT (min) values

The effect of processing conditions on OBC (%) and CFT (min.) values of the HOC oleomargarine samples can be seen from Figure 3. There was no significant effect of oil addition ratio on OBC value of the HOC samples. On the other hand, an increase in the OBC value was detected with the increase in the wax concentration. The effects of oil addition and wax ratios on the CFT value were curved and had the same trends. The increases in both affected the CFT value of oleomargarine and CFT value initially decreased, but after a certain level of oil addition or wax ratio was exceeded, its trend change and an increase in CFT was observed (Figure 3).

Similarly, the oil-binding capacity of the oleomargarine s obtained by the sunflower wax, beeswax, carnauba wax or monoglyceride addition to olive oil increased as the amount of gelling agents added to the oil increased (Yılmaz and Ögütçü, 2014b;c;a). In that study, the crystallization time was also studied and it was found to decrease with

increasing wax ratio. This outcome showed an in accordance with the trend observed in our study. OBC is a measure showing the degree of liquid oil entrapment in the gel network. It has also been noted in previous studies that an increase in the gelator ratio in oil results in higher OBC and lower gelation time.

3.2. Oleomargarine Production Optimization and Model Validation

By using the response surface methodology, optimum production formulation of oleomargarine samples produced by adding carnauba wax to the blended oils in which refined hazelnut oil was enriched with natural extra virgin olive oil was determined. Stickiness value and crystal formation time were minimized, while oil binding capacity (%) value was maximized. The final formulation determined was given in Table 10.

Table 10. Optimum conditions used in the production of oleomargarine

Sample	X1(Addition Oil Ratio)	X2 (Wax Ratio)	d (Desirability)
^a HOC	17.27	9.71	1.00

^a, HOC; Hazelnut oil, olive oil, carnauba wax

The oil addition and wax ratios were determined as 17.27% and 9.71%, respectively. Depending on the criteria selected for optimization, the "desirability value" was calculated as 1.0.

Table 11. Experimental data of the stickiness value of oleomargarines produced under optimum conditions and values of model estimation intervals

Run	Experimental Data	Model Prediction Intervals (95% Confidence Level)	d (Desirability)
	Stickiness Value (g force)	Stickiness Value (g force)	
^a HOC	-108.06±4.50	-126.25; -98.23	0.99

^a, HOC; Hazelnut oil, olive oil, carnauba wax

In order to experimentally verify the predictive value of the model, the stickiness values of oleomargarines produced under optimum conditions (oil addition ratio and wax ratio) were determined and its mean value was -108.06±4.50 which was in the confidence interval produced by model (Table 11). The models of stickiness was experimentally confirmed.

Table 12. Experimental data and model estimation intervals of OBC (%) and CFT (min.) values of oleomargarines produced under optimum conditions

Sample	Experimental Data		Model Prediction Intervals (95% Confidence Level)			
	OBC (%)	CFT (min.)	OBC (%)	d	CFT (min.)	d
^a HOC	92.38±0.53	8.03±0.04	94.87-100.00	1.0	8.97-9.23	1.0

^a, HOC; Hazelnut oil, olive oil, carnauba wax

Similar to the model for stickiness value, accuracies of the expressions corresponding to OBC (%) and CFT (min) also were experimentally checked. Confidence intervals for these responses were given in Table 12 with the mean values of experimental OBC (%) and CFT (min) results of oleomargarine produced at the optimal conditions. The mean values of OBC and CFT were found to be within the model estimation ranges given in Table 12, and the models obtained according to these results were experimentally verified.

