

# Regeneration behaviour of agro-industrial based waste materials. Barley husk, wheat bran and oat husk: a frying oil study

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This study aims to experimentally evaluate the influence of agro-industrial based wastes on improving the quality of sunflower oil. A synthetic adsorbent and the ashes of barley husk, wheat bran, and oat husk were selected and utilised as filtration-aid adsorbents for the regeneration of used frying oil.

The surface properties, crystal morphology, and framework structures of the ash-based adsorbents were characterized, and the mineral compositions of adsorbents were also determined. The results indicate that the crystal structure of adsorbent materials is responsible for its adsorption capacity and removal of impurities from the frying oil. Wheat bran ash was more effective in the adsorption of degradation products from oil, in reducing free fatty acid, *p*-anisidine values and also in preventing *trans*-fatty acid formation since it has the highest adsorption capacity and SiO<sub>2</sub> level. Oat husk ash drew more attention due to its largest surface area and ability to reduce the peroxide value of oils. Treatment of frying oil with agro-industrial based ashes have been found to improve the oil quality and exhibit an effect like Magnesol XL.

**Keywords:** Agricultural waste, Regeneration, Barley husk, Wheat bran, Oat husk

## 1. INTRODUCTION

Cereal by-products (husk, germ, bran etc.) have attracted industrial and academic researchers interested in agro-food based waste valorisation and management. In this research, barley husk, wheat bran, and oat husk derived silica-rich ashes were used as sustainable and eco-friendly regeneration materials for frying oils. Compared with Magnesol XL, a commercial adsorbent, wheat bran ash has many advantages, including lower free fatty acid content and *p*-anisidine values, lowest *trans*-fatty acid formation, and low cost (only needs combustion processes). Agro-industrial based adsorbent treatment exhibits innovative approach and an excellent performance for frying oil regeneration and has natural-derived and sustainable adsorption applications. This study contributes significantly to the existing literature because it provides data regarding BET surface area, SEM images, and XRD graphs of wheat bran and oat husk ashes for the first time.

Deep-fat frying is a complex and critical process, as well as a popular food preparation technique. Briefly, the frying process can be defined as a quick-cooking method of immersing the food into oil at around 180°C [1]. Desirable and undesirable physico-chemical reactions occur in frying oil depending on the type of oil, presence of oxygen, and frying temperature-time interactions. These reactions play a notable role in the compositional and organoleptic attributes of fried foodstuffs and frying oil stability [2, 3].

Wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.) and oat (*Avena sativa* L.) have a growing global demand. Wheat, barley, and oat harvest statistics were reported 765.2, 155.8 and 22.6 thousand metric tonnes according to 2019/20 forecast, respectively [4]. Not only cereals, but also their

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by-products (husk, germ, bran, etc.) have become commercially and industrially important since their positive-health roles have been documented in detail [5].

Recent researches discussed the current technologies used to remove solid and dissolved impurities, especially unwanted flavours, colours, and odour compounds from frying oils. Filtration with suitable filter-aid materials is the most widely used regeneration technique. The adsorbent treatments involving synthetic magnesium silicate, activated carbon etc. are preferred for purifying used frying oils [6, 7].

Among the potential adsorbent materials used to extend the shelf life of frying oils, silica-containing agro-industrial by-products or wastes have aroused much interest due to their low cost, framework structure, and high adsorption capacity. Biogenic silica forms can be obtained from both agricultural- and industrial-based wastes (furnace slag, coal fly etc) containing significant silica content [8, 9].

Choi et al. [10] reported that natural and powder forms of corncob as agricultural waste have effective adsorption capacities in aqueous solutions containing oil. According to researchers, the Langmuir model is more suitable to explain the spontaneous adsorption process, and the corncob is an inexpensive promising adsorbent due to its high and rapid adsorption capacity.

Choi and Gil [11] investigated the adsorption effectiveness of rice hull, barley hull, and soybean hull ashes to remove impurities from the degummed soybean oil. Ash-type and carbon-type adsorbents prepared from the aforementioned agricultural wastes and their removal capacities were compared to one another. Ash-type adsorbents were shown to be more successful in reducing (86%) the free fatty acid values in soybean oil, and carbon-type adsorbents were more effective in reducing colour compounds compared to an ash-type adsorbent.

Farag et al. [12] evaluated ashes obtained from rice, wheat, and barley hull to regenerate fried oil at 180°C for 20 h. Researchers indicated that treatment with all-natural adsorbent materials might reduce red-colour, viscosity, acidity, peroxide content, TBA and conjugated diene/triene values, and polar compounds compared to the non-treated frying oil. The highest refractive index and smoke point might be observed in oil treated with the synthetic adsorbent.

As mentioned above, different agro-industrial by-products or wastes were evaluated for the removal of undesired compounds from non-refined or fried oils. Moreover, there are no data on the adsorption effectiveness, surface morphology and characteristics by BET and SEM, X-ray diffraction spectrum of wheat bran ash and oat hull ash in literature to compare.

The aim of this study is to prepare adsorbent materials from agro-industrial wastes (barley husks, wheat bran and oat hulls) by controlled ashing and subsequently characterize the structure and morphology

of adsorbent materials. Findings obtained from this study includes comparison of the adsorption effectiveness of new adsorbent materials with commercial Magnesol XL for the regeneration of used frying oil.

## 2. MATERIAL AND METHODS

### 2.1. MATERIALS

Refined sunflower oil used as the frying media was kindly provided by Gümüş Gıda Industry and Trade Co. Inc. (Istanbul, Türkiye). Some important physico-chemical properties of the fresh oil were determined as 6.5% of total polar materials (TPM), 0.08% of free fatty acidity, and 1 meq active oxygen peroxides per kilogram of oil. Pre-fried and frozen French fries (Nimet, Türkiye) used in this study were purchased from local markets and stored at -18°C until frying and analyses.

### 2.2 PREPARATION OF THE ADSORBENT MATERIALS FROM AGRO-INDUSTRIAL BASED WASTE

Magnesol XL® (amorphous and odourless) was kindly provided by The Dallas Group of America (Whitehouse, NJ, USA). Barley (*Hordeum vulgare* L.) husk, wheat (*Triticum aestivum* L.) bran, and oat (*Avena sativa* L.) husk were obtained from Akın Aklif Agricultural Products Industry (Bursa, Türkiye) and Sağlık Agricultural Products Industry (Konya, Türkiye). Firstly, barley husk, oat husk, and wheat bran were cleaned to remove foreign materials, and then placed into the high temperature-resistant ceramic crucible. Burning process was performed in a programmable furnace (Nabertherm N500 LE, Germany) at 700°C for 12 h until it was completely ash (Fig. 1). Then, the ashes were cooled down to room temperature and stored in an airtight container.

