Original article

# Effect Of Hops Oil on Sunflower Oil Thermal Stability

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**Summary.** The aim of this study was to compare the effects of hops oil and butylated hydroxytoluene (BHT) on the thermal stability of sunflower oil. Oil samples were subjected to heat treatment at 180°C for 5 min and this process was repeated ten times. Free fatty acid (FFA), peroxide (PV), p-anisidine (p-AV), conjugated dienes (CD) and trienes (CT) values, induction time (IT) and fatty acid composition (FAC) were investigated after 0, 2, 5 and 10 heating cycles to evaluate chemical changes during heating. Antioxidant activities of oil samples were evaluated using DPPH radical scavenging and β -carotene bleaching assays. According to the results, the change in the FFA value of sunflower oils was not significant at the end of the ten heating cycles. The effect of the hops oil on PV and p-AV was found to be similar to that of BHT. Hops oil (1200 ppm) added sample (1.0) gave the closest CD value to the BHT group (0.8). Addition of BHT and hops oil prolonged the induction time of sunflower oil. Total monounsaturated fatty acids increased while polyunsaturated content decreased in all samples. Moreover, hops oil exhibited significantly higher antioxidant activity in sunflower oil compared to control.

**Key words:** hops oil, thermal stability, antioxidant, sunflower oil

## Introduction

Fats and oils, which have important functions in the human diet, can easily undergo oxidation in the presence of factors such as oxygen, heat, light, enzymes and metals. When the oxidation starts, unsaturated fatty acid molecules lose a hydrogen and turn into free radicals. The lipid radicals react with oxygen to form peroxyl, then attack a new fatty acid molecule to initiate a chain reaction. The chain reaction continues until an antioxidant stops it, or there is no more hydrogen to break (1).

Refined oils like sunflower oil are often used for frying foods. The sensory properties such as taste, appearance, and texture are provided by deep-frying, one of the most common and oldest cooking methods. This method cannot be duplicated by another; therefore, the demand increases day by day. Another reason why fried foods are preferred is that they can be prepared quickly and easily (2, 3). However, nutrition scientists do not recommend consuming large amounts of fried foods due to their high calorie, cholesterol, oxidized oil, trans fatty acids and unsaturated fatty acid contents (2, 4). During the frying process, high temperature (150–200 ) causes a series of chemical reactions, including oxidation, hydrolysis and polymerization of unsaturated fatty acids. As a result, the composition of the frying medium is changed by the formation of volatile chain scission products, non-volatile oxidized derivatives and dimeric, polymeric, or cyclic substances (5, 6). Considering the nutritional characteristics, canola, soybean, and sunflower oils with high polyunsaturated acid content have no stability at high temperatures (7).

Oxidation caused by increasing peroxide, aldehyde and ketones causes unpleasant changes in the oils' taste, odor and nutritional quality. Therefore, antioxidants should be used in refined oils due to the high

number of double bonds in their chemical structure. Synthetic antioxidants were suitable and advantageous agents to increase shelf-life and prevent the decrease in nutrition values until their toxicology was revealed. Consumers and manufacturers are trying to avoid using these synthetic antioxidants as much as possible and prefer natural and safer ingredients that can act as an antioxidant. Researchers have shown that oils extracted from herbs can increase the oxidative and thermal stability of edible oils and foods (8).

Hops (*Humulus lupulus* L.) has been cultivated since 200 A. D. and used to produce beer and alcoholic beverages for about 900 years. It is an important ingredient in the industry to give a bitter taste to beer all over the world. On the other hand, hops extracts have anticarcinogenic, antimicrobial and estrogen activities associated with their flavonoid and 8-prenylnaringenin contents (9).

This study aimed to improve the stability of sunflower oil against oxidation caused by frying temperature using hops oil. Two different concentrations of hops oil were used and the results were compared with butylated hydroxytoluene (BHT), a synthetic antioxidant, to comprehend whether hops oil contributed to oxidative stability. In addition, to the best of our knowledge, this is the first research investigating the effect of antioxidant activity of hops oil on thermal oxidation in sunflower oil.

