



Effect of Chemical Refining Steps on the Some Micro and Macro Element Content and Quality Parameters in Corn Oil

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ARTICLE INFO	ABSTRACT
<p><i>Research Article</i></p> <p>Received : 23/09/2020 Accepted : 05/02/2021</p> <p>Keywords: Chemically refining Heavy metal Food safety Food quality Corn oil</p>	<p>In this study, it was aimed to determine some element contents and some quality properties and to compare these parameters at each stage in the chemically refining process of crude corn oil. Color (lovibond tintometer), free fatty acidity, peroxide values and fatty acid compositions were determined in the samples of corn oil taken from consecutive stages of chemically refining. Also, the content of elements (Na, Mg, K, Ca, Fe, Pb, Cd, Ni, Mn, Zn, Co, Cr, P, Cu) was analyzed, by using inductively-coupled plasma-mass spectrometry (ICP-MS) and inductively-coupled plasma-optical emission spectrometry (ICP-OES) after microwave digestion. The color (Lovibond tintometer), free fatty acidity and peroxide values in the chemically refining process varied between 2.7-16, %0.09-2.12, 10.95-1.08 mEqO₂/kg, respectively. Oleic, linoleic and linolenic acid contents changed between 30.486-30.580%, 54.339-54.703% and 0.972-0.993%, respectively, in the chemically refining stages. While no <i>trans</i> fatty acids detected in crude corn oil and after degumming-neutralization step, very low amount of <i>trans</i> oleic acid (0.040%) and total <i>trans</i> linoleic acid (0.132%) was detected in bleached corn oil. The total <i>trans</i> fatty acid content little more increased in the last stage of the chemically refining. However, total <i>trans</i> fatty acid content of refined corn oil was < 0.3%. It was clearly seen that Na, Mg, K, P, Ca, Mn, Fe, Pb, Ni, Cr, Cu element contents decreased significantly at the end of the chemically refining process. Although Cd, Co and Zn elements were determined in crude corn oil, these elements were not detected in the refined corn oil. The results obtained showed that the chemically refining process effected some of the quality properties of corn oil and especially the changes in the element contents.</p>

Türk Tarım – Gıda Bilim ve Teknoloji Dergisi, 9(6): 982-990, 2021

Kimyasal Rafinasyon Aşamalarının Mısır Yağındaki Bazı Mikro ve Makro Element İçeriği ve Kalite Parametrelerine Etkisi

MAKALE BİLGİSİ	ÖZ
<p><i>Araştırma Makalesi</i></p> <p>Geliş : 23/09/2020 Kabul : 05/02/2021</p> <p>Anahtar Kelimeler: Kimyasal rafinasyon Ağır metal Gıda güvenliği Gıda kalitesi Mısır Yağı</p>	<p>Bu çalışmada, ham mısır yağının kimyasal rafinasyon sürecinde bazı element içerikleri ile bazı kalite özelliklerinin belirlenmesi ve bu parametrelerin her rafinasyon aşamasında karşılaştırılması amaçlandı. Kimyasal rafinasyonun aşamalarından alınan mısır yağı örneklerinde renk (lovibond tintometre), serbest yağ asitliği, peroksit değerleri ve yağ asidi bileşimleri tespit edildi. İlave olarak, indüktif eşleşmiş plazma/optik emisyon spektroskopisi (ICP-OES) ve indüktif eşleşmiş plazma/kütle spektroskopisi (ICP-MS) cihazlarında element (Na, Mg, K, Ca, Fe, Pb, Cd, Ni, Mn, Zn, Co, Cr, P, Cu) analizleri yapıldı. Kimyasal rafinasyon sürecinde renk (Lovibond tintometer), serbest yağ asitliği ve peroksit değerleri sırasıyla 2.7-16, %0.09-2.12, 1.08-10.95 mEqO₂/kg aralığında değişim gösterdi. Oleik, linoleik ve linolenik asit içerikleri kimyasal rafinasyon aşamalarında sırasıyla %30.580-30.486, %54.703-54.164 ve %0.993-0.972 aralığında değişti. Ham mısır yağında ve gum giderme-nötralizasyon aşamasından sonra <i>trans</i> yağ asidi belirlenemez iken, ağartılmış mısır yağında çok düşük miktarlarda <i>trans</i> oleik asit (%0.040) ve toplam <i>trans</i> linoleik asit (%0.132) tespit edildi. Toplam <i>trans</i> yağ asidi içeriği kimyasal rafinasyonun son aşamasında bir miktar artış gösterdi. Bununla birlikte, toplam <i>trans</i> yağ asidi içeriği %3'ün altında kaldı. Kimyasal rafinasyon işlemi sonunda Na, Mg, K, P, Ca, Mn, Fe, Pb, Ni, Cr, Cu element içeriklerinin çok önemli düzeyde azaldığı açık bir şekilde görüldü. Cd, Co ve Zn elementleri ham mısır yağında tespit edilmesine rağmen ise rafine mısır yağında bu elementler tespit edilemedi. Elde edilen sonuçlar kimyasal rafinasyonu prosesinin mısır yağının bazı kalite özelliklerine ve bilhassa element içeriklerine etkili olduğunu gösterdi.</p>

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Introduction

Edible oil is a required ingredient in human nutrition and in the production of certain foods. Edible oil technology is one of the leading sectors of today's food industry, whose production process starts from the field and continues in modern enterprises and goes to the houses where consumption occurs (Kuleaşan, 2004).

Edible oils are the most concentrated source of energy, they have a carrier function for fat-soluble vitamins, make food more delicious and contribute to the feeling of fullness after meals. In addition, edible oils are of great importance in human nutrition in terms of fatty acids that cannot be synthesized by the body (Nas et al., 2001). The chemical structure, metabolism, amount and quality parameters of oils consumed daily have a critical effect on health (Kostik et al., 2013).