3.3. Determination of Characteristic, Functional and Quality Parameters of Oleomargarines Produced under Optimum Conditions

Hardness and stickiness, OBC (%) and CFT (min), acidity and peroxide values, fatty acid composition and DSC melting profiles were determined as the characteristic parameters of oleomargarine produced under optimum conditions and given in Table 13 - 16. Similarly, total phenolic and sterol content of oleomargarins as their functional properties were determined spectrophotometrically and tocopherol profile was figured out chromatographically and all were also presented in Table 17. It has been stated that there is a correlation between hardness and spreadability, but this relationship is not perfect. Hardness is defined as the force required to compress the sample under a certain pressure, while stickiness is defined as the force required to remove the sample from the surface. Therefore, it has been determined that both hardness and stickiness values should be at moderate levels in order to obtain an ideal spreadability. A good quality margarine should be hard enough to maintain its fluidity at room temperature and sticky enough to adhere to the surface it is applied to.

Table 13. Oleomargarine of produced under optimum conditions and margarine average values of hardness and stickiness values

^a Sample	HOC	M
Hardness Value (g force)	612.34±5.85	417.96±8.50
Stickiness Value (g force)	-108.06±4.5	-168.72±7.74

^a, HOC; Hazelnut oil, olive oil, carnauba wax, M; Margarine

The hardness value of HOC sample was higher than the margarine, and the stickiness value was lower (Table 13).

Table 14. Quality parameters of oleomargarines produced under optimum conditions

Quality parameters	^a HO	OO	HOC
	0.13±0.0	0.86±0.0	0.55±0.0
Acidity (% oleic acid)	2	2	0
Peroxide Value (meq O ₂ /kg of oil)	5.20±0.0	6.66±0.1	6.45±0.0
	7	1	5
	0.033±0.0	0.043±0.0	0.037±0.0
Chlorophyll (mg/kg oil)	000	001	003
	0.021±0.0	0.111±0.0	0.036±0.0
Carotenoid (mg/kg oil)	001	000	000

^a, HO; Hazelnut oil, OO; Olive oil HOC; Hazelnut oil, olive oil, carnauba wax

The acidity and peroxide value of the oils used in the study were in the ranges of 0.13 – 0.86 and 5.20– 6.66, respectively. Similarly, HOC samples produced at the optimal conditions was also analyzed and the acidity was found as 0.55 and peroxide was 6.45 (Table 14). In the literature, peroxide values of oleogel samples prepared by adding 3, 7 and 10% beeswax and carnauba wax to fish, hazelnut, pomegranate seed oil and olive oil, coincidence results were seen to be with those in this study. In the other study of virgin olive oil oleogels acidity and peroxide values determined as 1.95 - 2.14 and 12.48 - 16.76, respectively (Yılmaz and Demirci, 2021). Researchers' reports that the oil and wax samples used in gelling were effective on acidity and peroxide values (Yılmaz ve Ögütçü, 2014b;a, Ögütçü vd., 2015, Ögütçü ve Yılmaz, 2015a). It is thought that reasons such as the methods of obtaining the wax samples, the melting point in the oil, the waiting time by contacting the air at the wax melting temperature are also effective on the peroxide value. In addition, since the peroxide value is maximum 5 in the margarine codex, alternatively produced oleomargarines should not exceed this limit. Total chlorophyll and carotenoids content of the oils used in the study were determined as 0.033-0.043 and 0.021- 0.111 mg/kg oil and the HOC oleomargarine sample was examined and chlorophyll and carotenoids were found to be 0.037 and 0.036 mg/k g oil, respectively (Table 14). As a result of the literature survey, this is the first time reporting total chlorophyll and carotenoid content of oleomargarine.