## Materials and Methods

### *Materials*

Sunflower oil was provided from an oil factory (Oruçoğlu Oil Factory, Afyonkarahisar, Turkey). It was subjected to refining process and did not contain any additives. Hops oil was supplied from Realec Natural and Synthetic Chemical, Enza Company (İzmir, Turkey). Beta carotene, linoleic acid, p-anisidine and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were provided from Sigma (St. Louis, MO). Butylated hydroxytoluene (BHT), glacial acetic acid, diethyl ether, ethanol (%96 v/v), ethyl acetate, phenolphthalein, n-hexane, isooctane, chloroform, methanol, potassium hydroxide, potassium iodide, starch and Tween-40 were provided from Merck (Darmstadt, Germany).

### *Sample preparation and thermal oxidation of oils*

A deep fryer (Tefal, Uno M, Rumilly, France) was first loaded with 2 liters of sunflower oil and heated to the desired temperature. Thermal oxidation of sunflower oil samples was performed at 180°C for 5 min The samples were cooled to room temperature and thermal oxidation was applied again for the following heating process. This process was repeated ten times for each sample. Analyzes were performed in the 2nd, 5th and 10th heating cycles. Sunflower oil samples were divided into four groups: additive-free sunflower oil (CON), sunflower oil with 100 ppm butylated hydroxytoluene (BHT), sunflower oil with 1200 ppm hops oil (HOPS1200) and sunflower oil with 2400 ppm hops oil (HOPS2400). All heat treatments were performed in triplicate (n = 3).

### *Determination of free fatty acid (FFA) and peroxide values (PV)*

The free fatty acid (FFA) contents and peroxide value (PV) of the oil samples were measured according to the IUPAC (10) and the official method of AOCS Cd8b-90 (11), respectively. All determinations were performed in triplicate (n = 3).

### *Determination of p-Anisidine value (p-AV)*

The p-anisidine value (p-AV), which gives information about the second oxidation products of peroxides (aldehydes and ketones), was determined according to the AOCS Cd18-90 (12). For this purpose, 0.1–0.4 g of the sunflower oil samples were dissolved in 10 mL isooctane. The absorbance of this oil solution ($A_1$) was measured against the isooctane (as blank) at 350 nm. Then, 5 mL of this solution and 1 mL of the p-anisidine solution (0.25% g/v glacial acetic acid) were mixed. In addition, 5 mL of isooctane and 1 mL of p-anisidine solution were transferred to another test tube (as blank). After 10 minutes, the absorbance value ($A_2$) was recorded at 350 nm against isooctane

containing p-anisidine. The p-anisidine value of the oil samples was calculated using the following formula (Eq. 1). All determinations were performed in triplicate (n = 3).

$$p-AV = 10x\frac{1.2x(A2-A1)}{w} \qquad \text{(Eq. 1)}$$

*Determination of conjugated dienes (CD) and conjugated trienes (CT) value*

The conjugated dienes (CD) and conjugated trienes (CT) values of the samples were measured according to AOCS Ti 1a-64 (13). Approximately 0.1 g of sunflower oil was weighed and dissolved in 10 mL isooctane. Then, the absorbance values were measured at 232 and 268 nm for CD and CT, respectively using a UV-visible spectrophotometer (Shimadzu UV-1240, Tokyo, Japan). All determinations were performed in triplicate (n = 3).

*Determination of induction time (IT) by Rancimat Method*

The Ransimat test is a method in which accelerated techniques are used to measure oxidative stability and to estimate the shelf life of fat and fatty foods. This test, recommended by Hadorn and Zurcher (14) as the rancimat method, was applied to determine the oxidative stability of the sunflower oil with or without hops oil or BHT. It is performed in a sealed tube where the sample is placed and applied at high temperature to accelerate oxidation. During the process, the oxidation products of volatile compounds such as acetic and formic acids in the sample are carried by air circulation into a container filled with distilled water. There is a significant change in the conductivity of the water phase when oxidation starts and the conductivity is measured, then the initial time of oxidation is recorded. The oxidative stability of the tested sample is related to the late beginning of the change in the conductivity value recorded as induction time (IT) (15).

The oxidative stability of the samples was determined by Duman et al. (16). In the analysis, 110°C constant temperature (743 Rancimat Metrohm, Herisau, Switzerland) was used to oxidize 3 g of oil. The flow rate of the air passing through the samples was set to be 20 L/hour. Ultrapure water with a conductivity of 0.055 µs was used in the study. All determinations were performed in triplicate (n = 3).

