Chemical Papers (2023) 77:5733–5750
https://doi.org/10.1007/s11696-023-02893-2

ORIGINAL PAPER

Evaluation of the antioxidant effect of propolis on thermal oxidation of sunflower oil using ATR-MIR spectroscopy

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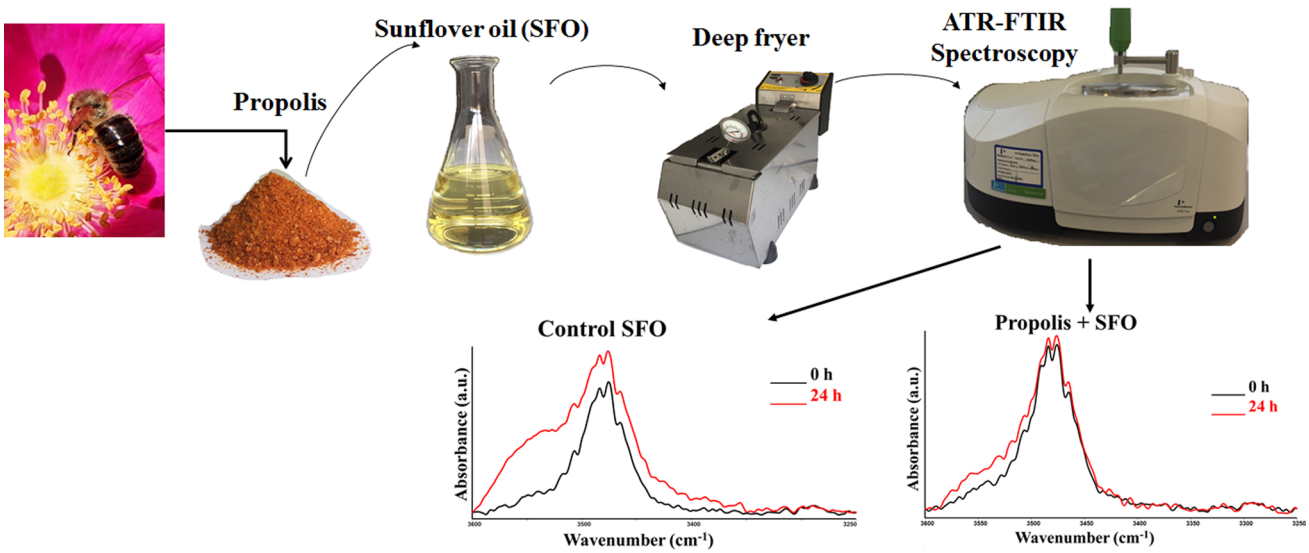
Received: 21 December 2022 / Accepted: 27 May 2023 / Published online: 6 June 2023

Abstract

This study was conducted to evaluate the effectiveness of propolis in improving the oxidative stability of sunflower oil (SFO) in comparison to buthylated hydroxytoluene (BHT), a synthetic antioxidant, under simulated frying conditions by using Attenuated Total Reflection-Mid Infrared (ATR-MIR) spectroscopy. Control, two different concentrations of propolis (1500 and 2000 ppm) and BHT added SFOs were heated at 180 °C for 24 h (8 h per day) and changes in the spectra of these oils sampled every 2 h were evaluated. The results revealed that the areas of the infrared bands related to primary and secondary oxidation products (the bands at 3482 and 1745 cm^{-1}) and to trans-unsaturated fatty acids (the bands at 987 and 965 cm^{-1}) increased and the areas of the bands related to cis fatty acids (the bands at 3009 and 722 cm^{-1}) decreased in the control SFO spectra after the heating process as a result of oxidation. 2000 ppm propolis delayed all these oxidation process, in a similar manner to BHT. Principal component analysis and chemical studies confirmed that propolis has a protective effect on the thermal oxidation of SFO. These results indicated that propolis could be recommended as an effective natural antioxidant and used instead of synthetic antioxidants in edible oil industry. This study also showed that ATR-MIR spectroscopy could be used as a fast and efficient technique to evaluate the oxidative stability of edible oils and the bands at 3482, 3009, 1745, 987, 965, 722 cm^{-1} can be used as biomarkers for oxidation.