Table 15. Fatty acid composition (%) of the oils used in the study, oleomargarines produced under optimum conditions and margarine

Fatty Acid	HO	OO	HOC	M
	0.00±0.00	0.00±0.00	0.00±0.00	3.78
Lauric Acid				
Myristic acid (C14)	0.04±0.00	0.00±0.00	0.03±0.00	2.02
Palmitic Acid (C16)	5.56±0.06	12.51±0.97	7.08±0.01	25.66
Stearic acid (C18)	2.73±0.02	3.18±0.08	2.83±0.02	10.86
∑SFA ^b	8.32±0.04	15.68±1.04	9.94±0.03	42.32
Palmitoleic acid (C16.1)	0.17±0.00	0.57±0.00	0.20±0.01	0.45
Oleic Acid (C18.1)	74.52±0.05	71.64±0.89	73.59±0.03	52.5
Gadoleic Acid (C20.1)	0.00±0.00	0.53±0.03	0.00±0.00	3.19
∑MUFA	74.69±0.05	72.74±0.86	73.79±0.03	56.14
Linoleic acid (C18.2)	16.80±0.08	10.65±0.14	15.59±0.02	0.0
Gamma Linolenic acid (C18.3)	0.19±0.00	0.58±0.05	0.46±0.03	0.89
Alpha Linolenic acid (C:18:3n3)	0.00±0.00	0.35±0.01	0.22±0.00	0.65
∑PUFA	16.99±0.09	11.58±0.18	16.27±0.02	1.49

^a M; Margarine HO; Hazelnut oil, OO; Olive oil, HOC; Hazelnut oil, olive oil, carnauba wax

^b ∑SFA: Total Saturated Fatty Acid, ∑MUFA: Total Monounsaturated fatty acid, ∑PUFA: Total Polyunsaturated Fatty acid, ^cnd: below the detectable value.

Hazelnut oil, olive oil, oleomargarine, and margarine were individually analyzed and each corresponding fatty acid composition was presented in Table 15. The saturated fatty acid percent (%) of hazelnut oil and olive oil were determined as 8.32% and 15.68%, respectively. As expected, saturated fatty acid percent of oleomargarine (9.94%) was in between 8.32 to 15.68% which was dependent partially on the mixing ratio in formulation followed during oleomargarine production. The corresponding value for margarine was determined as 42.32%. Total monounsaturated fatty acid content (%) of the oils varied from 72.74 - 74.69 and total polyunsaturated fatty acid content (%) was in between 11.58 - 16.99. Total monounsaturated fatty acid content (%) of oleomargarine and margarine were 73.79% and 56.14%, respectively. Table 15 also showed that total polyunsaturated fatty acid content (%) for oleomargarine and margarine were as 16.27% and 1.49%, respectively. The saturated fat content of the margarine sample was found higher than the HOC oleomargarine samples. The fatty acid composition of the oleomargarines produced in the study varies depending on the type of oil used in the mixture and the addition ratios in oil. Dominant monounsaturated fatty acid and polyunsaturated fatty acid were oleic acid (>70%) and linoleic acid (> 10%) for hazelnut oil, olive oil, and

oleomargarine, whereas those corresponding values were clearly lower for margarine (Table 15).

Table 16. DSC Values of oleomargarines produced under optimum conditions and margarine

	DSC Values	HOC	M
Crystallization (Tc)	^a Onsetc (°C)	68.77±1.0	19.52+0.6
	Peak (Tc. °C)	65.84±0.1	17.37+0.1
	Hc (J/g)	-1.52±0.1	-1.5+0.1
Melting (Tm)	Onsetc (°C)	66.64±0.1	42.72+0.3
	Peak (Tm. °C)	76.09±0.1	42.94+0.2
	Hm (J/g)	8.31±0.7	0.19+0.4

a, Onsetc; crystallization initiation temperature, Tc; crystallization temperature, Hc; crystallization enthalpy, Onsetm; melting start temperature, Tm; melting temperature, Hm; enthalpy of fusion. HOC; HOC; Hazelnut oil, olive oil, carnauba wax, M; Margarine