*Determination of fatty acids composition (FAC)*

The fatty acid composition of the samples was determined as fatty acid methyl esters (FAMEs). FAMEs were prepared according to ISO 5509 (17) and analyzed a Agilent 6890N Gas Chromatography (GC) equipment with a flame ionization detector (FID) and HP-88 column (i.d. = 0.25 mm, length = 60 m, film thickness = 0.2 µm, California, United States). Injector and FID temperatures were 270°C and 290°C, respectively. The oven temperature was kept at 165°C for 30 min then increased by 10°C/min and kept at 190°C for 20 min. Helium (16.4 psi) was used as carrier gas. Sample injection, split flow and split ratio were 0.2 µl, 0.4 ml/min, 1/70, respectively. Identification and quantification of FAMEs (area percent) by comparing the relative retention times of the peaks were accomplished with those of authentic standards.

*Antioxidant capacity assays*

The antioxidant capacity of the oil samples was measured by DPPH$^{\bullet}$ (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging and β-carotene bleaching assays which were performed according to methods developed Brand-Williams et al. (18) and Taga (19), respectively. Two hundreds µL of sample and 3 mL of 0.051 mM DPPH solution were mixed and incubated at room temperature for 30 min. The change in absorbance was measured at 517 nm, spectrophotometrically against blanks. DPPH scavenging activity of the oil samples was calculated using the following formula (Eq. 2) where $A_0$ was the absorbance of the blank (reacting mixture without the test sample), and $A_1$ was the absorbance of the reacting mixture with the test sample.

$$DPPH\ scavenging\ activity\ (\%) = \frac{(A0-A1)}{A0}\times 100 \qquad \text{(Eq. 2)}$$

For the β-carotene bleaching test, 1 mg of β-carotene was dissolved in 10 mL of chloroform. Next, 1 mL of β-carotene solution, 20 mg of linoleic acid and 200 mg of Tween 40 were mixed. Chloroform was removed from the mixture and stabilized by adding 50 mL of distilled water. 5 mL of the prepared emulsion was transferred to each tube. After adding 0.2 mL of diluted sample to the tubes, they were shaken. In the control experiment, 5 mL of emulsion and 0.2 mL of methanol were mixed. 20 mg of linoleic acid, 200 mg of Tween 40 and 50 mL of distilled water were used to zero the spectrophotometer (Shimadzu UV–1240, Tokyo, Japan). Then, the spectrophotometer was adjusted to 470 nm and the absorbance values of the control and samples were measured at t = 0. After the process, the samples were placed in a water bath at 50°C. The absorbance was measured every 15 minutes until the absorbance value of the control fell below 0.03. The absorbance values obtained at the end of 120 minutes and the antioxidant activities of the samples were calculated using the following formula (Eq. 3) and formula (Eq. 4), respectively. All determinations were performed in triplicate (n = 3).

The bleaching rate of β-carotene (R) was calculated by formula (Eq. 3) where a was the initial absorbance value and b was the absorbance value after 120 minutes

$$R = \frac{\ln(a/b)}{t} \qquad \text{(Eq. 3)}$$

The antioxidant activities of the samples (AA) were calculated by formula (Eq. 4) where $R_C$ was the bleaching rate of the control sample and $R_S$ was the bleaching rate of the oil sample.

$$AA(\%) = \frac{RC - RS}{RC} \times 100 \qquad \text{(Eq. 4)}$$

*Statistical analysis*

The tests were performed in triplicate and the results were expressed as mean ± standard deviation (SD). They were statistically analyzed by ANOVA using SPSS (version 11.5, SPSS Inc., USA). Duncan's multiple range test with a significance level of 0.05 was used to determine the differences between groups and heating cycles.

**Results and discussion**

The amount of FFA that reaches values above the standards causes undesirable changes in the sensory and nutritional values of oils and foods. FFA formation is a relevant indicator for investigating fat and oil rancidity (20). Heat treatment of oils/fats causes the release of fatty acids from glycerides by hydrolysis reactions and increases the number of FFA depending on the selected temperature. In this study, the FFA content increased from 0.168% to 0.209% in CON and BHT groups, from 0.168% to 0.189% and 0.176% in HOPS1200 and HOPS2400 groups, respectively. The change in the FFA value of all sunflower oils was slight but not significant at the end of the 10$^{th}$ heating cycle ($p>0.05$) (Fig 1a). BHT added sunflower oil showed the highest increase in FFA as much as the control sample, confirming that BHT had no retardation effect on sunflower oil deterioration (21). Fatty acids could evaporate from the surface at frying temperatures while being released by hydrolysis and oxidation. Therefore, although FFA is an indicator of oil quality, it should be evaluated together with other measurements since it is a dynamic value (21).