Graphical Abstract



Keywords Propolis · Sunflower oil · Oil oxidation · Attenuated total reflection-mid infrared (ATR-MIR) spectroscopy · Oxidative stability · Principal component analysis (PCA)

Extended author information available on the last page of the article

Abbreviations

$AlCl_3$	Aluminum chloride
ATR-MIR	Attenuated total reflection-mid infrared
BHA	Butylated hydroxyanisole
BHT	Buthylated hydroxytoluene
CAPE	Caffeic acid phenethyl ester
CD	Conjugated diene
CT	Conjugated triene
DPPH	2,2-Diphenyl-1-pcyrylhydrazyl
GA	Gallic acid
HPLC	High performance liquid chromatography
LDL	Low density lipoprotein
PCA	Principal component analysis
ppm	Parts per million
PRPLS	Propolis
QE	Quercetin
SFO	Sunflower oil
TBHQ	Tertiary butylhydroquinone
TFC	Total flavonoid content
TPC	Total phenolic content

Introduction

Deep frying is one of the most common cooking techniques used worldwide both in the food industry and houses. Fried foods are highly appreciated and preferred by people due to their taste and sensory properties (Zhang et al. 2020). However, since oil is subjected to high temperatures (150–200 °C) in the existence of humidity and atmospheric oxygen during the frying process, many undesirable reactions such as oxidation, hydrolysis, isomerization occur in oils, and unfortunately these reactions reduce the oil quality (Rossi et al. 2007). Lipid oxidation, which is the primary impairment process occurring in oils during heat treatment, causes the generation of free radicals and proceeds into radical chain reactions. During these oxidation reactions many unwanted compounds are generated, such as hydroxyperoxides, malondialdehydes, alkanes, alkenes (Choe and Min 2006). These chemicals affect the sensory properties and quality of oils and may cause various important health problems, such as cancer, increased lipid peroxidation and LDL, atherosclerosis and hypertension as reviewed by Ganesan and Xu (2020).

It has been known that oils with high polyunsaturated fatty acids such as sunflower oil (SFO), that is one of the most preferred frying oils due to its cheaper price, are very vulnerable to oxidation (Aleena et al. 2020). Therefore, it is very important to increase SFO's stability by preventing oxidation during the frying process. Adding an antioxidant is the simplest way to improve the stability of oils. Antioxidants are natural or synthetic compounds which delay or stop oxidation by inhibiting the generation of free radicals or preventing the spread of free radicals by various mechanisms. Synthetic antioxidants such as BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole) and TBHQ (tertiary butylhydroquinone) have been utilized for many years to improve the oxidative stability of oils (Shahidi 2000). However, the utilization of synthetic antioxidants is questioned since they may cause harmful effects on human health. Previous studies have shown that synthetic antioxidants have potential carcinogenicity, cytotoxicity and endocrine disrupter effects (Pop et al. 2013; Saito et al. 2003). Indeed, the use of synthetic antioxidants has been limited in the USA, Canada, Japan and numerous European countries (Wang et al. 2018a). Thus, due to the concerns about the harmful impacts of synthetic antioxidants on human health, the use of natural antioxidants has gained importance in recent years. In previous studies, natural products such as evening primrose extract (Niklová et al. 2001), rosemary essential oil fraction (Mezza et al. 2018), Nigella seed extract (Ammari et al. 2012) were used to increase the stability of SFO against oxidative stress as alternatives to BHT and it was shown that they had high protection potential. However, none of these studies were carried out at frying temperatures. Although these substances show high antioxidant activity, they are known to deteriorate easily at high temperatures due to their unstable structure (Aladedunye and Matthäus 2014). Since antioxidants to be used in frying oil should have a high thermal stability itself, there is a need for natural antioxidants resistant to high temperatures that can be used in frying oils. In previous studies it has been reported that polyphenols, which are abundant in some herbal extracts, are more resistant to high temperatures than endogenous natural antioxidants found in oils and synthetic antioxidants and thus display higher antioxidant activity in heated oils (Aladedunye and Matthäus 2014; Farag et al. 2007; Orozco-Solano et al. 2011).