### 2.3 CHARACTERIZATION OF THE ADSORBENT MATERIALS

Scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and



**Figure 1** - Agro-industrial based wastes and their ashes used in the regeneration of frying oils.

X-Ray Fluorescence (XRF) analyses were performed to characterize the agro-industrial based adsorbent materials.

The morphologies of agro-industrial based adsorbents were carried out by using a field mission scanning electron microscope (FE-SEM, JEOL JSM-7100F, JEOL Ltd., Japan) fitted with energy-dispersive X-ray (EDX) spectroscopy (Oxford Instruments, EDS X-Max). All samples were coated with a gold-palladium layer (80:20 wt. %) to prevent surface charges under the  $8 \times 10^{-1}$  mbar/Pa vacuum with an applied voltage of 10 mA. SEM images were acquired at an acceleration voltage of 15 kV.

The specific surface area and pore distribution were performed by QuadraSorb SI (Quantachrome Instruments, FL, USA). The adsorbent materials were first degassed under a vacuum at 150°C for 2 h, then the surface area, average pore size and total pore volume were determined using physical adsorption of  $N_2$  at -77K. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to calculate the mesopore distribution with Quantachrome Quadrawin 5.12 software (Quantachrome Instruments, FL, USA).

Adsorption capacity measurement of synthetic (Magnesol XL) and agro-industrial based adsorbents (ashes of barley husk, wheat bran and oat husk) were performed according to the technique of Taşpınar and Özgül-Yücel [6] expressed as mg oleic acid/g adsorbent.

The crystalline phases of all-natural adsorbent materials were measured by X-ray diffraction (Panalytical Empyrean, Netherlands) from 10° to 60° (2 $\theta$ ). The XRD patterns were generated using CuK $\alpha$  radiation ( $\lambda=1.54056$  Å) with at 45 kV and 40 mA. Data collection was analysed using X'Pert HighScore Plus software.

Elemental composition of the prepared ashes was analysed with X-ray fluorescence spectrometer (SPECTRO xSORT, SPECTRO Analytical Instruments GmbH).

## 2.4 FRYING PROCESS

Frying process was performed using a household fryer (Premiuer PDF 5615, Premier Electronics Ltd., İstanbul, Türkiye). Both the control oils (non-treatment) and treatment group oil samples (treated with Magnesol XL and agro-industrial based adsorbent materials) were heated up to 180° for totally 18h. The frying process was repeated for 6 h each day for three consecutive days. Before starting the frying process, enough frozen pre-fried French fries were defrosted entirely, and excess water was removed with a clean cloth. At the beginning of the experiment, all fryers were filled with 2 L of fresh sunflower oil. The frying process of totally 250 g French fries were performed for each day in each frying group. The fryers were stopped at the end of the sixth frying process on each frying day, and the adsorbent treatment process was carried out

to all treatment groups.

## 2.5 TREATMENT OF FRIED OILS WITH ADSORBENT MATERIALS

For this purpose, the oil remaining in the fryer was weighed at the end of each frying day (6 h). All adsorbent materials [Magnesol XL (MGO), barley husk ash (BHA), wheat bran ash (WBA), oat husk ash (OHA)] were added at 2% (w/w) composition into the oil at 100°C and stirred at 700 rpm for 30 min. Then the oil + adsorbent mixture was filtered through regular filter paper (Whatman no:1, 110 mm diameter) to remove adsorbent materials. Filtered oil was put back into the fryer and restarted the next day without any oil replenishment and then, 100 mL of filtered frying oil and 100 grams of French fries' samples were collected, labelled and kept frozen until the analyses.

## 2.6 QUALITY ASSURANCE TESTS ON ALL FRYING OIL AND FRIED POTATO SAMPLES

Total Polar Materials (TPM) levels (%) were measured using a commercial quick measuring device (Testo 270, Testo Inc., Germany) in the frying oils held at min 45°C temperature.

The apparent viscosity values of the oil samples were measured using a Brookfield Viscometer (model DV II+Pro, Brookfield Eng. Lab., Inc., MA, USA) at 25°C with no:18 spindle rotating at 30 rpm. Hach 2100 AN Turbidimeter (USA) was used to measure the turbidity values of frying oil samples.

Instrumental colour values were recorded as  $L^*$ ,  $a^*$ ,  $b^*$  from both oil and potato samples with a Minolta Colorimeter CR-400 (Minolta Camera Co., Osaka, Japan). Four replications were read on different locations of each sample. In addition, the hue angle, which describes the hue as well as the saturation index or chroma ( $C^*$ ), which describes the brightness or vividness of colour, were also calculated as described by Manjunatha et al. [13]. All the determinations were performed in triplicate and reported as mean values.

$$\text{Saturation index/chroma}(C^*) = \sqrt{a^{*2} + b^{*2}}$$

$$\text{Hue angle}(H^*) = \text{Tan-1} \left( \frac{b^*}{a^*} \right) \quad \text{Equation (1)}$$

Texture measurements of the French fries samples expressed as hardness value were assessed with a texture analyser (Brookfield CT3, Brookfield Engineering Labs lbc, Massachusetts, USA) equipped with TA39 probe (2 mm D, 20 mm L, motion speed 1.5 mm/s) on five different points on each fried potato sample. Texture measurements were carried out immediately after the end of each frying cycle. Before the absorbed fat content analysis, all fried potato samples were ground using a blender (Waring blender 8011EG, Waring Commercial, USA) and absorbed fat contents were quantified using petroleum ether solvent with automatic Soxtherm apparatus (Gerhardt Soxtherm Manager SX, Germany).

The free fatty acidity given as percent of linoleic acid and acid number (mg KOH/kg oil) values of the oil samples were determined by AOCS methods of Ca 5a-40 and Cd 3d-63 [14]. The peroxide and *p*-anisidine values referred as the primary and secondary oxidation products determined based on AOAC Methods [14] Cd 8-53 and Cd 18-90, respectively. These measurements were performed in triplicate for each oil samples. Total oxidation (TOTOX) value was calculated based on the following equation ( $TV=2PV+AV$ ) by Serjouie et al. [15].

The quantitative determination of fatty acid composition was carried out for each sample by methylation using the Ce 2-66 [14] and application of gas chromatograph (GC-FID) (Agilent Technologies 7890B, Palo Alto, CA, USA) according to Yılmaz & Aydeniz-Güneşer [16].