Corn (*Zea mays* L.) is a member of the Maydeae tribe Gramineae grass family (Lara and Saldivar, 2019). Corn is the most important cereal grain in terms of production today, has high value and economic importance worldwide (Lara and Saldivar, 2019; Food and Agriculture Organization, 2018). The majority of commercially produced corn oil is extracted from the seed (Arellano et al., 2019). Corn oil exhibits excellent oxidative stability in many uses, such as when used as a frying oil. Corn oil contains high levels of unsaturated fatty acids, the main components of which are linoleic and oleic acids. As with other vegetable oils, the fatty acid composition of corn oil depends on factors such as climatic conditions, growing season and genotype. Refined corn oil; besides being used as salad oil and frying oil, it is used to obtain technical oils as raw materials in various lipid modification processes. It has an important place among vegetable oils due to its usefulness in a variety of food uses and has excellent sensory and nutritional properties (Arellano et al., 2019; O'Brien, 2008). High quality refined corn oil can be obtained by refining free fatty acids and phospholipids from crude oil.

Undesirable components such as free fatty acids (FFAs), phospholipids and pigments can negatively affect oil quality in terms of taste, appearance, physicochemical properties, and oxidative stability (Jiang et al., 2015, Zhu et al., 2015). Vegetable oils must be refined in order to be consumed. In general terms, refining vegetable oils refers to the separation of triglycerides from oil-insoluble impurities. The purpose of refining is to produce partially refined oils for hydrogenation or fully refined oils with good taste, odor, appearance properties and shelf life with high efficiency and low cost. Substances other than triglycerides in crude oil differ in amount and variety according to the conditions of cultivation and storage, as well as the processes applied to seed and crude oil. The refining processes should be directed towards obtaining a high and permanent quality end product from raw materials of different properties. In order to achieve this purpose or in other words, to obtain an acceptable product with refining methods, the crude oil should contain low levels of non-triglycerides (Taşan et al., 2011). Chemical refining includes degumming, neutralization, bleaching, winterization and deodorization processes (Taşan, 1999).

Whether edible oils are of consumable quality can also be evaluated by determining some trace metals. The body needs some metals in trace amounts. However, it is stated that high amounts of heavy metals have carcinogenic, mutagenic, teratogenic and endocrine disrupting effects, while others may cause neurological and behavioral changes. In addition, freely available heavy metals can break the molecular bonds and increase the production of free radicals, thereby causing oxidative stress (Angioni et al., 2006; Ali et al., 2013). Oxidative stress disrupts the antioxidant defense system of cells and can lead to cell damage and cell death (Mudipalli, 2008; Das et al., 2008).

The aim of this study is, during the refining of crude corn oil by chemical refining technique; to determine and compare some physical and chemical properties, oxidative stability values, geometric isomerization that may occur in fatty acids at some stages of refining applications and changes that can be seen in 14 different element contents.

Material and Method

Material

The research material was taken from the refining unit of private refining company located in the province of Edirne, which applies chemically refining technique to crude corn oil. This refining company, which applies the refining process to crude corn oils, imports raw corn oils from abroad.

In the study, corn oil samples were taken from the crude corn oil, which entered the chemical refining unit, and the combined degumming-neutralization, bleaching, winterization and deodorization stages of the chemical refining unit respectively.

The sampling process was carried out in three different production periods with an interval of 10 days; during these production periods, the same crude corn oil was used and the same refining parameters (temperature, pressure, addition of alkali, use of bleaching earth, processing times etc.) were applied.

During the combined degumming-neutralization stage, heating up to 90°C was applied, in addition, 1 L 85% phosphoric acid for per 1000 kg and 7 L sodium hydroxide solutions for per 1000 kg added; in the bleaching stage, heating up to 100°C, addition of 12 kg synthetic silica bleaching earth for per 1000 kg and 750 mm Hg vacuum applied; 2 kg perlite for per 1000 kg was added in the winterization; in the deodorization stage, heating was applied to 150-170°C.

The samples taken were filled in 1 L brown glass bottles with no overhead gap to protect against oxidation. Analyzes in which element contents were determined were carried out in laboratories within Tekirdağ Namık Kemal University Scientific and Technological Research Application and Research Center (NABILTEM) and Yıldız Technical University Science and Technology Application and Research Center. A significant part of the analysis was done immediately without wasting time in the vegetable oil factory where samples were obtained and refining was applied.

Method

Determination of Color Value

The color values of the samples were determined with the Lovibond tintometer PFXi-880 and a 5 ¼ " cuvette was used for measuring operations (Anonymous, 1990).

Determination of % Free Fatty Acidity Value

The free fatty acid value is stated as the percentage of oleic acid in the total free fatty acids according to the IUPAC 2.201 (Anonymous, 1987) method.

Determination of Peroxide Value

Peroxide value; it is a measure of the amount of active oxygen in oils, the amount of peroxide oxygen in 1 kg of oil, in milliequivalentgrams. IUPAC 2.501 (Anonymous, 1987) method was used to determine the peroxide value of the samples examined.

Determination of Fatty Acid Composition

The oil samples examined were converted to fatty acid methyl esters by BF₃-methanol according to AOCS Ce 2-66 method (AOCS, 1992). Chromatograms showing fatty acid compositions were obtained by injecting 0.5 µl of fatty acid methyl esters into the gas chromatography (GC). Agilent 6890 N model gas chromatography (Agilent, USA) (Anonymous, 2002), flame ionization detector (FID) and HP-88 (Coated with 88% cyanopropylmethyl-aryl polysiloxane, silica capillary column, 100 m × 250 µm i.d., 0.20 µm film) column were used. Carrier gas helium, carrier gas flow 1ml / min. The peaks of GC chromatograms were tentatively identified by comparing the retention times and area percentages with those of authentic standards of fatty acid methyl esters obtained from Nu-Chek-Prep Inc. (Elysian, MN). Methyl esters of *trans*-9-elaidic and *cis-trans* isomers of linoleic acid were purchased from Supleco Inc. (USA). Samples were separately analyzed in triplicate. The final results were expressed as relative percentage of individual fatty acid.