Propolis (PRPLS), which is considered one of the most valuable sources of polyphenols in nature, is a resinous substance formed by honey bees with raw materials gathered from various parts of plants to protect the hive from foreign invaders. The most important active components of PRPLS are flavonoids, phenolic acids, phenolic acid esters and terpenoids, which make up 70% of the total amount of it and they all have high antioxidant activity (Bankova et al. 2000). In general, polyphenolic compounds may constitute as much as 58% of this amount and flavonoids constitute 20% of this 58% (Kurek-Górecka et al. 2013). It has been shown that these compounds scavenge free radicals and thus protect biomolecules such as lipids, proteins, vitamins, etc., from oxidative damage (Villaño et al. 2007). It has also been shown that they have many positive impacts on human health such as preventing cardiovascular diseases, diabetes and cancer (Shetty and Wahlqvist 2004). Therefore, the use of PRPLS in foods as an antioxidant provides many beneficial impacts

on health as well as protecting the food from oxidative damage. The protective effects of PRPLS on various foods have been demonstrated in previous studies. For instance, it has been shown that the addition of PRPLS protected milk (Cottica et al. 2015), apple juice (Luis-Villaroya et al. 2015) and various non-carbonated beverages (Vasilaki et al. 2019) from oxidation during the pasteurization process. In addition, it has been shown that PRPLS could be utilized to increase the shelf life of fish oil (Ucak 2018), shibuta (Duman and Özpolat 2015), chicken breast fillets (Mehdizadeh and Langroodi 2019) and beef meatballs (Vargas-Sánchez et al. 2014).

The most widely used methods for measuring the oxidative status of oils are chemical techniques, such as the determination of peroxide value, anisidine value, conjugated dienes-trienes, etc. However, these techniques often require toxic and harmful solvents and a long time for analysis. In recent years, ATR-MIR (Attenuated Total Reflection-Mid Infrared Infrared) spectroscopy, which is created by attaching an ATR device to MIR spectroscopy, has gained popularity for assessing the thermal stability of oils (Meenu et al. 2022). This technique allows to obtain information about the structural changes in molecules in a simple and non-destructive way and has many advantages for oil analysis. For example, in this technique, a little amount of sample is enough and the oil to be analyzed is put directly on the crystals of the ATR attachment. In addition, it makes precise analysis in a very short time, does not need sample pre-treatment procedures and allows monitoring of different functional groups simultaneously. By analyzing infrared bands, which represent the typical vibrational modes of each functional group, valuable qualitative and quantitative data can be acquired (Cakmak-Arslan et al. 2020). In previous studies, ATR-MIR spectroscopy has been utilized efficiently for the evaluation of the oxidative stability of hazelnut and extra virgin olive oils during frying (Cakmak-Arslan 2022), investigating the impacts of temperature on the quality of some vegetable oils (Poiana et al. 2013), examining the effects of different cooking techniques on oil quality (Ciemniewska-Żytkiewicz et al. 2014), etc.