PV is one of the quality criteria for fats and oils, including peroxides and hydroperoxides formed in the initial stages of lipid oxidation reactions (22). In this study, PV measurement was carried out in heat-treated sunflower oil with hops oil and BHT to show the primary oxidation degree. The effect of hops oil and BHT on PV of sunflower oil samples during different heating cycles is given in Fig. 1b. According to the results, the PV of all samples after heating ranged from 2.84 meq $O_2$/kg oil to 6.20 $O_2$ /kg oil. There was a significant loss with the heating process in PV at the end of the 10$^{th}$ heating cycle for all groups, while the PV of HOPS1200 group was as low as the BHT group at the 5$^{th}$ and 10$^{th}$ heating cycle. However, the PV value of HOPS2400 was remarkable at the end of heating. The high concentrations of oleic (32.96%) and linoleic (55.43%) acids that affect peroxide formations of hops oil may explain why this group gave the highest PV value, contrary to expectations. According to other researchers who obtained data close to our results, the decrease in PV during heating or frying was explained as the reduction in the solubility of

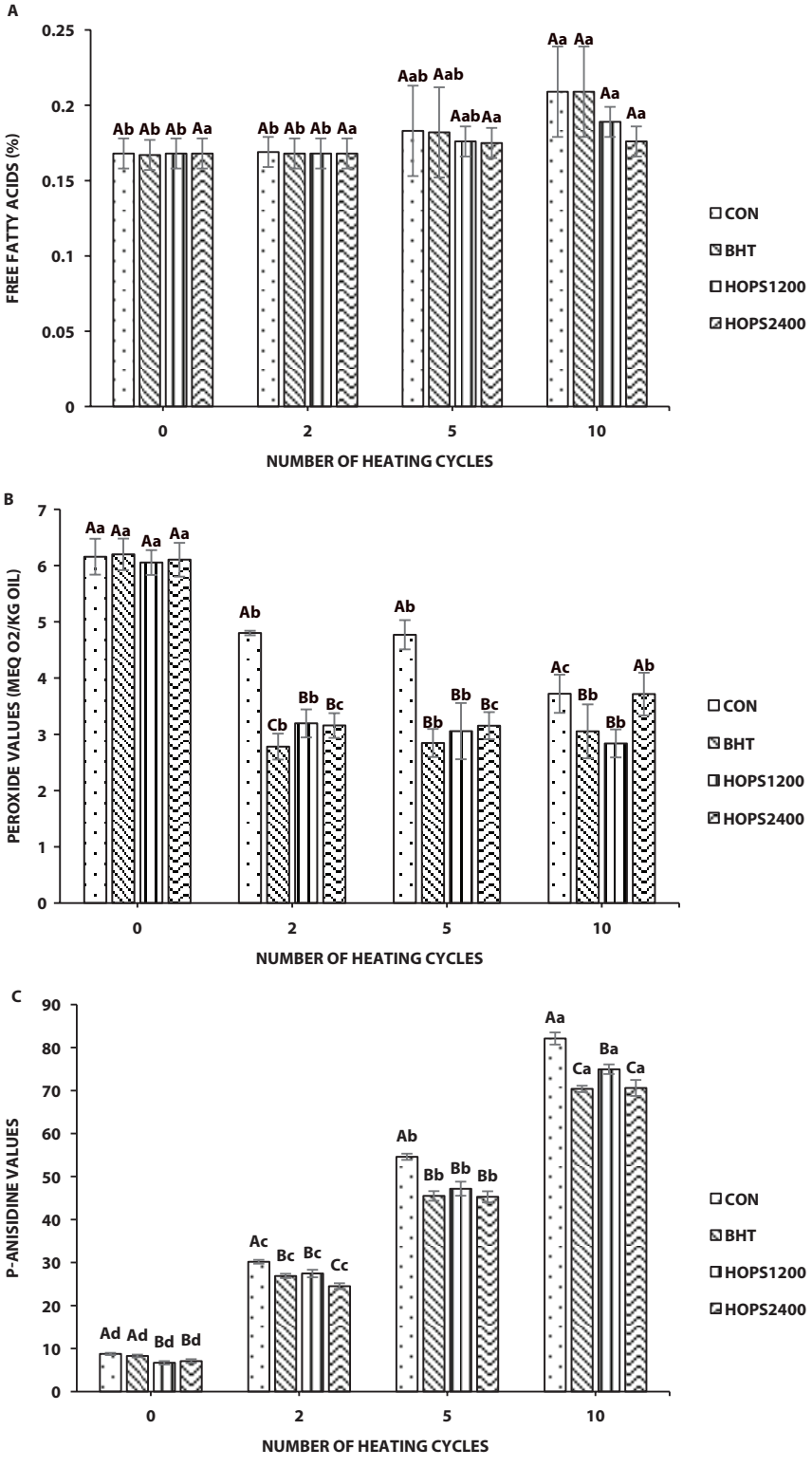


**Figure 1.** Free fatty acid (a), peroxide (b) and p-anisidine (c) values of oil samples. Values followed by different uppercase (A-D) and lowercase (a–d) letters show significant difference between samples and heating cycle, respectively ($p<0.05$). CON: Control, BHT: Oil with 100 ppm butylated hydroxytoluene (BHT), HOPS1200: oil with 1200 ppm hops oil, HOPS2400: oil with 2400 ppm hops oil

the oxygen required for peroxide formation due to the high temperature (5, 23, 24). In addition, peroxides, which are precursors of secondary oxidation products, can be reduced by conversion into compounds such as aldehydes and ketones in high-temperature applications (23). For these reasons, the researchers suggest that the peroxide value alone cannot be sufficient to evaluate the degree of oxidative degradation (25).

The p-AV is considered the index of volatile and nonvolatile aldehyde compounds in fats/oils (26). This value is calculated according to the absorbance of the color formed (350nm) as a result of the reaction of aldehydes and ketones, which are the secondary oxidation products of hydroperoxides. The changes in p-AV of sunflower oil samples during the heat treatment at 180°C are presented in Fig. 1c. There was a positive linear relationship between p-AV and the number of heat treatments