Determination of Element Contents with Inductively Coupled Plasma / Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma / Mass Spectroscopy (ICP-MS)

In order to eliminate the organic compounds in the oil samples and to transfer the inorganic compounds to the soluble phase, the solubilization processes were carried out using the closed system wet burning method. For this purpose, the NovaWAVE model automated microwave digestion system was used. All samples and standards were used by diluting with ultra-pure water.

The concentration of Na, Mg, K, Ca, P elements was determined with the Inductively Coupled Plasma / Optical Emission Spectroscopy (ICP-OES) device equipped with the SPECTROBLUE model Smart Analyzer Vision software. The concentration of Fe, Pb, Cd, Ni, Mn, Zn, Co, Cr, and Cu elements was determined with the Agilent 7700 model Inductively Coupled Plasma / Mass Spectroscopy (ICP-MS) device.

In the process, 0.5 g of samples were weighed. Samples were placed in microwave tubes and 9 ml of HNO₃ and 3 ml of H₂O₂ were added. The lids of the microwave containers were closed and placed in the microwave oven,

burning was performed in the appropriate program. In the first 15 minutes, a temperature of 145°C was reached gradually. It was held under these conditions for 5 minutes. After this stage, the temperature reached 175°C in 5.5 minutes. In these conditions, gradual combustion took place by keeping it in 4.5 minutes. After burning, the caps of the cooled tubes were opened in the fume hood, the lid and the walls of the container were rinse well. Some ultrapure water was added to the samples and filtered using filter papers. After dissolution, the filtrate was taken and completed to 25 mL (NMKL, 2011).

Elemental analyzes of prepared samples were performed in Inductively Coupled Plasma / Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma / Mass Spectroscopy (ICP-MS) devices. Standard solutions at the desired concentrations for Na, Mg, K, Ca, Fe, Pb, Cd, Ni, Mn, Zn, Co, Cr, P and Cu were prepared from CPI International's 1000 mg/L stock solutions. The same processes were applied in the blind sample. Three parallels were studied for each sample and the results are averaged.

Statistical analysis

Variance analysis was applied to the data obtained as a result of the study by using SPSS package program according to random trial pattern. Duncan multiple comparison test applied to important variation sources (Soysal, 1998).

Results and Discussion

Color Values

The average of Lovibond tintometer color values of corn oil samples taken from each of the process stages of the unit where chemically refining was applied in three different production periods were shown in Table 1. Yellow color did not change in corn oil samples; the red color appears to be an average of 16 units in crude corn oil and an average of 2.7 units at the end of refining. While the red color value of crude oil samples was 16.0 on average, this value decreased to 9.3 in the degumming-neutralization stage. Decrease in the bleaching and winterization stages to an average of 5.2 and 5.0, respectively, continued. After the deodorization process, it decreased to an average of 2.7. As a result of variance analysis, these changes were found statistically significant at the level of P<0.01. Xie et al. (2019); in their study, they determined the effect of chemically refining on the color value of soybean oil. Color value was determined as 4.30±0.20 in crude oil; after neutralization, decolorization and deodorization, it was determined as 2.50±0.10, 1.10±0.10 and 0.20±0.00, respectively. Chewa et al. (2016) determined the L*, a* and b* color values of crude and chemically refined kenaf (*hibiscus cannabinus*) seed oil. L*, a* and b* color values in crude oil were determined as 11.55±0.29, 91.94±0.15 and 14.50±0.54, respectively. At the end of the chemical refining process, it was determined as 6.57±0.15, -2.14±0.07 and 6.43±0.28, respectively.

Table 1. Changes of quality indices in corn oil during chemical refining¹

Quality indices	Crude	Degummed- Neutralized	Bleached	Winterized	Deodorized
Color	16.0±0.2 ^a	9.3±0.57 ^b	5.2±0.05 ^c	5.0±0.05 ^c	2.7± 5.43 ^d
FFA (%)	2.12±0.08 ^c	0.13±0.01 ^b	0.11±0.01 ^{ab}	0.10±0.00 ^a	0.09±0.00 ^a
PV (mEqO ₂ /kg)	10.95±0.11 ^d	12.54±0.12 ^c	3.89±0.50 ^b	6.76±0.20 ^c	1.08±0.03 ^a

¹Each value is an average of three determinations, the mean ± standard deviation (SD). The means in each row with different letter (a-d) are significantly different (P<0.01, Duncan's multiple range test). FFA = free fatty acid, PV = peroxide value.

In the degumming-neutralization stage, which is the first stage of the refining processes, the red color value decreased significantly ($P<0.01$), and the color unfolded. Some researchers have reported that the lightening of the color was due to the reduction of the color substance and the reduction of acidity during the neutralization stage (Taşan, 1999). With the bleaching process, which aims to lighten the color using bleaching soil, the color value was reduced significantly ($P<0.01$). On the other hand, there was a statistically insignificant decrease in the winterization stage. According to the data obtained in our study, the lightening continued with deodorization process. It is reported that the reason for this might be that naturally occurring pigments in oil undergo chemical changes at high temperatures and become discolored. (Karaali 1981).

% Free Fatty Acidity Value

The average of free fatty acidity values of corn oil samples taken from each of the process steps of the unit where chemical refining was applied in three different production periods were shown in Table 1. It can be seen that oil samples tend to decrease in free fatty acid values during chemical refining process stages. The free fatty acid value, which was 2.12% in crude corn oil, decreased to 0.09% by deodorization process at the end of the refining process.