Although there are a few reports on the use of PRPLS as an antioxidant in various foods, to the best of our knowledge, there are no studies regarding the protective effects of PRPLS against thermal oxidation in SFO. Since it is known that the polyphenols in PRPLS have high antioxidant activity and are resistant to high temperatures, we thought that PRPLS can be used as a natural antioxidant in frying oils. Thus, the purpose of this study is to evaluate the effectiveness of PRPLS in improving the oxidative stability of SFO during the heating process. For this purpose, first the structural and compositional changes resulting from lipid oxidation in SFO under simulated frying temperature were monitored by ATR- MIR spectroscopy and then the protective effect of two different concentrations of PRPLS in comparison to a synthetic antioxidant, buthylated hydroxytoluene (BHT), on these changes was evaluated with the same technique. Principal component analysis (PCA), which is a chemometric method, was used to confirm the ATR-MIR results. In addition, the specific absorptivities of conjugated dienes (CDs) and conjugated trienes (CTs), which are directly related to oxidation products, were also measured to support the ATR-MIR results.

Materials and methods

Propolis (PRPLS) extract preparation

PRPLS samples, collected from Düzce province (Turkey) in the summer of 2021, were obtained from Düzce University Beekeeping Research and Application Center. Raw PRPLS was kept in a deep freezer (− 20 °C) till extraction. Since ethanol is the best solvent for the polyphenols and is not toxic for humans, ethanolic extraction of PRPLS was preferred (Mouhoubi-Tafinine et al. 2016). PRPLS samples were ground, 30 g of PRPLS was mixed with 150 mL (1:5 w/v) ethanol (96%) and kept in the dark for 5 days with continuous stirring and filtered using a filter paper. The alcohol was vaporized under reduced pressure at 40 °C in a rotary evaporator (Heidolph, Germany). Then the resinous product was dissolved in ethanol (70%) and left for 1 day in the dark with continuous stirring (Rizvi et al. 2020). The obtained extract was kept at − 80 °C for 1 day and then powdered in a lyophilizer (Christ Alpha 1–2 LD plus, Germany) at 0.97 atm pressure at − 52 °C (Wang et al. 2018b). The powdered PRPLS samples were kept in the dark at + 4 °C until they were used.

PRPLS extract characterization

HPLC component analysis

For the HPLC component analysis of PRPLS, a modified Aliyazicioglu et al. (2013) method was used. The standards of caffeic acid phenethyl ester (CAPE), quercetin and kaempferol, the phenolic compounds quantified in this study, were obtained from Sigma-Aldrich (quercetin ≥ 95.0%, kaempferol ≥ 90.0%, CAPE ≥ 97.0%). 5 g of PRPLS extract was completed to 45 ml with ethanol (96%). The solution was vortexed for 2 h after 15 min of ultrasonic extraction. Then it was filtered, vialed and injected to the HPLC device (Shimadzu LC-20AT) equipped with PDA detector (SHIMADZU SPD-M20A). The experiment was carried out isocratically using methanol/ultrapure water (75:25) as mobile phase at a flow rate of 1.0 mL/min on an ODS column (5 µm, 4.6 × 250 mm). Separation of components in the extracts was conducted in a 15-min run. Identification was achieved based on the retention

times of the standards which were previously detected separately and quantification was done by determining the peaks with the help of PDA detector. CAPE was detected at 325 nm, quercetin and kaempferol were detected at 254 nm.

Total phenolic content (TPC) analysis

TPC of the ethanolic extract of PRPLS was measured by using the Folin-Ciocalteu method (Baltas et al. 2016; Singleton and Rossi 1965). Gallic acid (GA) (Sigma-Aldrich, USA) was used as the standard phenolic compound. Briefly, 1360 µL distilled water, 40 µL PRPLS extract, 800 µL 0.5 N Folin reagent and 800 µL Na_2CO_3 (7.5%) (Sigma-Aldrich, USA) were added to a test tube. After 30 min of incubation, the absorbance was read at 760 nm in a UV–Vis spectrophotometer (Shimadzu, UV-1800). The experiments were carried out in triplicate and the results were given as mg GAE/g.