in all groups. According to the statistical analysis results, the number of heating had a significant effect on the increase in p-AV ($p<0.05$). The p-AV values of CON, BHT, HOPS1200 and HOPS2400 groups were detected 82.10, 70.39, 74.96 and 70.60, respectively, at the end of $10^{th}$ heating cycle. The inhibitory effect of the HOPS2400 on p-AV formation was found to be stronger or similar to that of the BHT ($p>0.05$). These results are consistent with several studies where different frying temperatures were applied. Wang et al. (27) found that 1200 ppm essential coriander oil contributed to delaying the formation of anisidine in sunflower oil under 24-day accelerated storage conditions as well as synthetic antioxidants. Yeo et al. (28) investigated the effect of sesamol on the thermal stability of lard at four different temperatures (90, 120, 150 and 180°C). According to the results of the study, the highest p-AV value was detected in the sample with tocopherol, followed by BHA, sesamol and TBHQ at 150°C. In another study investigating the effect of Greek sage and summer savory extracts on the thermal oxidative stability of various edible oils, it was determined that summer savory extract was effective on the p-AV value of sunflower oil after 10 hours of heat treatment at 180°C (26). In the study reported by Inanc and Maskan (29), it was stated that carvacrol affected on the p-AV value as much as BHT even after several frying processes.

CD and CT values that provide important information about the oxidative status of oils measured for each sample are given in Table 1. The results of the study showed that CD and CT values increased with the increase in the number of heating significantly in all oil samples ($p<0.05$). The statistical analysis demonstrated that the effect of BHT, HOPS1200 and HOPS2400 was not significant ($p>0.05$) on the increase in CT formation in all heating cycles. Although the CD level of BHT added oil (0.83) was lower than HOPS1200 group (0.97), it gave the closest value to the BHT group. In a study investigating the effect of carvacrol on the thermal oxidative stability of palm oil (29), the change in CD values was higher than CT, which was in line with our results. The reason for that was attributed by the researchers to the linoleic acid concentration higher than that of the linolenic acid in oils such as sunflower oil (29, 30). Considering the linoleic and linolenic acid concentrations of sunflower oil used in our study, we agree with the above statement.