While the free fatty acid value of crude oil samples averaged 2.12%, this value increased to 0.13% in the degumming-neutralization stage. On the other hand, after bleaching, winterization and deodorization process stages, on average 0.11%; it was determined as 0.10% and 0.09%. As a result of variance analysis, these changes were found statistically significant at the level of $P < 0.01$. Drira et al. (2018) determined the effects of chemical refining steps on pomace olive oil, free fatty acid. The free fatty acid (%) level of 6.90 ± 0.10 in crude oil is 4.74 ± 0.07 after the winterized stage; 0.20 ± 0.00 after the neutralization stage; 0.28 ± 0.00 after decolorization and 0.14 ± 0.00 after deodorization. Liu et al. (2019a) determined the free fatty acid (%) content of crude coconut oil as 5.70 ± 0.03 ; after degumming, neutralization, bleaching and deodorization process stages, it decreased to 5.87 ± 0.14 , 0.32 ± 0.01 , 0.39 ± 0.02 and 0.12 ± 0.01 respectively.

The high rate of free fatty acids that can be found in oils adversely affects the taste and smell and durability of the oil, therefore, high amount of fatty acids in edible vegetable oils is considered as a factor that reduces quality. Free fatty acidity can occur during the ripening period of the seed, as well as mechanical damage, storage and transportation conditions in the seed, and processing conditions during extraction of crude oil can significantly affect the content of free fatty acid (Nas et al., 2001, Taşan and Demirci, 2003). As the free fatty acids are converted into soap solutions with the use of alkali in chemical refining, the most important reduction occurred in the combined degumming-neutralization phase ($P<0.01$), no significant change was observed after the combined degumming-neutralization phase. Effective factors in the neutralization phase; temperature, duration, concentration of the base solution used, the amount of free fatty acid content of the oil and other impurities (Taşan, 1999).

Peroxide Value

The average of peroxide values of corn oil samples taken from each of the process steps of the unit where chemical refining was applied in three different production periods were shown in Table 1. Peroxide value; it was determined as the highest degumming-neutralization stage and the lowest deodorization stage, on average $12.54 \text{ mEqO}_2/\text{kg}$ and $1.08 \text{ mEqO}_2/\text{kg}$, respectively.

The peroxide value, which increased to $12.54 \text{ mEqO}_2/\text{kg}$ during the degumming-neutralization stage, decreased significantly during the bleaching phase and became $3.89 \text{ mEqO}_2/\text{kg}$. The peroxide value, which reached $6.76 \text{ mEqO}_2/\text{kg}$ again during the winterization stage, was determined as $1.08 \text{ mEqO}_2/\text{kg}$ after deodorization stage.

As a result of variance analysis, the differences between the processing stages of the chemical refining method were found to be statistically significant at the level of $P<0.01$. Xie et al. (2019) determined the peroxide value of crude soybean oil to $3.50 \pm 0.18 \text{ (mmol/kg)}$; this value was determined as 6.12 ± 0.14 , 5.07 ± 0.20 and $0.81 \pm 0.07 \text{ (mmol/kg)}$ in neutralized oil, bleached oil and deodorized oil, respectively. Liu et al. (2019a) aimed to determine the effects of chemical refining on the quality of coconut oil, they determined the peroxide value of crude coconut oil as $6.02 \pm 0.22 \text{ mg/kg}$. The peroxide value decreased at each stage of the refining process (5.16 ± 0.14 , 2.60 ± 0.06 , 3.52 ± 0.10 and $0.55 \pm 0.10 \text{ mg/kg}$, after degumming, neutralization and bleaching respectively), at the end this value was found to be $0.24 \pm 0.00 \text{ mg/kg}$ in deodorized oil. Liu et al. (2019b) determined peroxide values in raw and refined rice bran oil. Peroxide values found $5.29 \pm 0.20 \text{ (mmol/kg)}$ in crude oil, $3.92 \pm 0.19 \text{ (mmol/kg)}$ in degumming oil, $0.34 \pm 0.07 \text{ (mmol/kg)}$ in neutralized oil, $0.59 \pm 0.27 \text{ (mmol/kg)}$ in bleached oil and $0.65 \pm 0.13 \text{ (mmol/kg)}$ in deodorized oil. These results in the literature are in agreement with the results of our study.

It is normal to have very little oxidative deterioration in oily raw materials. Because these deterioration products can be removed by refining processes. Mechanical damage during harvesting, storage and transportation and pretreatments applied can cause oxidative deterioration reactions (Taşan, 1999).

In the increase at degumming-neutralization stage, where the peroxide number reaches the highest values, the possibility of oil contact with air and the processing time can be considered to be effective. Rate and type of bleaching soil in the bleaching stage, temperature, duration and vacuum, are effective factors in the decrease in peroxide value. The peroxide value was significantly removed in the deodorization stage of the chemical refining.

Fatty Acid Compositions

Fatty acid compositions of corn oil samples taken from each of the process stages of the unit where chemical refining was applied in three different production periods were shown in Table 2. Also mean values of fatty acid compositions, total saturated fatty acids, total monounsaturated fatty acids, total polyunsaturated fatty acids, total unsaturated fatty acids, total *trans* fatty acids, total polyunsaturated fatty acids to total saturated fatty acids are shown in Table 2.

Table 2. Average values of fatty acid compositions in the process of refining steps (%)¹