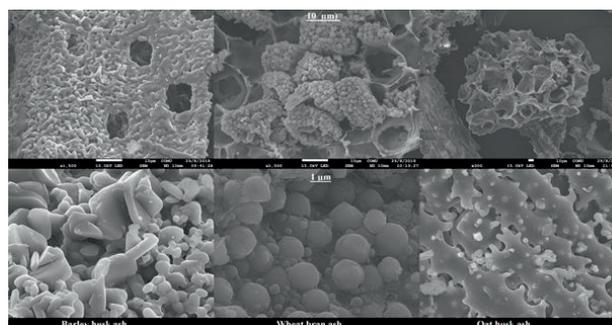
## 2.7 STATISTICAL ANALYSIS

All frying process (control and adsorbent treatment groups) were replicated two times. All analyses in frying oil and French fries' samples were done at least three times within each replicate of the treatments. All findings were reported as mean values  $\pm$  SD for Table II, as mean values  $\pm$  SE for Table III. Comparison of the treatment groups was done with ANOVA and Tukey's tests. Statistical analyses were completed with Minitab ver. 16.1.1 [17] and SPSS [18] package programs at 5% significance level.

## 3. RESULTS AND DISCUSSION

### 3.1. CHARACTERIZATION OF THE ADSORBENT MATERIALS

Morphological features such as pore radius, pore-volume, surface area, crystalline structure have critical importance on the adsorption effectiveness of adsorbent materials [11]. Especially, a positive relationship ( $r^2 = 0,891$ ,  $p = 0,017$ ) among pore volume and higher ad-



**Figure 2** - Surface morphology images of barley husk ash, wheat bran ash and oat husk ash by SEM.

sorption performance was also observed in frying oils. SEM was used to visualise the surface morphology of agro-waste based adsorbent materials used in the regeneration of frying oils. SEM images taken at magnifications of 1500x (10 nm) and 5000x (1 nm) revealed that wheat, barley, and oat ashes have a heterogeneous surface distribution and quite different crystallites and pore structures. Barley husk ashes drew much attention due to their strip and needle-shaped crystal structure. The wheat bran ashes have a globule/capsule-shaped structure, and oat husk ashes have a porous and amorphous structure (Fig. 2).

The BET analysis (Tab. I) was used for determining the critical surface characteristics of the agro-industrial based adsorbent materials. The surface area and pore volume of oat husk ash were higher than those of the barley husk ash and wheat bran ash.

As can be seen from Figure 1 and data on Table I, there are distinct similarities between the BET surface area and SEM images. It is clearly noticeable that ashes of oat husk (92.37 m<sup>2</sup>/g) and wheat bran (55.78 m<sup>2</sup>/g) have a much larger surface area than that of barley (0.82 m<sup>2</sup>/g). The pore radius values ranged from 10.71 Å to 46.55 Å. It can be brought to the attention that the lowest pore volume value was

**Table I** - Surface characteristics of the agro-industrial based adsorbent materials used in the regeneration of frying oils

Adsorbent material	BET surface area (m <sup>2</sup> /g) (p=0.00)	BJH surface area (m <sup>2</sup> /g) (p=0.00)	Pore Radius (Å) (p=0.00)	Pore Volume (cm <sup>3</sup> /g) (p=0.00)	Adsorption Capacity (mg oleic acid/g) (p=0.004)
Barley husk ash (BHA)	0.82 $\pm$ 0.01 <sup>C</sup>	1.52 $\pm$ 0.11 <sup>C</sup>	46.55 $\pm$ 0.50 <sup>A</sup>	0.02 $\pm$ 0.001 <sup>C</sup>	2.19 $\pm$ 0.07 <sup>B</sup>
Wheat bran ash (WBA)	55.78 $\pm$ 0.10 <sup>B</sup>	4.75 $\pm$ 0.05 <sup>B</sup>	10.74 $\pm$ 0.04 <sup>B</sup>	0.03 $\pm$ 0.01 <sup>B</sup>	10.22 $\pm$ 0.46 <sup>B</sup>
Oat husk ash (OHA)	92.37 $\pm$ 1.55 <sup>A</sup>	6.81 $\pm$ 0.84 <sup>A</sup>	10.71 $\pm$ 0.03 <sup>B</sup>	0.05 $\pm$ 0.01 <sup>A</sup>	5.07 $\pm$ 2.89 <sup>B</sup>
Magnesol XL (MGO) (Withiam and Sinclair, 2008; Na-Ranong et al., 2015)	from 400 to 445.4	-	95	from 0.57 to 0.88	23.80 $\pm$ 2.13 <sup>A</sup>

<sup>A-C</sup> Means followed by different uppercase letters represent significant differences for the same properties in each adsorbent material ( $p < 0.05$ )

recorded with barley husk ash despite its 4-fold larger pore radius than wheat bran ash and oat husk ash. Choi & Gil [11] compared the surface area, pore volume, pore diameter of ash-type and carbon-type of rice husk, barley husk, and soybean husk ashes. According to research, rice husk and barley husk carbon-type adsorbents have 100-times larger surface areas and 7-8 times larger pore volume than those of the rice hull and wheat bran ash-type adsorbents. The surface area, total pore volume, and pore radius for barley husk ash were determined to be 20 m<sup>2</sup>/g, 0.08 cm<sup>3</sup>/g, and 165.4 Å, respectively. Moreover, researchers also reported 345 m<sup>2</sup>/g surface area, 0.37 cm<sup>3</sup>/g pore volume, and 101.4 Å pore radius for commercial silica adsorbents.