Total flavonoid content (TFC) analysis

TFC of the ethanolic extract of PRPLS was measured using the aluminum chloride ($AlCl_3$) (Sigma-Aldrich, USA) calorimetric method (Chandra et al. 2014). Quercetin (QE) (Sigma-Aldrich, USA) was used as the standard flavonoid compound. Briefly, 4000 µL distilled water, 100 µL PRPLS extract, 100 µL QE solution and 100 µL $AlCl_3$ were added to a test tube. The mixtures were incubated for 60 min. Then absorbance was read at 415 nm in a UV–Vis Spectrophotometer (Shimadzu, UV-1800). The experiments were carried out in triplicate and the results were given as mg QE/g.

DPPH radical scavenging activity

DPPH radical scavenging activity analysis was performed according to Marghitas et al. (2009). Briefly, 1 ml of different concentrations of PRPLS extract (1/10, 2/10, 3/10, 4/10, and 5/10) were put in different test tubes and made up to 10 mL with 1 M DPPH (dissolved in 99% methanol). These mixtures were incubated for 30 min in the dark. Absorbance values were measured at 515 nm using a UV–Vis spectrophotometer (Shimadzu, UV-1800). Results were expressed as IC_{50} (concentration required to clear 50% of DPPH) mg/mL.

Sunflower oil (SFO) samples

SFO produced in 2021 was bought from a local market. SFO samples were divided into 4 groups, as control (without PRPLS and BHT), 1500 ppm and 2000 ppm PRPLS added and 100 ppm BHT (Sigma-Aldrich, USA) added. BHT added oil was prepared as a positive control. Since the maximum allowed dose of BHT in frying oils in Turkey is 100 ppm (Official Gazette 2008), this amount was chosen to add to the oil. The amount of PRPLS to be added to the oils was determined by preliminary studies. In order to decide the PRPLS amount, different concentrations of PRPLS extracts (from 1000 to 2000 ppm) and 100 ppm BHT were added to the SFOs and heating procedure was applied. At the end of the heating procedure, some specific infrared bands were analyzed. Based on these results, it was decided to add 1500 and 2000 ppm PRPLS to the oils.

Determination of fatty acid content of sunflower oil

The fatty acid composition of SFO was determined according to Yang et al. (2016). An Agilent 7890 gas chromatograph combined with an Agilent 5975C mass spectrometer (GC–MS; Agilent Technology, CA, USA) was used. The device was equipped with an Agilent HP-5MS (30 m × 0.25 mm × 0.25 µm) column. Wiley and NIST (Wiley Registry of Mass Spectral Data, 7th Edition, NIST 98 Library) was used as the library.

Thermal treatment of sunflower oil samples

Before beginning the heating procedure, 5 mL of oil samples were taken as control and transferred to amber glass vials. For the heating process of the oil, a commercially available fryer with a capacity of 3 L (Remta, Turkey) was used. A liquid thermometer was put in the fryer to control the temperature of the oil. 2.5 L of SFO was heated at 180 °C for a total time of 24 h over 3 consecutive days (8 h per day) and 5 mL samples were taken from these oils every 2 h until the end of the heating procedure. In the current study, the same conditions used in some restaurants were tried to be created by accepting that a restaurant uses oil for 24 h, equivalent to using oil for an average of 8 h a day for 3 days (Yılmaz and Aydeniz 2011). In many previous studies on the thermal stability of frying oils, the heating time we used in this study was used (Cakmak-Arslan 2022; Saoudi et al. 2016; Smith et al. 2007). The oil samples were kept at + 4 °C in amber glass vials until analysis. The heat treatment of each sample was performed in duplicate (Cakmak-Arslan 2022).

Acquisition of ATR-MIR spectra

Infrared spectra of SFOs were obtained with a Spectrum Two MIR spectroscopy connected to the ATR accessory (Perkin-Elmer Ltd., UK). 5 µL of oil samples were pipetted on the ATR crystal and the spectra were recorded with 32 scans at 4 cm^{-1} resolution in the 4000 to 450 cm^{-1} region at room temperature. The ATR crystal was cleaned using ethanol before each new sample and a new background spectrum was obtained before each measurement. In order to make the results more reliable, 3 spectra were obtained from each oil

sample. Therefore, 6 spectra were recorded for every heating time period and by averaging these 6 spectra, one spectrum representing each heating time period was obtained.