Fatty acids (%)		Crude	Degummed- Neutralized	Bleached	Winterized	Deodorized
Myristic acid	C14:0	0.026±0.00	0.029±0.00	0.029±0.00	0.029±0.00	0.028 ±0.00
Palmitic acid	C16:0	10.580±0.05 ^a	11.114±0.00 ^b	11.095±0.00 ^b	11.253±0.04 ^b	11.147±0.03 ^b
Palmitoleic acid	C16:1	0.090±0.00	0.038±0.00	0.041±0.00	0.060±0.00	0.057±0.00
Stearic acid	C18:0	2.167±0.00 ^a	2.065±0.00 ^b	2.073±0.00 ^b	2.064±0.00 ^b	2.051±0.00 ^b
Elaidic acid	C18:1 ^{trans} ²	-a	-a	0.040±0.00 ^b	0.039±0.00 ^b	0.039±0.00 ^b
Oleic acid	C18:1	30.580±0.03 ^a	30.472±0.00 ^a	30.461±0.00 ^a	30.492±0.02 ^a	30.486±0.00 ^a
Linoelaidic	ΣC18:2 ^{trans} ³	-a	-a	0.132±0.00 ^b	0.131±0.00 ^b	0.175±0.00 ^c
Linoleic acid	C18:2	54.703±0.08 ^a	54.449±0.00 ^{ab}	54.243±0.01 ^{ab}	54.097±0.03 ^b	54.164±0.04 ^{ab}
Linolenic acid	C18:3	0.993±0.00 ^a	0.970±0.00 ^a	0.970±0.00 ^a	0.968±0.00 ^a	0.972±0.00 ^a
Arachidic acid	C20:0	0.505±0.00	0.500±0.00	0.546±0.00	0.506±0.01	0.513±0.01
Eicosadienoic acid	C20:2	0.050±0.00	0.055±0.00	0.058±0.00	0.051±0.00	0.052±0.00
Gadoleic acid	C20:1	0.306±0.00	0.308±0.00	0.312±0.00	0.310±0.00	0.316±0.00
Total Saturated Fatty Acids		13.278 ^a	13.708 ^b	13.743 ^b	13.852 ^b	13.739 ^b
Total Monounsaturated Fatty Acids		30.976 ^a	30.818 ^a	30.854 ^a	30.901 ^a	30.898 ^a
Total Polyunsaturated Fatty Acids		55.746 ^a	55.474 ^b	55.403 ^b	55.247 ^c	55.363 ^{bc}
Total Unsaturated Fatty Acids		86.722 ^a	86.292 ^{ab}	86.257 ^{ab}	86.148 ^b	86.261 ^{ab}
Total Unsaturated / Total Saturated		6.531	6.295	6.276	6.219	6.278
Total Trans Fatty Acids		-a	-a	0.172 ^b	0.170 ^b	0.214 ^c

¹Each value is an average of three determinations, the mean ± standard deviation (SD), and are expressed as a weight percentage of total FA methyl esters. The means in each row with different letter (a-c) are significantly different ($P < 0.01$, Duncan's multiple range test). ²Constituted of C18:1Δ9 *trans*, ³Sum of only Δ9_{cis}, Δ12 *trans* and Δ9 *trans*, Δ12 *cis* isomers for the C18:2.

A total of 12 types of fatty acids were determined in the corn oil samples taken from the refining unit during three different production periods. In some corn oil samples, elaidic acid (*trans* oleic acid) and linoelaidic acid (total *trans* linoleic acid) formations were also encountered. According to the data obtained in the study, the most common fatty acids in corn oil samples were palmitic (C16:0), oleic (C18:1) and linoleic (C18:2) acids. Next comes stearic acid (C18:0) in proportions exceeding 2% and linolenic (C18:3) acid in a ratio that approximates 1%. Other fatty acids, myristic (C14:0), palmitoleic (C16:1), arachidic (C20:0), eicosadienoic (C20:2), gadoleic (C20:1), were well below 1%.

When Table 2 is examined, it is seen that 4 types of saturated fatty acid were detected in corn oil samples taken and examined in three different production periods; C14:0, C16:0, C18:0 and C20:0. While total saturated fatty acid was 13.278% in crude corn oil, it was determined as 13.739% as a result of refining although the total saturated fatty acids showed some fluctuation during the chemically refining process, it was found that only the degumming-neutralization stage was effective and this difference was statistically significant at the level of $P < 0.01$. It can be seen that the ratio of C16:0 was between 10.580-11.253 on average, reaching an average of 11.114% with the degumming-neutralization process and an average of 11.253% during the winterization stage. The highest mean value for C18:0 was determined in crude corn oil (2.167%) and the lowest mean value was determined in deodorized corn oil (2.051%). As a result of variance analysis, it was observed that the differences occurred for C16:0 and C18:0 were statistically significant ($P < 0.01$). For both saturated fatty acids C16:0 and C18:0, degumming-neutralization, bleaching, winterization and deodorization output were determined to be statistically identical with each other.

The process of winterization in refining can generally reduce the amount of high-melting saturated fatty acids such as palmitic and stearic acids (Taşan and Demirci, 2003). In the studies of Karaali (1981) and Taşan and Demirci (2003), the refinement of sunflower oil has

determined decreases in palmitic and stearic acid ratios. In our study, as explained in the statistical evaluation, statistically significant changes were observed after applying degumming-neutralization process to crude corn oil, and the next steps did not have any effect. Liu et al. (2019a) determined the fatty acid composition of coconut oil treated by chemical refining. The amount of highest rates fatty acids C12:0, C14:0 and C16:0 and total amount of saturated fatty acids in crude oil changed from 38.11±0.13, 19.43±0.46, 13.17±0.27, 82.72±0.19 to 40.31±0.13, 19.54±0.28, 12.50±0.08, 85.41±0.36 at the end of deodorization. It may also be due to the different processing parameters used in the refining methods applied in the differences observed in these studies.

Three kinds of monounsaturated fatty acids, C16:1, C18:1 and C20:1 are determined in corn oil samples taken and examined in three different production periods. While the ratio of total unsaturated fatty acids was 30.976% in crude corn oil, it was determined as 30.889% as a result of refining process. As a result of variance analysis, the differences occurred during the refining process were found to be statistically insignificant ($P > 0.01$). On the other hand, three types of polyunsaturated fatty acids, C18:2, C18:3 and C20:2, have been determined, and an average of 55.746% in crude corn oil and 55.363% at the end of refining process. The average value of total unsaturated fatty acids, consisting of total mono and polyunsaturated fatty acids, was determined as 86.722% in crude corn oil, and the average of deodorization output at the end of refining was 86.261%. In addition, while the total unsaturated / total saturated fatty acids ratio was 6.531% in crude corn oil, this value decreased to 6.278% as a result of deodorization process. Liu et al. (2019b) investigated the effects of refining process on rice bran oil. They determined saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acid amounts ranged from 19.28±0.03 to 19.55±0.01 from 39.67±0.07 to 40.31±0.06 and from 39.61±0.02 to 35.41±0.06 in crude and deodorized oil, respectively.