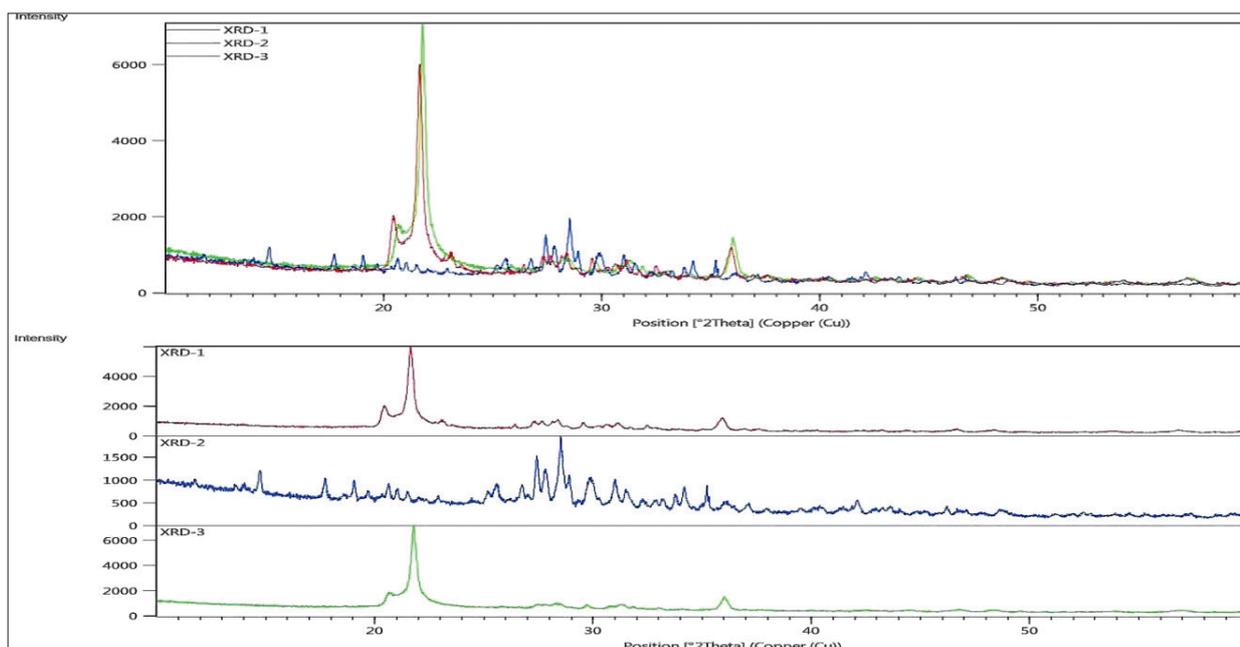
Barley husk ash used in this study mainly yielded a smaller surface area (0.82 m<sup>2</sup>/g), pore volume (0.0019 cm<sup>3</sup>/g), and pore radius (46.55 Å) compared to the findings of Choi and Gil [11]. It was believed that the differences in surface properties was caused by the ashing temperature preferred by researchers.

The crystal structure of the barley husk ash, wheat bran ash, and oat husk ash were characterized individually and comparatively by XRD (Fig. 3). Some crystal structures existed in the XRD pattern of barley husk ash and oat husk ash. SEM images also supported the fact that barley and oat husk ashes contain similar strip-shaped structures. Other impurity peaks and different X-ray broken positions were detected in the XRD patterns of wheat bran ashes. Moreover, wheat bran ashes have more intense crystal structures (Fig. 3). Regarding the d-spacing of all ash samples, BHA has a bigger d-spacing with 4.10269 Å than WBA with 3.12844 Å and OHA with 4.07894 Å. Compared to the other two ashes, it can be con-

cluded that the spherical-shaped crystal structure of WBA is responsible for its higher adsorption capacity and effective removal of impurities from the frying oil. In a recent study [19], spherical-shaped and non-spherical biochar were developed and tested to remove paracetamol from water. The researchers reported that spherical biochar's X-ray diffraction intensity and degree of crystallinity were higher than that of non-spherical biochar, spherical-shaped biochar exhibited higher porosity, surface area and total pore volume than non-spherical biochar. All these characteristics mentioned above prove that the spherical-shaped crystal structure has an increasing effect of adsorption capacity.

There is no BET data, SEM or XRD image data available, especially for wheat bran and oat husk ashes in the literature to compare. Nevertheless, there are relatively limited studies in literature on barley husk and wheat husk. It was thought that the adsorption performance of the wheat bran layer used in this study might exhibit remarkable differences compared with wheat husk reported in the literature.

The main crystalline phases of all agro-industrial-based adsorbent materials were listed in Table II. All tested agricultural-based adsorbent materials can be distinguished by their elemental compositions. The five major elements identified among the three ash-type adsorbents are SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, MgO, and CaO. Although the BHA and OHA exhibited similar crystal structure, their SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, MgO contents and adsorption behaviours toward degradation products in used frying oil were statistically different. Among all agro-industrial-based adsorbent materials, WBA contained the highest SiO<sub>2</sub> and CaO levels with a value of 87% and 3.33%, respectively.



**Figure 3** - X-ray diffraction spectras of agro-industrial based adsorbent materials (XRD-1: barley husk ash, XRD-2: wheat bran ash, XRD-3: oat husk ash)

**Table II** - Crystalline composition of the barley husk, wheat bran and oat husk ashes as adsorbent materials used in the regeneration of frying oils

Constituent (%)	Barley husk ash (BHA)	Wheat bran ash (WBA)	Oat husk ash (OHA)
MgO	11.64 <sup>A</sup>	<3.60 <sup>B</sup>	<1.39 <sup>C</sup>
Al <sub>2</sub> O <sub>3</sub>	<0.26 <sup>A</sup>	<0.33 <sup>A</sup>	<0.13 <sup>B</sup>
SiO <sub>2</sub>	1.27 <sup>B</sup>	87.00 <sup>A</sup>	75.8 <sup>A</sup>
P <sub>2</sub> O <sub>5</sub>	41.57 <sup>A</sup>	16.65 <sup>B</sup>	6.98 <sup>C</sup>
SO <sub>3</sub>	1.07 <sup>B</sup>	3.04 <sup>A</sup>	1.82 <sup>B</sup>
Cl	0.23	0.31	0.41
K <sub>2</sub> O	23.35 <sup>A</sup>	13.12 <sup>B</sup>	6.08 <sup>C</sup>
CaO	1.78 <sup>B</sup>	3.33 <sup>A</sup>	1.93 <sup>B</sup>
TiO <sub>2</sub>	<0.020	0.04	<0.017
MnO	0.33	0.09	0.11
Fe <sub>2</sub> O <sub>3</sub>	0.28	0.77	0.25
NiO	0.008	0.016	0.006
CuO	0.03	0.02	0.01
ZnO	0.13	0.07	0.01
Rb <sub>2</sub> O	<0.01	0.01	0.01
SrO	0.007	0.005	0.013

<sup>A-C</sup> Means followed by different uppercase letters represent significant differences for the same properties in each adsorbent material ( $p < 0.05$ )

SiO<sub>2</sub> content is accepted as an excellent diagnostic parameter because of its high chemical resistance and high stability at temperatures as high as 500-600°C. Hegedüs et al. [20] announced a new modified zeolite-type adsorbent called E4 (Ebsorb-4), which has a high silicon content (73%) and a specific surface of 40 m<sup>2</sup>/g. Based upon their high silicon content, researchers claimed that it could lead to improvements of adsorption ability to small molecules such as water, ammonia, methanol, or hydrogen sulphide, and it was claimed as environmentally-friendly, non-toxic and reusable material.