Thermal properties of oleomargarine and margarine were summarized in Table 16. Crystallization temperature and melting temperature of the oleomargarine sample were found to be as 65.84 °C and 76.09 °C, respectively. The crystallization temperature of the margarine was 17.37 °C and the melting temperature was 42.92 °C. The crystallization and melting temperature of the HOC sample was found to be higher than that of margarine. Similar to our results, it was reported that oleomargarine produced using carnauba wax had high crystallization and melting temperature values (Öğütçü, 2014). DSC melting profiles of oleomargarine samples (3, 7 and 10% carnauba wax add to olive oil) were investigated and crystallization temperature, melting temperature, crystallization enthalpy, and melting enthalpy was found to be varied in the ranges of 50.77 – 61.17 °C, 65.83 – 76.0 °C, -10.57 - -15.51 J/g, and 10.39 – 14.81 J/g, respectively. They reported that as wax concentration increased, the crystallization temperature of the oleogels decreased and the melting temperature increased (Öğütçü and Yılmaz, 2014). Carnauba wax oleogel DSC melting profiles was determined onset melting point 60 °C and peak point 85°C (Tabibiazar et al., 2020). The thermal properties of the prepared thyme and cumin-flavored virgin olive oil-sunflower wax oleogels examined. Crystallization onset temperature, peak temperature and crystallization enthalpy was found to be varied in the ranges of 60.55 – 61.37 °C, 58.72 – 59.54 °C, -11.44 - -8.58 J/g, respectively. Melting onset temperature, peak temperature and melting enthalpy was found to be varied in the ranges of 48.41 – 53.51 °C, 62.53 – 62.83 °C, 12.73- 13.64 J/g, respectively (Yılmaz and Demirci, 2021).

Table 17. Functional Properties of oils used in the study and oleomargarine produced under optimum conditions

Sample	HO	OO	HOC
Total Phenolic Substance (mg GAE / kg oil)	61.59±2.20	193.79±2.20	83.52±1.48
Sterol (mg β-sitosterol / kg oil)	866.21±4.58	1160.60±8.02	1052.92±24.05
Alpha tocopherol (α) (mg/ kg oil)	618.64±0.53	171.13±0.19	616.53±1.27
Beta tocopherol (β) (mg/ kg oil)	27.61±0.20	37.43±0.2	27.14±0.53
Gamma tocopherol (γ) (mg/ kg oil)	85.89±0.45	Nd	85.72±0.08

HO; Hazelnut oil, OO; Olive oil, HOC; Hazelnut oil, Olive oil, Carnauba wax, nd, no detectable

The functional properties of HOC oleomargarine sample and oils were examined the total phenolic substance (mg/kg oil), total sterol (mg/kg oil) and tocopherol (mg/kg oil) content of samples were determined and given in Table 17. Total phenolic content (mg GAE/kg oil) of hazelnut oil, olive oil and HOC samples were as 61.59 mg/kg oil, 193.79 mg/kg oil and 83.52 mg/kg oil, respectively. Being as tocopherols, α, β and γ tocopherol were chromatographically detected and their amounts were calculated. They were in the ranges of 171.13 - 618.64 mg/kg oil, 27.14 - 37.43 mg/kg oil, and nd- 85.89 mg/kg oil, respectively. Total sterol amount was in between 866.21 mg/kg oil to 1160.60 mg/kg oil. It varies depending on the oil type and addition ratios.

4. DISCUSSION AND CONCLUSIONS

Vegetable oils are important due to the nutritional contents like essential fatty acids, bioactive, and fat-soluble vitamins. Additionally they are good energy sources. In recent years, consumers have changed their diet behaviors to healthy, natural and functional foods instead of eating behaviors like meeting some part of nutritional and energy requirements by fats used in the diet and/or fats in the food composition. The worldwide accepted dietary recommendation for health is to reduce the total saturated fat and trans fatty acid intake in the diet.

Solid fats used in the diet; are produced as breakfast, kitchen and food industry margarine according to its usage area. The composition of margarine varies depending on the national standards of the countries and the type of margarine. The ratio of saturated fatty acids in the composition of margarine is considerably higher than vegetable oils.