In the chemically refining processes, C18:1 fatty acid average between 30.461-30.580%, C18:2 fatty acid average between 54.097-54.703% and C18:3 fatty acid average between 0.968-0.993% was determined.

Some changes can be seen in monounsaturated and polyunsaturated fatty acids as a result of treatment with water, alkali-acid, bleaching earth used during refining processes, high temperatures, oxidative events caused by air contact, changes that can be seen in saturated fatty acids during winterization stages, effects such as geometric isomerization phenomenon (Taşan, 1999). Çalışkan (2008) states that unsaturated fatty acids (oleic, linoleic) in corn oil were not affected by refining processes, only a decrease in linolenic acid values during deodorization. In our study, some reduction in linolenic acid was determined. Similarly, there was a decrease in the oleic acid ratio in the refining process. However, these changes are not statistically significant as a result of statistical evaluations. Chewa et al. (2016) identified C18:1, followed by C18:2 and C16:0, as the most common fatty acid in crude and refined kenaf seed oils. After refining processes, they identified a significant decrease in saturated fatty acids and a significant increase in total monounsaturated fatty acids. Xie et al. (2019) determined the fatty acid composition of soybean oil, which was chemically refined. The most common fatty acids found in crude soybean oil are C18:2, followed by C18:1 and C16:0. While these three fatty acid (%) in crude oil were 54.06±0.08, 22.69±0.01 and 10.6±0.02, respectively, they were determined after deodorization at 54.60±0.09, 22.41±0.0 and 10.89±0.04, respectively. Karayiğit (2018) determined total saturated fatty acid value of sunflower oil applied chemical refining was 10.24±0.003% in crude oil and 10.01±0.003% in deodorized oil; total polyunsaturated fatty acid value was determined as 64.50±0.003 in crude oil and 64.88±0.005 in deodorized oil. In light of the evaluations in the literature, it shows that there is very little difference between the rates of mono and polyunsaturated fatty acids of crude oils and refined oils.

An average of 0.040% elaidic acid (*trans* oleic acid, C18:1*t*) was determined in bleached corn oil samples taken and analyzed in three different production periods. There

was no increase in elaidic acid in corn oil samples, which came out of the deodorization stage, and was found to be 0.039% on average. In our study, *trans* fatty acid was not determined in crude corn oil samples. Also, linoelaidic acid (*trans* linoleic acid, 0.132%) was detected in bleached corn oil. By increasing this value, linoelaidic acid was detected in the deodorized corn oil as 0.175%. After the bleaching stage, the total *trans* fatty acid content little more increased in the last stage of the chemically refining. However, total *trans* fatty acid content of refined corn oil was < 0.3%.

Due to the high temperatures and durations applied at the stages of obtaining crude oil from oilseeds, *trans* fatty acid formations can be encountered even in vegetable crude oils. The differences in the fatty acid composition of the deodorized oil with different operating parameters used in the deodorization stage can lead to the formation of *trans* fatty acids at different rates and types (Taşan and Demirci, 2003; Taşan et al., 2011). Xie et al. (2019); determined the change in *trans* fatty acid (%) level of chemically refined soybean oil. Total *trans* fatty acid level was determined as 0.11±0.01 in crude oil, this value was 0.11±0.04 after neutralization; it was determined as 0.14±0.02 after the decolorizing stage and 1.08±0.07 after the deodorization stage. In various studies, it was stated that geometric isomerization occurred depending on the high temperature and long time parameters used at deodorization stage (Taşan and Demirci, 2003).

Element Contents

The average of the element content values of corn oil samples taken from chemical refining stages are shown in Table 3. Corn oil samples taken from the refining unit in three different production periods were analyzed for 14 elements in total, and changes in the refining stages were determined. Identified elements were sodium (Na), magnesium (Mg), potassium (K), phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), cobalt (Co), chromium (Cr) and copper (Cu) elements. Duncan multiple comparison test was performed on the major variation sources, and the groups are shown in Table 3.

Table 3. Average values of element contents in the process of refining steps (ppm)¹

Elements	Crude	Degummed- Neutralized	Bleached	Winterized	Deodorized
Na	38.00±0.35 ^a	10.01±0.16 ^b	9.52±0.45 ^b	8.80±0.48 ^b	8.97±0.79 ^b
Mg	21.14±0.09 ^a	1.14±0.02 ^b	0.28±0.01 ^c	0.92±0.00 ^b	1.38±0.01 ^b
K	11.74±1.07 ^a	1.12±0.38 ^c	7.55±1.05 ^b	11.02±0.65 ^a	9.78± 0.16 ^{ab}
P	107.13±0.31 ^a	1.14±0.10 ^b	0.97±0.12 ^b	1.06±0.15 ^b	0.264±0.05 ^c
Ca	108.21±0.79 ^a	31.29±0.33 ^c	36.83±0.56 ^c	54.97±0.29 ^b	8.27± 0.32 ^d
Mn	0.096±0.00 ^a	0.107±0.00 ^a	0.045±0.00 ^b	0.018±0.00 ^c	0.018±0.00 ^c
Fe	4.65±0.02 ^a	3.29±0.22 ^b	1.48±0.02 ^c	0.75±0.01 ^d	0.54±0.01 ^e
Pb	0.227±0.01 ^a	0.183±0.00 ^b	0.148±0.00 ^{bc}	0.123±0.00 ^c	0.089± 0.00 ^d
Cd	0.057±0.00 ^a	0.004±0.00 ^b	ND ²	ND	ND
Ni	0.899±0.01 ^a	0.482±0.01 ^b	0.284±0.02 ^c	0.319±0.01 ^c	0.102±0.00 ^d
Zn	1.97±0.03 ^a	0.17±0.02 ^b	ND	ND	ND
Co	0.047±0.00 ^a	0.029±0.00 ^b	0.014±0.00 ^c	ND	ND
Cr	1.42±0.02 ^a	0.071±0.01 ^c	0.149±0.00 ^b	0.204±0.01 ^b	0.079±0.00 ^c
Cu	0.148±0.00 ^a	0.053±0.00 ^d	0.063±0.00 ^{cd}	0.086±0.00 ^b	0.078±0.00 ^{bc}