Similar to the findings reported by Hegedus [20], our results demonstrated that the highest SiO<sub>2</sub> content in WBA contributes to achieving the highest adsorption capacity and the effective removal of free fatty acids, *trans-form* fatty acids and peroxides from used frying oil.

According to Farag et al. [12], Mn (429–352 ppm), Si (310–295 ppm) and Ca (129–107 ppm) were determined as major minerals in wheat bran and barley hull ashes, respectively. Moreover, their Fe and Al contents were detected close to those of the Magnesol XL.

Wang et al. [21] compared ash composition and characteristics of barley straw and its husk by XRD and XRF analyses. Researchers observed that barley husk has higher ash content (4.9%) and SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Cl levels (31.77, 1.55, 23.21, and 2.26%, respectively) compared to that of barley straw ash. Major crystalline compounds in barley husk and straw ashes obtained by combustion at 550°C were identified as SiO<sub>2</sub>, KCl, and K<sub>2</sub>SO<sub>4</sub>. The barley husk ash used in this study contained lower SiO<sub>2</sub> and CaO than indicated by Wang et al. [21] and its K<sub>2</sub>O and SO<sub>3</sub>

contents were similar to the findings reported.

Wang et al. [21] drew attention to the fact that only silicates and potassium phosphates were identified as main crystalline phases in barley husk at 800°C combustions and that potassium and calcium salts could be released from the main ash structure after 550°C. In another study [22], the increment of temperature from 524°C to 962°C caused 10.5-18.5% weight loss for rice straw ash and 5.5-14.6% weight loss for wheat straw ash. Moreover, SiO<sub>2</sub> content in wheat straw ash rose from 57.5% to 66.9% with the progress in temperature. The increase in Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> contents were also positively correlated with temperature.

This temperature-weight loss phenomenon was agreed upon in many publications. It was thought that the differences in the crystal structure might be associated with different combustion temperatures used in literature.

### 3.2 PHYSICO-CHEMICAL PROPERTIES OF THE TREATED FRYING OILS

Polar substances with amphiphilic characters are the most reliable and critical indicators for detecting the degradation reactions in frying oils [23]. In this study, measured TPM values (Tab. III) in all frying oil samples increased with frying time. Treatment with oat husk ash resulted in the highest TPM values, followed by barley husk ash and wheat bran ash treated oil samples at the end of 18 h of frying. According to frying oil regulations (FDA), the maximum percentage of polar compounds in used frying oil should not exceed 25%; on reaching that level; the oil must be changed or refreshed [24]. Under these frying conditions, it was determined that adsorbent materials obtained

from agro-industrial based waste and Magnesol XL did not exceed the legal limit even at the end of 18 h of frying (Tab. III). Magnesol XL treatment resulted in the best reductions in the TPM contents of the fried oil samples. Wheat and barley hull ashes exhibited similar performances in adsorbing the polar materials from fried sunflower oil.

It was observed that the viscosity values also followed a similar trend to TPM values for deep frying. However, both commercial (Magnesol XL) and agro-industrial-based adsorbent materials were not effective in preventing frying-induced viscosity enhancements. The viscosity values of oil samples treated with barley husk and wheat bran ashes were almost half of that of the values of oil samples treated with oat husk ash. It was considered that the higher initial viscosity value (81.65 cP) of oat husk ash treated oil samples resulted in a higher-end viscosity value (100.60 cP).

According to Chatzilazarou et al. [25], the increase in viscosity of used frying oils was due to the polymerization reactions, which produces high-molecular-weight components through carbon-carbon and/or carbon-oxygen-carbon bridges among the fatty acids.

The changes in viscosity values of fried sunflower oil were examined by Farag et al. [12] and a gradual and significant increase was detected in the viscosity of oil samples taken at the end of the frying process (20 h). Sunflower oils treated with barley hull ash and wheat hull ash have a relative flow time of 7-8 min as measured by Ostwald viscometer.

Chroma and hue angle values can be defined as the intensity of colour and combination of colour co-ordinate parameters, respectively [13]. Formation of red, yellow, and blue coloured pigments during the frying process was highly correlated with oxidized fatty acids, pyrolytic condensation products, peroxides, al-

dehydes, and oil-soluble particles, according to Blumenthal & Stier [26].

The experimental data of the CIE colour parameters such as lightness ( $L$ ), chroma ( $C^*$ ), and hue angle ( $h^*$ ) values are presented in Table IV. The  $L$  values of adsorbent treated oil samples decreased linearly; on the contrary, chroma values of adsorbent treatment oil samples increased with frying time. The most expected results on  $L$  values were obtained in oils treated with agro-industrial based adsorbent materials. OHA, which have the largest surface area, is more successful in reaching lighter (the highest  $L^*$  value) than that of BHA and WBA at the end of frying. It is believed that the larger surface area will be effective in removing colour substances.

Jacobson [27] concluded that degradation reactions occurred in frying oils due to an increase in the non-polar or unsaturated carbonyl compound contents and resulted in the accumulation of the compounds in the fried foods leading to the formation of darker pigments in the frying oils. Under these experimental conditions, control and Magnesol XL treatment groups exhibited similar  $L^*$  and hue values.

The hue angle value of WBA was 102.260 at the initial frying time (6 h), and this value reached 140.10 at the end of frying time (18 h). Also, the hue angles of BHA, OHA, and control groups decreased during the deep-frying period. It was considered that the variations in Hue angle values were due to the increase in redness value of the oil and loss of moisture and pigment content, especially due to the Maillard reaction. French fries, donuts, fried fish chips, potato chips, and others are popular frying products liked by consumers worldwide. Textural characteristics like firmness, hardness, and crispness were accepted as critical quality attributes of the fried foods [28]. In this study, the firmness values and adsorbed fat contents of the

**Table III** - Some physical properties measured in the frying oil samples treated with synthetic and agro-industrial based adsorbent materials