In this project, it was aimed to produce, optimize and characterize oleomargarine, which does not contain *trans* fat, is low in saturated fat and rich in mono or polyunsaturated fatty acids, by enriching hazelnut oil with natural extra virgin olive oil and gellated using carnauba wax. As the ratio of gelling agent added to the oil mixtures increased, it was determined that the hardness and stickiness and OBC (%) values of oleomargarines increased, while the CFT (min.) value decreased. Color

values varied according to the type of oil used in the production of oleomargarine, and the addition ratio of oil and wax. Type and ratios of added oleogelator were effective on the melting and crystallization temperatures. The acidity and peroxide values of edible oils were within the limits specified by the codex, according to the Turkish Food Codex Communique on Olive Oil and Oils Named by Plants. Oleomargarine is an alternative product to margarine and its acidity value (% oleic acid) is maximum 1.5 and peroxide value (meq O₂ /kg of oil) is 5 in the margarine codex values. The fatty acid composition (%) of edible oils and oleomargarine produced from these oil mixtures were found to be rich in mono and polyunsaturated fat content, but low in saturated fat content. When the margarine and oleomargarine samples were compared, the saturated fat content of the margarine sample was found to be considerably higher than the HOC oleomargarine samples. Fatty acid composition, total phenolic substance amounts, sterol (β -sitosterol) and tocopherol compositions of oleomargarines changed depending on the oil addition ratios used in the mixture.

In short, in this study, optimum conditions for oleomargarine production (oil addition ratio 17.27% and wax ratios 9.71%) were determined by using different vegetable oil mixtures and carnauba wax, and it is thought that these basic results will contribute significantly to oleomargarine production and food industry.

Acknowledgment

We would like to thank Suleyman Demirel University Scientific Research Projects Management Unit, which financially supported the thesis with the project numbered 4849-YL1-17 for the conduct of this study.

Ethics Committee Approval

N/A

Peer-review

Externally peer-reviewed.

Author Contributions

All authors have read and agreed to the published version of manuscript.

Conflict of Interest

All authors declare that they have no conflict of interest.

REFERENCES

- Alasalvar, C., Shahidi, F., Ohshima, T., Wanasundara, U., Yurttas, H.C., Liyanapathirana, C.M., Rodrigues, F.B. (2003). Turkish Tombul hazelnut (*Corylus avellana* L.). 2. Lipid characteristics and oxidative stability. *Journal of Agricultural and Food Chemistry*, 51(13), 3797-3805.
- Alimentarius, C. 2001). Codex standard for olive oil, virgin and refined, and for refined olive-pomace oil. *Codex stan*, 8, 25-39.
- AOCS. 1997). Fatty acid composition by gas chromatography, in method Ce 1 - 62. Official Methods and Recommended Practices of the American Oil Chemists' Society.
- AOCS, O. (1998). methods and recommended practices of the American Oil Chemists' Society. American Oil Chemists' Society, Champaign, IL, USA.
- Aşık, H.U., Özkan, G. (2011). Physical, Chemical and Antioxidant Properties of Olive Oil Extracted from Memecik Cultivar. *Academic Food Journal/Akademik GIDA*.
- Ayadi, M., Grati-Kamoun, N., Attia, H. (2009). Physico-chemical change and heat stability of extra virgin olive oils flavoured by selected Tunisian aromatic plants. *Food and Chemical Toxicology*, 47(10), 2613-2619.
- Aydın, S., Özkan, G., Yorulmaz, A. (2020). Effect of Variety, Maturity and Malaxation Conditions on Sterol Profile of Olive Oil. *Academic Food Journal*, 18(1), 87-95.
- Bozdoğan Konuşkan, D. (2008). Determination of Some Properties of Solvent Extracted Oils of Olive Oil Halhalı, Sarı Hasebi And Gemlik Varieties Grown in Hatay And Comparison with Olive Oils Obtained Bymechnical Method. *Food Engineering Department Institute of Naturel And Applied Science University of Cukurova, Adana, Turkey*.
- Brandt, M., Moss, J., Ferguson, M. (2009). The 2006–2007 Food Label and Package Survey (FLAPS): nutrition labeling, trans fat labeling. *Journal of Food Composition and Analysis*, 22, S74-S77.
- Cevik, S., Ozkan, G., Kiralan, M., Bayrak, A. (2014). Effect of harvest time on physicochemical quality parameters, oxidation stability, and volatile compounds of extra virgin olive oil. *Acta Alimentaria*, 43(4), 526-537.
- Da Pieve, S., Calligaris, S., Nicoli, M.C., Marangoni, A.G. (2010). Shear nanostructuring of monoglyceride organogels. *Food Biophysics*, 5(3), 211-217.
- Dassanayake, L.S.K., Kodali, D.R., Ueno, S., Sato, K. (2009). Physical properties of rice bran wax in bulk and organogels. *Journal of the American Oil Chemists' Society*, 86(12), 1163.
- De Greyt, W.F., Petrauskaitė, V., Kellens, M.J., Huyghebaert, A.D. (1998). Analysis of tocopherols by gas liquid and high performance liquid chromatography: a comparative study. *Lipid/Fett*, 100(11), 503-507.
- Delil, S.O.S., Özkan, G., Karacabey, E. (2022). Phenolic Transition from Olive Fruits at Different Ripening Stages to Olive Oil: Process Optimization and Determination by Spectrophotometric and Chromatographic Methods. *Food Analytical Methods*, 1-14.
- Durmaz, G., Gökmen, V. (2019). Effect of refining on bioactive composition and oxidative stability of hazelnut oil. *Food research international*, 116, 586-591.