¹Each value is an average of three determinations, the mean ± standard deviation (SD). The means in each row with different letter (a-d) are significantly different (P<0.01, Duncan's multiple range test). Element LOD (ppb) = Na:20.65; Mg:8.316; K:50; Ca:40; Fe:1.056; Pb:17; Cd:0.7297; Ni:4.098; Mn:0.5189; Zn:1.566; Co:2.713; Cr:2.517; P:10; Cu:2.009. ²ND: Not Detected.

Na element value, which was 38 ppm in crude corn oil, decreased to 8.97 ppm in refined oil on the other hand, the Mg element value decreased to 1.38 ppm. As a result of variance analysis, the differences formed by refining were found to be statistically significant ($P < 0.01$). The highest decrease in the Na element content was determined after the degumming-neutralization process, while the Mg element value decreased with the degumming-neutralization and bleaching processes, it increased as a result of winterization and deodorization processes. Taşan and İmer (2018) determined Na content of cold pressed sunflower, hazelnut, flaxseed and sesame oil as 4.45 ± 0.32 , 7.93 ± 1.41 , 9.73 ± 1.18 and 8.69 ± 1.92 ppm respectively, and determined Mg content as 10.16 ± 1.95 , 11.93 ± 1.47 , 5.49 ± 0.75 and 15.18 ± 2.91 ppm respectively. Karayiğit (2018) was determined Na amount in crude sunflower oil as 271.61 ppm and 0 ppm in deodorized oil. Yüksel (2010) determined the content of Mg element in refined corn oil samples in the range of 0.003-0.027 ppm and 0.157-0.372 ppm in some sunflower oil and vegetable oil mixtures. The element contents in oilseeds and oily fruits may differ significantly depending on the distribution of elements in the soil, environmental and climatic conditions, variety characteristics and processing conditions (Tuna, 2011).

While the K and Ca element value in crude corn oil was 11.74 ppm and 108.09 ppm, respectively, it was observed that these values decreased with degumming-neutralization process and increased with bleaching and winterization processes. As a result of the refining process, the K and Ca element value decreased to an average of 9.78 ppm and 8.27 ppm, respectively. As a result of analysis of variance, the differences formed by refining were found to be statistically significant ($P < 0.01$). Yüksel (2010) while determining the Ca element values in the refined corn oil between 0.053-0.111 ppm, was significantly lower than the values we find. Taşan and İmer (2018) determined the content K element in cold pressed sunflower, hazelnut, flaxseed and sesame oil as 7.10 ± 1.43 , 9.69 ± 1.39 , 4.40 ± 0.49 and 16.26 ± 3.79 ppm, respectively and determined the content of the element Ca in the same cold press oils as 54.16 ± 5.52 , 52.65 ± 8.56 , 24.58 ± 1.57 and 39.02 ± 4.68 ppm, respectively. Karayiğit (2018) determined the K and Ca amounts in crude sunflower oil as 1.55 ppm and 2.73 ppm and the K and Ca amounts in deodorized sunflower oil as 0 ppm.

On the other hand, P element value has been determined as 0.264 ppm in refined corn oil by continuously decreasing with refining steps from 107.13 ppm at the beginning of the refining process. As a result of analysis of variance, the differences formed by refining were found to be statistically significant ($P < 0.01$). Güler (2009) states that the phosphorus contained in vegetable oils was caused by phospholipids and its amount depends on the type of oilseed, soil and climatic conditions. The degumming-neutralization stage to the P element content was the most important stage and the P content has also decreased due to the phospholipids removed. Various researchers report that the P element content must be reduced before deodorization process (Taşan, 1999). Taşan and İmer (2018) determined the content of P element in cold pressed sunflower, hazelnut, flaxseed and sesame oil as 22.39 ± 4.41 , 36.49 ± 3.08 , 17.43 ± 2.35 and 50.10 ± 10.78 ppm respectively. Karayiğit (2018) determined the amount

of P in crude and deodorized sunflower oil as 967.39 ppm and 217.69 ppm. It is understood that the P value obtained in our study is quite reasonable compared to the values given in the literature.

Fe and Mn element values, which were 4.65 ppm and 0.096 ppm at the beginning, decreased to an average of 0.54 ppm and 0.018 ppm at the end of the refining. As a result of analysis of variance, the differences formed by refining were found to be statistically significant ($P < 0.01$). Karayiğit (2018) determined the amount of Mn and Fe in crude and deodorized sunflower oil as 0.10 ppm, 25.65 ppm and 0.04 ppm, respectively. According to the results of our study, the Fe value found in crude corn oil decreased by 88.4%. Bakırcıoğlu et al. (2013) Fe values determined by using different analysis methods in refined corn oil vary between 0.730-8.390 ppm. Yüksel (2010) determined Fe values in the range of 0.211-0.435 ppm in refined corn oils, and the findings are close to our results. Kabaran (2015); determined that Fe content in olive oil samples produced in the Güzelyurt region is 875.06 ± 806.85 ng/ml on average. Fe acts as a catalyst in the oxidation of oils due to its prooxidant property. For this reason, it is inconvenient to have very high levels in fats and it must be removed from the oil by refining (Güler, 2009).