Frying time (h)	Control	Agro-industrial based adsorbent materials			
		Magnesol XL (MGO)	Barley husk ash (BHA)	Wheat bran ash (WBA)	Oat husk ash (OHA)
TPM (%)					
6	10.00 ± 0.46 <sup>Aa</sup>	8.62 ± 0.24 <sup>Aa</sup>	9.25 ± 0.72 <sup>Aa</sup>	9.38 ± 0.12 <sup>Ab</sup>	11.88 ± 1.38 <sup>Ab</sup>
12	10.25 ± 0.43 <sup>Aa</sup>	9.00 ± 0.20 <sup>Aa</sup>	9.25 ± 0.72 <sup>Aa</sup>	10.00 ± 0.29 <sup>Aab</sup>	8.50 ± 0.29 <sup>Ac</sup>
18	11.50 ± 0.20 <sup>Ba</sup>	10.75 ± 0.14 <sup>Ba</sup>	12.25 ± 0.14 <sup>Ba</sup>	12.75 ± 0.14 <sup>Ba</sup>	16.50 ± 1.44 <sup>Aa</sup>
p=0.01					
Viscosity (25°C, cP)					
6	57.94 ± 1.53 <sup>Ba</sup>	49.75 ± 1.78 <sup>Ba</sup>	49.705 ± 0.36 <sup>Bb</sup>	54.71 ± 2.72 <sup>Ba</sup>	81.65 ± 4.99 <sup>Ab</sup>
12	41.68 ± 0.96 <sup>Cb</sup>	45.97 ± 2.00 <sup>Ca</sup>	63.62 ± 1.47 <sup>Ba</sup>	57.17 ± 1.44 <sup>BCa</sup>	86.80 ± 4.10 <sup>Ab</sup>
18	47.06 ± 1.29 <sup>Cab</sup>	46.35 ± 0.782 <sup>Ca</sup>	52.46 ± 0.50 <sup>BCab</sup>	62.54 ± 2.72 <sup>Ba</sup>	100.60 ± 0.92 <sup>Aa</sup>
p=0.01					

<sup>A-C</sup> Means followed by different uppercase letters represent significant differences for the same absorbent material in each frying time

<sup>a-c</sup> Means followed by different lowercase letters represent significant differences in each frying time for the absorbent materials (p<0.05)

**Table IV - Color parameters of the frying oil samples, and absorbed fat contents and firmness values of the French fries samples**

Frying time (h)	Control	Magnesol XL (MGO)	Agro-industrial based adsorbent materials			Total (p=0.01)
			Barley husk ash (BHA)	Wheat bran ash (WBA)	Oat husk ash (OHA)	
L* value						
6	38.17 ± 0.62	38.95 ± 0.65	38.34 ± 0.64	37.80 ± 0.67	37.12 ± 0.71	38.07 ± 0.297 <sup>a</sup>
12	37.29 ± 0.69	39.53 ± 0.27	36.39 ± 0.77	34.94 ± 1.56	38.43 ± 0.35	37.31 ± 0.50 <sup>ab</sup>
18	38.29 ± 0.39	38.76 ± 0.39	35.67 ± 0.51	34.59 ± 1.43	36.51 ± 0.74	36.76 ± 0.47 <sup>b</sup>
Total (p=0.01)	37.91 ± 0.33 <sup>AB</sup>	39.08 ± 0.26 <sup>A</sup>	36.80 ± 0.48 <sup>BC</sup>	35.77 ± 0.79 <sup>C</sup>	37.35 ± 0.40 <sup>ABC</sup>	
Chroma values						
6	9.33 ± 0.07 <sup>ABa</sup>	7.94 ± 0.25 <sup>Ba</sup>	11.13 ± 0.74 <sup>Ab</sup>	10.43 ± 0.01 <sup>ABa</sup>	8.85 ± 0.29 <sup>ABb</sup>	
12	8.98 ± 0.68 <sup>Aa</sup>	8.66 ± 0.12 <sup>Aa</sup>	10.30 ± 1.17 <sup>Ab</sup>	10.45 ± 0.13 <sup>Aa</sup>	10.57 ± 0.48 <sup>Aa</sup>	
18	11.29 ± 0.52 <sup>Ba</sup>	8.35 ± 0.44 <sup>Ca</sup>	14.85 ± 0.40 <sup>Aa</sup>	12.72 ± 0.20 <sup>ABa</sup>	13.87 ± 0.59 <sup>Aa</sup>	
p=0.01						
Hue values						
6	103.66 ± 0.31	103.79 ± 0.31	101.53 ± 0.67	102.26 ± 0.19	103.11 ± 0.23	
12	102.57 ± 0.66	103.58 ± 0.36	101.09 ± 0.25	100.13 ± 0.76	102.83 ± 0.06	
18	102.20 ± 0.69	103.93 ± 0.05	95.724 ± 0.32	140.1 ± 41.80	100.91 ± 0.82	
French fries sample						
Firmness (gram)						
6	217.80 ± 15.7	197.30 ± 16.8	269.00 ± 20.8	203.0 ± 16.3	231.80 ± 22.0	
12	248.90 ± 35.9	224.20 ± 23.3	291.20 ± 19.3	176.60 ± 11.0	255.40 ± 25.0	
18	173.80 ± 28.5	201.90 ± 14.4	243.60 ± 21.3	246.20 ± 26.3	255.90 ± 23.0	
Total (p=0.01)	213.50 ± 16.7 <sup>B</sup>	207.80 ± 10.5 <sup>B</sup>	267.90 ± 112 <sup>A</sup>	208.60 ± 12.1 <sup>B</sup>	247.70 ± 13.1 <sup>AB</sup>	
Absorbed fat content (%)						
6	5.40 ± 0.09	4.78 ± 0.07	6.08 ± 0.02	5.46 ± 0.03	6.12 ± 0.33	5.57 ± 0.17 <sup>c</sup>
12	7.33 ± 0.64	5.30 ± 0.11	10.57 ± 2.05	7.81 ± 0.80	6.79 ± 0.64	7.56 ± 0.67 <sup>b</sup>
18	11.97 ± 0.77	6.25 ± 0.03	14.83 ± 1.63	13.35 ± 1.21	10.69 ± 1.67	11.42 ± 1.06 <sup>a</sup>
Total (p=0.01)	8.2 ± 1.26 <sup>A</sup>	5.45 ± 0.27 <sup>AB</sup>	10.49 ± 1.73 <sup>AB</sup>	8.87 ± 1.53 <sup>B</sup>	7.87 ± 1.02 <sup>C</sup>	

A-C Means followed by different lowercase letters represent significant differences in each frying time for the adsorbent materials

a-c Means followed by different uppercase letters represent significant differences for the same adsorbent material in each frying time (p<0.05)

French fries were analysed during the whole frying period. Table IV shows that the adsorbent treatments significantly influenced the firmness and adsorbed fat content of French fries. Under these frying conditions, fried potato samples have different firmness profiles in all frying groups. However, firmness values of potato samples fried in control and BHA groups decreased, and firmness values of potato samples fried in MGO, WBA, and OHA did not follow the same trend and increased up to 18 h.