- Isabel Minguez-Mosquera, M., Rejano-Navarro, L., Gandul-Rojas, B., SanchezGomez, A.H., Garrido-Fernandez, J. (1991). Color-pigment correlation in virgin olive oil. *Journal of the American Oil Chemists' Society*, 68(5), 332-336.
- Karasu, S. (2015). Determination of Quality Parameters of Salad Dressing Prepared with Cold Pressed Oil. *Namık Kemal University Graduate School of Natural and Applied Sciences Department of Food Engineering*.
- Kesen, S., Sönmezdağ, A.S., Kelebek, H., Selli, S. (2016). Fatty Acids Composition of Crude and Refined Hazelnut Oils. *Çukurova J. Agric. Food Sci.*, 31(1), 79-84.
- Legault, L., Brandt, M.B., McCabe, N., Adler, C., Brown, A.-M., Brecher, S. (2004). 2000–2001 food label and package survey: an update on prevalence of nutrition labeling and claims on processed, packaged foods. *Journal of the American Dietetic Association*, 104(6), 952-958.
- Marangoni, A.G., Garti, N. (2011). *Edible oleogels: structure and health implications*. AOCS Press, v + 340 pp.s, Champaign.
- Matthäus, B., Özcan, M. (2011). Determination of fatty acid, tocopherol, sterol contents and 1, 2-and 1, 3-diacylglycerols in four different virgin olive oil. *Journal of Food Processing and Technology*, 2(4).
- Mensink, R.P., Zock, P.L., Kester, A.D., Katan, M.B. (2003). Effects of dietary fatty acids and carbohydrates on the ratio of serum total to HDL cholesterol and on serum lipids and apolipoproteins: a meta-analysis of 60 controlled trials. *The American journal of clinical nutrition*, 77(5), 1146-1155.
- Moskowitz, H.R. (1987). *Food texture: Instrumental and sensory measurement*. M. Dekker.
- Nas, S., Gökalp, H.Y. (2001). *Vegetable oil technology*, Ataturk University Press.
- Öğütçü, M., Yılmaz, E. (2014). Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas y Aceites*, 65(3), 040.
- Öğütçü, M., Yılmaz, E. (2015). Characterization of hazelnut oil oleogels prepared with sunflower and carnauba waxes. *International Journal of Food Properties*, 18(8), 1741-1755.
- Öğütçü, M. (2014). *Preparation Of Edible Oleogels and Evaluation of their Food Product Usabilities*. Çanakkale Onsekiz Mart University Graduate School of Natural and Applied Sciences Doctoral Dissertation in Food Engineering, 299p, Çanakkale, Turkey.
- Paquot, C., Hautfenne, A. (1987). *Standard methods for the analysis of oils, fats and derivatives*. Blackwell scientific publications Oxford.
- Pehlivanoglu, H., Demirci, M., Toker, O.S. (2017). Rheological properties of wax oleogels rich in high oleic acid. *International journal of food properties*, 20(sup3), S2856-S2867.