The IT provides important information about the ability of edible oils to resist oxidation. In the present study, the IT result of all sunflower oil samples decreased when the heating number increased (Table 1). It was observed that BHT followed by HOPS 2400 provided good protection to sunflower oil against oxidative degradation in all heating cycles. There have been various results in the literature regarding the IT of edible oils with some plant-derived compounds after heat treatment. Horuz and Maskan (5) examined the effects of frying temperature (150–180°C) and concentration of four plant-based active components on IT of corn and palm oils. They were reported that carvacrol showed a significant effect in both oils. In another study, IT values of 200, 400, and 600ppm Olive Waste Cake ethanol Extract added sunflower oil (OWC). After heating, although IT values were 8 h in the control sample, it increased 12.5, 17.8 and 25.5 h, in 200, 400, 600 ppm OWC added oils, respectively (31). Yang et al. (32) investigated the effect of rosemary extract on the oxidative stability of vegetable oil. They found that IT was significantly higher for all oils containing rosemary extract than those containing synthetic antioxidants. Although the IT of the hops oil-added samples was lower than those with BHT, their antioxidant activities were as high as BHT at

**Table 1.** Conjugated dienes (CD), conjugated trienes (CT) and induction period of oil samples

| | Samples | Number of heating cycles | | | |
|---|---|---|---|---|---|
| | | 0 | 2 | 5 | 10 |
| **Conjugated diene values** | **CON** | $0.29\pm0.03^{Bd}$ | $0.77\pm0.02^{Ac}$ | $1.18\pm0.07^{Ab}$ | $1.46\pm0.04^{Aa}$ |
| | **BHT** | $0.25\pm0.00^{Bc}$ | $0.32\pm0.03^{Cc}$ | $0.57\pm0.09^{Bb}$ | $0.83\pm0.03^{Da}$ |
| | **HOPS1200** | $0.45\pm0.04^{Ac}$ | $0.45\pm0.01^{Bc}$ | $0.69\pm0.06^{Bb}$ | $0.97\pm0.02^{Ca}$ |
| | **HOPS2400** | $0.45\pm0.01^{Ac}$ | $0.46\pm0.01^{Bc}$ | $0.73\pm0.04^{Bb}$ | $1.36\pm0.02^{Ba}$ |
| **Conjugated triene values** | **CON** | $0.10\pm0.00^{Ac}$ | $0.14\pm0.00^{Ab}$ | $0.16\pm0.01^{Ab}$ | $0.21\pm0.02^{Aa}$ |
| | **BHT** | $0.10\pm0.00^{Ac}$ | $0.13\pm0.00^{Abc}$ | $0.15\pm0.01^{Ab}$ | $0.19\pm0.02^{Aa}$ |
| | **HOPS1200** | $0.10\pm0.01^{Ac}$ | $0.14\pm0.00^{Ab}$ | $0.15\pm0.02^{Ab}$ | $0.20\pm0.00^{Aa}$ |
| | **HOPS2400** | $0.10\pm0.00^{Ad}$ | $0.13\pm0.00^{Ac}$ | $0.16\pm0.01^{Ab}$ | $0.20\pm0,00^{Aa}$ |
| **Induction period (h)** | **CON** | $4.32\pm0.01^{Ca}$ | $3.95\pm0.01^{Cb}$ | $3.91\pm0.01^{Db}$ | $3.86\pm0.02^{Dc}$ |
| | **BHT** | $5.10\pm0.02^{Aa}$ | $4.77\pm0.01^{Ab}$ | $4.65\pm0.01^{Ac}$ | $4.28\pm0.01^{Ad}$ |
| | **HOPS1200** | $4.84\pm0.02^{Ba}$ | $4.54\pm0.01^{Bb}$ | $4.31\pm0.01^{Cc}$ | $4.06\pm0.01^{Cd}$ |
| | **HOPS2400** | $5.06\pm0.01^{Aa}$ | $4.78\pm0.01^{Ab}$ | $4.60\pm0.02^{Bc}$ | $4.22\pm0.01^{Bd}$ |

Values followed by different lowercase (a–d) and uppercase (A-D) letters show significant difference for each raw and column ($p<0.05$), respectively. CON: Control, BHT: Oil with 100 ppm butylated hydroxytoluene (BHT), HOPS1200: oil with 1200 ppm hops oil, HOPS2400: oil with 2400 ppm hops oil.

the end of the 5th and 10th heating cycle, suggesting that hops oil might have lost some of its volatile components that have antioxidant activity during the Ransimat test.