Similarly, intermittent frying led to a gradual decrease in fat absorption values, ranging from 4.78% to 14.83% for all frying groups. The potato samples fried in BHA absorbed higher oil content than the other frying oils, followed by the WBA and OHA groups. French fries fried in sunflower oil treated with barley husk ash were characterized with the highest content of firmness (g) and absorbed fat content (%).

Changes in the chemical properties of all frying oil samples can be examined in Table V. The formation of free fatty acids and peroxides can result in the accumulation of unhealthy compounds as well as provide a rancid taste and unpleasant sensory properties to fried food [29].

Free fatty acid and acid number values in the control sample, BHA, WBA and OHA samples, increased with frying time. In contrast, the lowest increments for free fatty acid and acid number values were recorded in oils treated with Magnesol XL. All agro-industrial-based adsorbent experimental groups demonstrated higher levels of free fatty acid compared to Magnesol XL treated sample. Nevertheless, WBA has the closest and lowest free fatty acidity value to Magnesol XL when compared to the other two ashes.

According to Official Notification of the Control Criteria of Frying Fats/Oils [30], the maximum tolerable acid number value is 2.5%, and samples in this study had acid values lower than the limit value throughout 18 h of frying.

Oxidation indicators such as peroxide and *p*-anisidine values developed during deep-frying have importance due to the possibility of using them to predict the shelf-life of oil and to monitor the behaviour of oil degradation [31].

Although the initial peroxide values (6 hours) for WBA and OHA samples were higher than the other frying groups, the peroxide values for all frying groups except WBA and OHA samples increased with the frying time. Compared to BHA, OHA and WBA, which have a much higher surface area, are thought to have a significant effect (lowest peroxide values) in the reduction of primary oxidation products. Especially, the relationship between spherical-shaped crystal structure and high adsorption capacity supports the positive effect of WBA in the removal of oxidation and hydrolysis products.

The *p*-anisidine value, which is accepted as the indicator of secondary oxidation products, can monitor oil degradation [32]. At the end of the frying period,

*p*-anisidine values reached the highest point in all frying oil samples. WBA had the lowest TOTOX value than the other frying oil samples and prevented *trans*-fatty acid formation during frying.

Faraq et al. [12] reported that the acid and peroxide values gradually increased and reached unacceptable values during the deep-frying period. Acid and peroxide values of sunflower oils treated with barley hull ash and wheat hull ash changed between 1–1.5 mg KOH/g oil and 2–4 meq active oxygen/kg oil. The increment trends for viscosity, TPM, acid, and peroxide values reported by Faraq et al. [12] were similar to the findings of this study.

The changes in the fatty acid composition of all treatment groups and the control group at the end of the frying period are given in Table VI. As expected, palmitic acid and linoleic acid were the primary saturated and monounsaturated fatty acids in sunflower oil, respectively [33]. The highest saturated fatty acid (C14-C16-C18) content was determined in MGO samples, and it was seen that this situation was statistically significant. Linoleic acid, as the major unsaturated fatty acid was shown to have very close results in all frying groups, even though OHA had the lowest linoleic acid content. There were no statistical differences in oleic acid contents among MGO, BHA, and WBA.

The fatty acid content, and especially *trans* fatty acid formation, was accepted as one of the most significant indicators for evaluating the usage life of frying oils. The occurrence of *trans* fatty acids depends on the hydrogenation or thermal refining processing, frying process, frying oil type, fatty acid composition, frying time, and the applied temperature [34]. It can be noted that the WBA sample had no elaidic acid (C18:1 *n9t*) formation and also contained the lowest amount of linolelaidic acid (C18:2 *n6t*). The high adsorption capacity of WBA may be related to the removal of more *trans* acids from frying oil compared to BHA and OHA. Moreover, agro-industrial based adsorbent materials were as effective as commercial adsorbent Magnesol XL in reducing the formation of *trans* fatty acid. The regenerative effect of tested adsorbents in the oil is quite remarkable. It is possible to say that WBA and OHA have a positive impact on reducing *trans* fatty acid formation.

#### 4. CONCLUSION

Treatment of used frying oils with the agro-industrial based adsorbents is getting special attention due to their high SiO<sub>2</sub> contents and adsorption performances. The valorisation of agro-industrial based adsorbent materials for frying oil regeneration could be a sustainable solution for waste management and a reduction of the environmental burden. This study can be appreciated as an important contribution to the existing literature because it provides data on the BET surface area, SEM images, and XRD graphs of wheat bran and oat husk ashes for the first time.

**Table V** - Some chemical properties measured in the frying oil samples treated with synthetic and agro-industrial based adsorbent materials