Pb and Cd element values were determined as 0.222 ppm and 0.057 ppm in crude corn oil samples. The Pb element value showed continuous decreases in refining processes and decreased to an average of 0.089 ppm at the end of refining, while the Cd element was not detected after the degumming-neutralization phase. As a result of variance analysis, the differences formed by refining were found significant ($P < 0.01$). These results in crude corn oil may be a strong sign that there is a contamination in the food chain that starts from the soil and reaches the human. Cd element can also be found in crude corn oil for reasons such as being in agricultural areas, mixing with industrial processes or contaminating with phosphorus fertilizers. Bakırcıoğlu et al. (2013) determined the Pd value in refined corn oil in the range of 0.034-1.356 ppm, while determined the Cd amount in corn oil samples as 0.017 ± 0.002 mg/kg. Küçükolbaşı et al. (2014) identified Pb element in crude corn oil as 1.9 ppm and in refined corn oil as 0.04 ppm, while it was decreased by approximately 97.80%. They determined the Cd element as 1.1 ppm in crude corn oil and 0.0006 ppm in deoderized corn oil with 99.90% reduction. In our study, the Cd was found in the crude corn oil at a lower rate, while the result of the bleaching process was completely disappeared. Taşan and İmer (2018) determined the content of Pb element in cold pressed sunflower as 0.58 ppm. In our study, the rate of reduction caused by refining was approximately 62.8%.

Similarly, the Zn element was determined only in crude corn oil samples and samples taken after degumming-neutralization process. The result of statistical evaluation is the same as Cd element. Küçükolbaşı et al. (2014) detected 0.05 ppm Zn element with 4.7 ppm in crude corn oil and 98.94% reduction in deodorized corn oil after refining. As a result, the differences arising from the refining process were statistically significant ($P < 0.01$). Taşan and İmer (2018); determined the content of Zn element in cold pressed sunflower, hazelnut, flaxseed and sesame oil as 0.58 ± 0.10 , 0.32 ± 0.07 , 0.39 ± 0.06 and 0.24 ± 0.07 ppm respectively.

While the Ni element value in crude oil was 0.899 ppm on average, it decreased to 0.102 ppm by refining. Cr decreased with degumming-neutralization and deodorization processes, but increased by bleaching and wintering processes. As a result of analysis of variance, while the differences formed by refining were found significant ($P < 0.01$). Martinez et al. (2011) could not determine the Ni element in refined corn, soy, sunflower and olive oil. Bakırcıoğlu et al. (2013) reported three different results for their Ni element value in refined corn oil using three different methods: 0.034 ppm, 0.924 ppm and 1.356 ppm. They determined the value of Cr element in refined corn oil in the range of 0-0.546 ppm. It approaches the value of 0.079 ppm we find. Karayığit (2018) while determining the amount of Ni in crude and deodorized sunflower oil as 0.17 ppm and 0 ppm, Güleç (2013); determined that Cr content in natural virgin olive oils ranged between 134.78 ± 1.58 - 534.27 ± 1.58 ng/mL.

On the other hand, while the average Cu element value in crude corn oil samples was 0.148 ppm, as a result of refining, it decreased by 47.3% compared to crude corn oil and was found to be 0.078 ppm in deodorized corn oil. It is seen that degumming-neutralization phase has the biggest effect. As a result of analysis of variance, the differences formed by refining were found to be statistically significant ($P < 0.01$). Küçükkolbaşı et al. (2014) determined the Cu element content of refined corn oil as 0.018 ppm with 99.84% decrease with refining process. Bakırcıoğlu et al. (2013) determined values in the range of 0,568-1,658 ppm in refined corn oil, which is considerably higher than our results. Karayığit (2018) determined the amount of Cu in crude and deodorized sunflower oil as 0.01 ppm and 0.25 ppm. Cu, which has a wide range of uses, is released into the environment with industrial powders, mineral enrichment and wastewater. The feeding of fertilizers of animals fed with Cu additives into the soil also leads to Cu accumulation (Haktanır and Arcaç, 1998).

It is stated that the number of elements are quite high in different plant organs, the number of different elements reaches 60, and a significant part of these elements is absolutely necessary for the development of plants. The soil structure and climate conditions where the plant is grown, the storage conditions of the product, the crude oil processing conditions of the oil source and the food processing equipment used are effective on the element content in the crude oils obtained from oil seeds and oily fruits (Taşan, 1999; Güler, 2009; Yüksel, 2010).

On the other hand, trace metals are among the most common environmental pollutants, and heavy metals, which can be found in different proportions in soil, water and air, cause pollution above a certain concentration (Tuna, 2011). In addition to the health risks they cause, heavy metals in oil break down the hydroperoxides in the fatty acid chain, allowing the formation of free hydrogen and hydroxyl ions in the environment. The ions formed cause the formation of new active radicals in the chain (Başoğlu, 2006). For these reasons, it is necessary to determine the amount of especially heavy metals in edible vegetable oils in order to prevent situations that may pose a health hazard.

Conclusions

The results of the study revealed that the chemical refining process applied to crude corn oil had a positive effect on the physicochemical properties of corn oil. The refining process applied; it ensured that the color value of corn oil was illuminated to a level that can be liked by the consumer, it lowered the free fatty acid value, which negatively affected the durability of the oil, to the desired levels, and the peroxide value has been reduced far below the legal limits accepted by the chemical refining process applied. It has been observed that the fatty acids determined in the fatty acid composition of the crude corn oil are preserved by taking part in the legal limits at the end of the refining process. The values of all the elements studied showed a decrease in different rates compared to crude corn oil with the effect of refining. The refining processes are effective in reducing the amounts of heavy metals, and in this respect, it can be seen that the refining has a positive effect on reducing the risk of health by decreasing the relatively heavy metal values of vegetable oils, and the adverse effects of the oxidative stability that may be caused by these metals can be prevented to some extent. These results reveal the necessity to control various element contents in oil sources to be used in refined oil production, oil seeds and oily fruits and crude oils obtained from them. It is imperative that heavy metals, which cause important health problems, are constantly monitored in vegetable oil products and more effective legal regulations are implemented.

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