FAC may change during the heating process and that affects the taste and nutrition quality of oils. The major FAC of sunflower oil treated with hops oil, BHT and untreated samples during 10 heating cycles are shown in Table 2. The first four fatty acids in the unheated control group according to their concentrations were linoleic (63.47%), oleic (25.10%), palmitic (6.00%) and stearic (3.62%) acids. Total monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids obtained from the unheated control group were 25.24% and 63.79%, respectively. In addition, as the number of heat treatments augmented, the amounts of palmitic acid, stearic acid, oleic acid and total MUFA increased. In contrast, linoleic acid and total PUFA concentration decreased in all samples after 10 heating cycles. Researchers consider that heat treatment causes polymerization, pyrolytic, hydrolytic and other chemical reactions and reorganization of double bonds in fatty acids (33, 34). Günal et al. (35) studied the effect of extract obtained from olive oil by-products and soy lecithin on the thermal stability of sunflower oil during deep frying. According to their results, which are in line with ours, while the linoleic acid content of the oil samples with deep-frying temperature was greatly reduced, oleic, palmitic and stearic acid increased significantly. They reported that lecithin and the extract from olive oil by-products had a weak effect on changing of sunflower oil fatty acid profile during heat treatment. In another study, a significant decrease was observed in the linoleic and palmitic acid content of sunflower oil during the deep-frying process (34).

The results of DPPH scavenging activity and β-carotene bleaching values are given in Table 3. According to the results, a significant decrease was observed in both capacity assays after heat treatment in all oil samples compared to the unheated group. The results obtained from the DPPH assay at the end of the $10^{th}$ heating cycle showed that both hops oil concentrations provided as much radical scavenging activity as BHT ($p>0.05$). In addition, at the end of the same heating cycle, β-carotene bleaching values showed that HOPS1200 (59.58%) and HOPS2400 (62.22%) had

**Table 2.** The major free fatty acid compositions of oil samples (%)

| | Samples | Number of heating cycles | | | |
|---|---|---|---|---|---|
| | | 0 | 2 | 5 | 10 |
| C16:0 | CON | 6.00 | 5.95 | 6.10 | 6.17 |
| | BHT | 6.02 | 6.04 | 6.10 | 6.11 |
| | HOPS1200 | 5.96 | 5.99 | 6.06 | 6.14 |
| | HOPS2400 | 6.04 | 6.03 | 6.16 | 6.08 |
| C18:0 | CON | 3.62 | 3.65 | 3.67 | 3.71 |
| | BHT | 3.62 | 3.64 | 3.67 | 3.69 |
| | HOPS1200 | 3.65 | 3.65 | 3.67 | 3.71 |
| | HOPS2400 | 3.65 | 3.66 | 3.66 | 3.71 |
| C18:1 | CON | 25.10 | 25.17 | 25.30 | 25.47 |
| | BHT | 25.01 | 25.13 | 25.23 | 25.38 |
| | HOPS1200 | 25.10 | 25.20 | 25.27 | 25.45 |
| | HOPS2400 | 25.16 | 25.19 | 25.29 | 25.45 |
| C18:2 | CON | 63.47 | 63.33 | 63.09 | 62.73 |
| | BHT | 63.50 | 63.34 | 63.08 | 62.94 |
| | HOPS1200 | 63.40 | 63.24 | 63.00 | 62.76 |
| | HOPS2400 | 63.26 | 63.18 | 63.00 | 62.76 |
| ΣMUFA | CON | 25.24 | 25.33 | 25.46 | 25.65 |
| | BHT | 25.17 | 25.56 | 25.41 | 25.55 |
| | HOPS1200 | 25.26 | 25.36 | 25.47 | 25.64 |
| | HOPS2400 | 25.32 | 25.37 | 25.44 | 25.66 |
| ΣPUFA | CON | 63.79 | 63.67 | 63.42 | 63.1 |
| | BHT | 63.83 | 63.67 | 63.43 | 63.28 |
| | HOPS1200 | 63.76 | 63.61 | 63.44 | 63.15 |
| | HOPS2400 | 63.62 | 63.60 | 63.38 | 63.17 |

CON: Control, BHT: Oil with 100 ppm butylated hydroxytoluene (BHT), HOPS1200: oil with 1200 ppm hops oil, HOPS2400: oil with 2400 ppm hops oil.