Measurement of conjugated dienes (CDs) and conjugated trienes (CTs)

CDs and CTs were determined by specific absorptivity values at 232 and 270 nm, respectively. Oil samples were mixed with cyclohexane (1:100 v:v) and the absorbances of the samples were measured using a UV–visible spectroscopy (T80 + UV/VIS Spectrometer, PG Instruments Ltd.) at 232 and 270 nm on a 1 cm quartz cuvvete (Besbes et al. 2004). The measured absorbances were used to calculate the specific absorptivities of CDs and CTs according to Rohman et al. (2011).

Data analysis

The analyses of ATR-MIR bands were performed using Spectrum 100 software (Perkin-Elmer). To characterize the oxidative process, the bands at 3482, 3009, 1745, 987, 965 and 722 cm^{-1}, which have been suggested to be used as biomarkers in previous oxidation studies, were analyzed (Cakmak-Arslan 2022; Guillén and Cabo 2000; Poiana et al. 2015). The areas under these infrared bands were calculated from the interactive baseline-corrected spectra. A linear regression analysis was performed in order to determine the relationship between the spectral data and heating time (Cakmak-Arslan 2022; Poiana et al. 2013). The correlation coefficients (Pearson's coefficients), the curves and the equations of the curves were obtained by using Microsoft Excel v14.

PCA, which is a highly convenient chemometric method for interpreting complex multivariate datasets, was used to monitor the discrimination of oils in different heating-time intervals. This unsupervised classification technique allows dimensionality reduction and visualization of the information existing in the original data in the form of a few principal components (PCs) while maintaining the maximum possible variability (Berrueta et al. 2007). PCA was performed by utilizing Unscrambler X 10.4 (Camo, NO) multivariate analysis (MVA) software. The analysis was performed on the baseline corrected and vector normalized spectra in the whole region (4000–450 cm^{-1}). The results of PCA were given as score and loading plots.

Results and discussion

Characterization of sunflower oil

The fatty acid composition of SFO is given in Table 1. As expected, the most abundant fatty acid is linoleic acid, which is a polyunsaturated fatty acid, with 55.44%. In previous studies it has been determined that the amount of linoleic acid was between 50.85 and 60.20% in SFOs collected from different regions of Turkey and some other countries (Arslan 2018; Asnaashari et al. 2015; Kozłowska and Gruczyńska 2018; Ozulku et al. 2017). Although there were minor differences between the amounts of other fatty acids contained in SFO, the linoleic acid amount measured in this study is in accordance with the previous studies. These differences might be assigned to differences in plant genotype and environmental conditions, such as water supply and temperature (Kozłowska and Gruczyńska 2018).

Characterization of PRPLS extract

In this study, the amounts of CAPE, quercetin and kaempferol, which are known to have high antioxidant activity among the phenolic compounds in PRPLS, were determined (Garrido et al. 2012). The amount of CAPE, which is a good marker of PRPLS, was determined as 6.164 ± 0.0037 mg/g. This value is consistent with the values presented by Ozkok et al. (2021), in which PRPLS was obtained from 23 different regions of Turkey and Ahn et al. (2007), in which PRPLS was obtained from various areas of China, and higher than those presented by Andrade et al. (2017) in which PRPLS was collected from the northeastern region of Brazil. The quercetin (0.470 ± 0.0029 mg/g) and kaempferol (1.563 ± 0.0038 mg/g) amounts of PRPLS were also in agreement with the literature (Andrade et al. 2017; Kumazawa et al. 2004). The TPC of PRPLS was 105.45 ± 0.10 mg GAE/g and TFC of it was 48.01 ± 1.19 mg QE/g. These results are consistent with the values reported in the literature. In previous studies carried out to assess the TPC of Turkish PRPLSs with different botanical origins, it