Frying time (h)	Control	Magnesol XL (MGO)	Agro-industrial based adsorbent materials		
			Barley husk ash (BHA)	Wheat bran ash (WBA)	Oat husk ash (OHA)
Free fatty acidity (% linoleic acid)					
6	0.35 ± 0.034 <sup>Aa</sup>	0.43 ± 0.04 <sup>Aa</sup>	0.29 ± 0.02 <sup>Aa</sup>	0.23 ± 0.06 <sup>Aa</sup>	0.35 ± 0.04 <sup>Aa</sup>
12	0.51 ± 0.07 <sup>Aa</sup>	0.33 ± 0.03 <sup>Aa</sup>	0.33 ± 0.04 <sup>Aa</sup>	0.30 ± 0.03 <sup>Aa</sup>	0.40 ± 0.05 <sup>Aa</sup>
18	0.50 ± 0.04 <sup>Aa</sup>	0.23 ± 0.06 <sup>Ba</sup>	0.47 ± 0.04 <sup>Aa</sup>	0.37 ± 0.02 <sup>Aa</sup>	0.55 ± 0.04 <sup>Aa</sup>
p=0.01					
Acid value (mg KOH/g)					
6	0.69 ± 0.07 <sup>Aa</sup>	0.86 ± 0.06 <sup>Aa</sup>	0.59 ± 0.04 <sup>Aa</sup>	0.45 ± 0.13 <sup>Aa</sup>	0.69 ± 0.087 <sup>Aa</sup>
12	1.02 ± 0.14 <sup>Aa</sup>	0.67 ± 0.06 <sup>Aa</sup>	0.66 ± 0.07 <sup>Aa</sup>	0.59 ± 0.06 <sup>Aa</sup>	0.80 ± 0.10 <sup>Aa</sup>
18	1.01 ± 0.07 <sup>Aa</sup>	0.46 ± 0.11 <sup>Ba</sup>	0.95 ± 0.07 <sup>Aa</sup>	0.75 ± 0.04 <sup>Aa</sup>	1.09 ± 0.07 <sup>Aa</sup>
p=0.01					
Peroxide value (meq active oxygen/kg oil)					
6	4.25 ± 0.54	4.72 ± 0.59	3.89 ± 0.06	5.71 ± 0.78	4.71 ± 0.62
12	4.75 ± 0.63	5.04 ± 0.77	4.26 ± 0.40	5.28 ± 0.45	5.58 ± 0.15
18	5.00 ± 0.45	5.34 ± 0.48	6.05 ± 0.25	4.61 ± 0.61	3.43 ± 0.72
p=0.277					
p-Anisidin values					
6	35.17 ± 0.31 <sup>Ac</sup>	29.47 ± 0.106 <sup>Bc</sup>	35.38 ± 0.10 <sup>Ac</sup>	27.52 ± 0.45 <sup>Bc</sup>	28.32 ± 0.28 <sup>Bc</sup>
12	55.59 ± 0.16 <sup>Ab</sup>	42.87 ± 0.089 <sup>Cb</sup>	46.05 ± 0.14 <sup>Bcb</sup>	44.03 ± 0.14 <sup>Cb</sup>	47.54 ± 0.44 <sup>Bb</sup>
18	60.83 ± 0.76 <sup>Ca</sup>	54.38 ± 0.14 <sup>Ea</sup>	63.83 ± 0.33 <sup>Ba</sup>	56.53 ± 0.60 <sup>Da</sup>	78.26 ± 0.58 <sup>Aa</sup>
p=0.01					
TOTOX value					
6	42.50 ± 0.31 <sup>Ab</sup>	38.69 ± 1.82 <sup>Ac</sup>	43.077 ± 0.35 <sup>Ac</sup>	40.88 ± 2.52 <sup>Ac</sup>	37.56 ± 2.59 <sup>Ac</sup>
12	66.13 ± 0.08 <sup>Aa</sup>	55.495 ± 0.99 <sup>Bb</sup>	55.32 ± 1.79 <sup>Bb</sup>	55.62 ± 0.18 <sup>Bb</sup>	58.543 ± 0.243 <sup>ABb</sup>
18	70.48 ± 3.05 <sup>Ba</sup>	66.01 ± 0.20 <sup>Ba</sup>	75.66 ± 0.27 <sup>Ba</sup>	65.78 ± 1.37 <sup>Ba</sup>	85.86 ± 3.83 <sup>Aa</sup>
p=0.01					

A-E Means followed by different lowercase letters represent significant differences in each frying time for the adsorbent materials

a-c Means followed by different uppercase letters represent significant differences for the same adsorbent material in each frying time (p<0.05)

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## Declaration of competing interest

The authors declare they have no known competing financial interests or personal relationships that could have appeared as to influence the work reported in this paper.

## Authors' contributions

Özcan Suzan: Master student; Methodology, Formal analysis. Aydeniz-Guneser Buket: Conceptualization; Investigation; Writing-review & editing; Supervisor; Project administration.

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**Table VI - Fatty acid composition of the frying oil samples treated with synthetic and agro-industrial based adsorbent materials after 18 h of frying**

Fatty acid	p value	Control	Magnesol XL (MGO)	Agro-industrial based adsorbent materials		
				Barley husk ash (BHA)	Wheat bran ash (WBA)	Oat husk ash (OHA)
Myristic acid (C14:0)	0.01	0.07 ± 0.01 <sup>E</sup>	0.28 ± 0.01 <sup>A</sup>	0.12 ± 0.01 <sup>B</sup>	0.09 ± 0.01 <sup>D</sup>	0.10 ± 0.01 <sup>C</sup>
Palmitic acid (C16:0)	0.01	6.41 ± 0.02 <sup>E</sup>	7.63 ± 0.02 <sup>A</sup>	7.28 ± 0.01 <sup>B</sup>	7.08 ± 0.01 <sup>D</sup>	7.21 ± 0.02 <sup>C</sup>
Palmitoleic acid (C16:1)	0.01	0.03 ± 0.01 <sup>D</sup>	0.05 ± 0.03 <sup>A</sup>	0.04 ± 0.01 <sup>B</sup>	0.03 ± 0.01 <sup>C</sup>	0.03 ± 0.01 <sup>C</sup>
Stearic acid (C18:0)	0.01	3.07 ± 0.03 <sup>E</sup>	3.34 ± 0.09 <sup>A</sup>	3.24 ± 0.06 <sup>C</sup>	3.19 ± 0.02 <sup>D</sup>	3.31 ± 0.09 <sup>B</sup>
Oleic acid (C18:1 n9c)	0.01	31.88 ± 1.60 <sup>C</sup>	32.70 ± 2.30 <sup>B</sup>	32.65 ± 2.45 <sup>B</sup>	32.73 ± 2.20 <sup>B</sup>	35.05 ± 4.19 <sup>A</sup>
Elaidic acid (C18:1 n9t)	0.736	0.068 ± 0.01	0.043 ± 0.01	0.05 ± 0.01	nd	0.04 ± 0.01
Linoleic acid (C18:2 n6c)	0.658	54.14 ± 3.02	54.31 ± 2.81	55.27 ± 0.01	55.31 ± 3.20	52.67 ± 1.19
Linoleic acid (C18:2 n6t)	0.823	0.23 ± 0.06	0.26 ± 0.05	0.27 ± 0.05	0.19 ± 0.03	0.24 ± 0.04
Linolenic acid (C18:3 n6)	0.01	0.128 ± 0.01 <sup>AB</sup>	0.11 ± 0.01 <sup>AB</sup>	0.05 ± 0.01 <sup>D</sup>	0.12 ± 0.01 <sup>A</sup>	0.04 ± 0.01 <sup>C</sup>
Gamma linolenic (C18:3 n6)	0.01	0.04 ± 0.01 <sup>A</sup>	0.02 ± 0.01 <sup>B</sup>	0.02 ± 0.01 <sup>B</sup>	0.01 ± 0.01 <sup>B</sup>	0.01 ± 0.01 <sup>C</sup>
Arachidonic acid (C20:4 n6)	0.01	0.05 ± 0.01 <sup>A</sup>	0.04 ± 0.01 <sup>B</sup>	0.05 ± 0.01 <sup>C</sup>	0.04 ± 0.01 <sup>B</sup>	0.05 ± 0.01 <sup>B</sup>

<sup>A-E</sup> Means followed by different lowercase letters represent significant differences in fatty acids (p<0.05)  
nd: not determined

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