**Table 3.** DPPH scavenging activity and ß-carotene bleaching values of oil samples

| | Samples | Number of heating cycles | | | |
|---|---|---|---|---|---|
| | | 0 | 2 | 5 | 10 |
| **DPPH scavenging activity (%)** | **CON** | $41.01\pm1.12^{Ca}$ | $39.22\pm2.00^{Ca}$ | $34.91\pm0.69^{Cb}$ | $28.22\pm1.98^{Bc}$ |
| | **BHT** | $53.44\pm1.01^{Aa}$ | $51.34\pm1.25^{Ab}$ | $41.28\pm0.87^{Ac}$ | $36.01\pm0.36^{Ad}$ |
| | **HOPS1200** | $42.56\pm1.93^{Ca}$ | $41.05\pm1.58^{BCa}$ | $37.69\pm2.78^{Bb}$ | $35.44\pm1.59^{Ab}$ |
| | **HOPS2400** | $48.83\pm2.72^{Ba}$ | $42.77\pm2.38^{Bb}$ | $40.64\pm1.76^{Ab}$ | $35.66\pm0.98^{Ac}$ |
| **ß-carotene bleaching assay (%)** | **CON** | $50.57\pm1.59^{Ca}$ | $45.94\pm1.99^{Cb}$ | $40.37\pm0.62^{Cc}$ | $39.39\pm2.41^{Cc}$ |
| | **BHT** | $70.19\pm1.85^{Aa}$ | $69.11\pm0.84^{Aa}$ | $64.94\pm0.43^{Ab}$ | $55.75\pm0.85^{Bc}$ |
| | **HOPS1200** | $66.97\pm1.75^{Ba}$ | $64.75\pm2.16^{Bab}$ | $62.98\pm0.97^{Bb}$ | $59.58\pm1.19^{Ac}$ |
| | **HOPS2400** | $68.48\pm0.64^{ABa}$ | $66.51\pm0.06^{ABb}$ | $63.87\pm0.22^{ABc}$ | $62.22\pm0.26^{Ad}$ |

Values followed by different lowercase (a–d) and uppercase (A-D) letters show significant difference for each raw and column ($p<0.05$), respectively. CON: Control, BHT: Oil with 100 ppm butylated hydroxytoluene (BHT), HOPS1200: oil with 1200 ppm hops oil, HOPS2400: oil with 2400 ppm hops oil.

higher activity than BHT (55.75%) ($p<0.05$). There have been various results in the literature regarding the antioxidant activity of edible oils with some natural or synthetic antioxidants after heat treatment. These results suggest that plant extracts are suitable for protecting oils against thermal oxidations. Chiou et al. (36) examined the effect of olive oil extract polyphenols on the DPPH radical scavenging activity of sunflower oil and a 1.5-fold increase in antioxidant activity was reported after heating at frying temperature. In another study, DPPH values of sunflower oil with sesame ligans (1.2%) increased 60% and 40% at the end of 90 and 120 min heating, respectively (37). Zeb and Ullah (38) showed that spinach leaf extract could improve the radical scavenging activity compared to oxidized control sunflower oil after heat treatment. Zunin et al. (39) found that after heat treatment at 180°C was applied to virgin olive oil containing carnosic acid, the radical scavenging activity rapidly decreased and even to zero after 5 hours of heating.

In conclusion, using different natural sources to increase the thermal stability of oils has been reported in the literature, but the effect of hops oil on sunflower oil was examined for the first time in the research described here. Overall, results showed that although FFA values did not change significantly among sunflower oils, HOPS1200 and BHT added samples had the lowest PV values. p-AV significantly increased after the 10$^{th}$ heating cycle and the effect of hops oil was important on p-AV compared to the control sample. No significant differences between the CT values of samples were recorded, while the HOPS1200 group gave the closest CD value to the BHT group. Hops oil and BHT addition were effective at increasing the antioxidant activities of oil samples. This study showed that hops oil might be a useful alternative to control the oxidation of sunflower oil during heat treatment owing to antioxidant properties.

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