Table 1 Fatty acid composition of SFO

Fatty acids	(%)
Myristic acid (C14:0)	0.762
Palmitic acid (C16:0)	12.78
Stearic acid (C18:0)	5.30
Oleic acid (C18:1)	27.33
Linoleic acid (C18:2)	55.44
α-Linolenic acid (C18:3)	1.11
Arachidic acid (C20:0)	1.28

was determined as 87.62–127.39 GAE/g by Silici (2008), as 16.13–178.34 GAE/g by Keskin (2018), as 27.48–199.69 GAE/g by Ozdal et al. (2019). Similarly, the TFC content was reported as 1.24–51.23 mg QE/g by Keskin (2018) and as 30.73–291.75 mg QE/g by Ozdal et al. (2019) in consistence with our results. Concerning the antioxidant activity of PRPLS, evaluated by DPPH scavenging method, a value of IC_{50} was determined as 1.98 ± 0.005 mg/mL. Although the value we determined is consistent with the values determined Marghitas et al. (2009) for Romanian PRPLS (0.3–5.6 mg/mL), it is lower than the values reported by Rosli et al. (2016) for Malaysian PRPLS (4.27 mg/mL).

Assessing the thermal oxidation of SFO and antioxidant effect of PRPLS using ATR-MIR spectroscopy and chemical parameters

The infrared spectrum of SFO is composed of various bands originating from the vibrations of different functional groups in the oil. Figure 1 depicts the infrared spectra of unheated and 24 h heated SFO in the 3650–500 cm^{-1}. In this figure, the major bands are marked and their descriptions according to the literature are given in Table 2. As seen from this figure, there are notable differences between some of the infrared bands of the unheated and heated SFO spectra (band no: 1, 2, 7, 17, 18, 19).

The intensities of and/or the areas under the infrared bands originating from certain molecules are proportional to the concentrations of those functional groups in the sample. Therefore, in infrared spectroscopy studies to have information about the amount of the molecules represented by those functional groups, the areas under the infrared bands can be analyzed (Cakmak-Arslan et al. 2020). In this study, by analyzing the infrared regions containing the bands with notable differences, information about the changes in the content, structure and composition of the SFO during the heating process was obtained. In addition, to assess the relationship between the analyzed spectral parameters and the heating time, linear regression analysis was made using the obtained spectral data.

Lipid oxidation, which is the primary degradation process in oils during the course of heating, consists of numerous simultaneous or successive reactions. It takes place as a consequence of the reaction of oxygen in the medium with the double bonds in the fatty acid chains. In the initial step of oxidation, an H atom is detached from fatty acids under the influence of high temperature, resulting in a lipid alkyl radical. By binding molecular oxygen instead of the H detached from the fatty acid, hydroperoxides, which are known as primary oxidation products, are formed. Peroxides are unstable compounds and responsible for the continuation of oxidation by acting as a catalyst, and after that autooxidation continues as a free radical chain reaction. With the decomposition of these compounds, secondary oxidation products, such as ketones, aldehydes, hydrocarbons, acids, etc., are formed (Choe and Min 2006). To monitor the lipid oxidation during the heating period efficiently, measuring of primary and secondary oxidation products is required.