- Pehlivanoglu, H., Ozulku, G., Yildirim, R.M., Demirci, M., Toker, O.S., Sagdic, O. (2018). Investigating the usage of unsaturated fatty acid-rich and low-calorie oleogels as a shortening mimetics in cake. *Journal of food processing and preservation*, 42(6), e13621.
- Pehlivanoğlu, H., Demirci, M., Toker, O.S., Konar, N., Karasu, S., Sagdic, O. (2018). Oleogels, a promising structured oil for decreasing saturated fatty acid concentrations: Production and food-based applications. *Critical reviews in food science and nutrition*, 58(8), 1330-1341.
- Roller, S., Jones, S.A. 1996). *Handbook of fat replacers*. CRC Press.
- Rudel, L.L., Morris, M. (1973). Determination of cholesterol using o-phthalaldehyde. *Journal of Lipid Research*, 14(3), 364-366.
- Singleton, V.L., Rossi, J.A. (1965). Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *American journal of Enology and Viticulture*, 16(3), 144-158.
- Society, A.O.C. 1998). *Method Cj 1–94. Official methods and recommended practices*.
- Tabibiazar, M., Roufegarinejad, L., Hamishehkar, H., Alizadeh, A. (2020). Preparation and characterization of carnauba wax/adipic acid oleogel: A new reinforced oleogel for application in cake and beef burger. *Food Chemistry*, 333, 127446.
- Thakur, D., Singh, A., Prabhakar, P.K., Meghwal, M., Upadhyay, A. (2022). Optimization and characterization of soybean oil-carnauba wax oleogel. *LWT*, 157, 113108.
- Tüfekci, F. (2018). *Investigating the Fatty Acid Composition of Hazelnuts Produced at the Black Sea Region*. Istanbul Aydın University, Department of Food Engineering, 179p, Istanbul, Turkey.
- Wassell, P., Bonwick, G., Smith, C.J., Almiron Roig, E., Young, N.W. (2010). Towards a multidisciplinary approach to structuring in reduced saturated fat based systems—a review. *International journal of food science & technology*, 45(4), 642-655.
- Yılmaz, E., Demirci, Ş. (2021). Preparation and evaluation of virgin olive oil oleogels including thyme and cumin spices with sunflower wax. *Gels*, 7(3), 95.
- Yılmaz, E., Öğütçü, M. (2014a). Properties and stability of hazelnut oil organogels with beeswax and monoglyceride. *Journal of the American Oil Chemists' Society*, 91(6), 1007-1017.
- Yılmaz, E., Öğütçü, M., (2014b). Comparative analysis of olive oil organogels containing beeswax and sunflower wax with breakfast margarine. *Journal of food science*, 79(9).
- Yılmaz, E., Öğütçü, M., (2014c). Comparative analysis of olive oil organogels containing beeswax and

sunflower wax with breakfast margarine. Journal of food science, 79(9), E1732-E1738.

Yorulmaz, A.Y. (2009). Determination of Phenolic, Sterol and Triglyceride Structures of Turkish Olive Oils. Ankara University Graduate School of Naturel and Applied Sciences Department of Food Engineering, Ankara, Turkey.