In MIR spectroscopy studies, information about the primary and secondary oxidation products can be obtained simultaneously in a system by analyzing the 3600–3250 cm^{-1} region (Talpur et al. 2015). Figure 2A–D

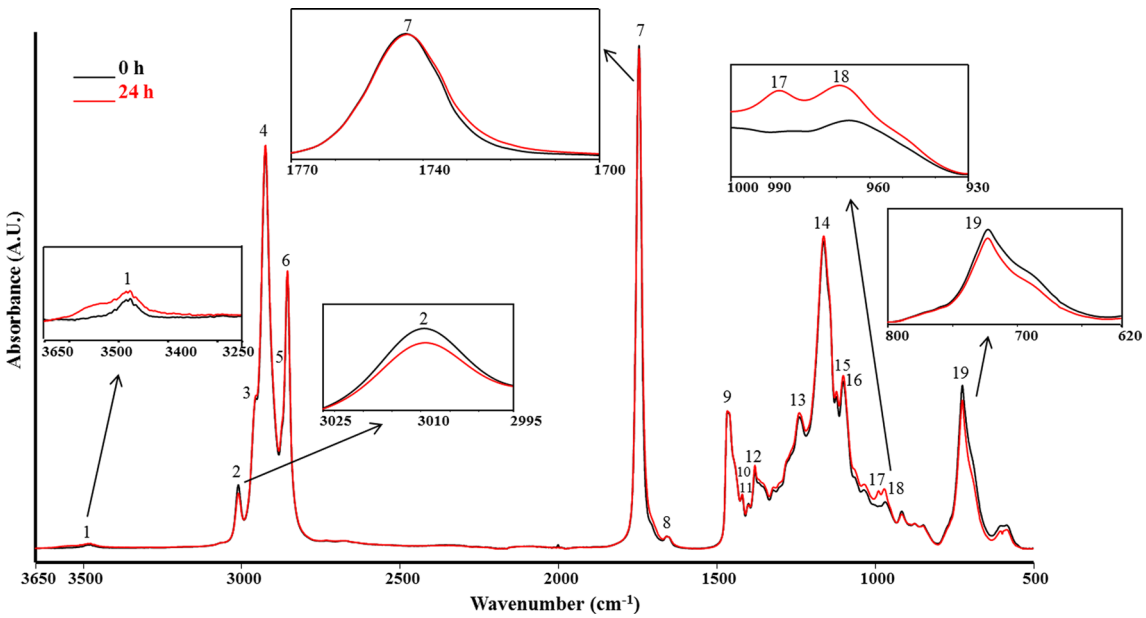


Fig. 1 ATR-MIR spectra of the unheated and 24-h heated SFO in the 3650–500 cm^{-1}

Table 2 Main absorption bands in the infrared spectrum of SFO (Arslan 2018; Cakmak-Arslan 2022; Guillén and Cabo 2002; Guillén and Cabo 2000; Poiana et al. 2015)

Band Number	Wavenumber (cm^{-1})	Definition of functional groups and vibration modes
1	3482	–C=O (ester) of triglycerides
2	3009	=C–H (cis) symmetric stretching of double bonds
3	2954	–C–H (antisym) stretching of CH_3 groups
4	2923	–C–H (antisym) stretching of CH_2 groups
5	2871	–C–H (sym) stretching of CH_3 groups
6	2856	–C–H (sym) stretching of CH_2 groups
7	1745	–C=O (carbonyl ester) stretching of triglycerides
8	1654	–C=C (cis) stretching of olefins
9	1462	–C–H bending of CH_2 groups
10	1418	–C–H bending (rocking) vibration of cis-disubstituted olefins
11	1398	=C–H (cis) bending in-plane vibrations of olefinic groups
12	1378	–C–H bending vibrations of CH_2 groups
13	1238	–C–O (ester) stretching and –C–H bending of CH_2 groups
14	1160	–C–O (ester) stretching and –C–H bending of CH_2 groups
15	1119	–C–O (ester) stretching
16	1097	–C–O (ester) stretching
17	987	Conjugated –C–H (trans) bending vibrations of olefinic groups
18	965	–C–H bending of isolated trans olefins
19	722	CH_2 rocking and out-of- plane vibrations of cis-disubstituted olefins

depicts the MIR spectra of unheated and heated SFO for 6, 12, 18, 24 h in the 3600–3250 cm^{-1} region of control (without PRPLS or BHT), 1500 and 2000 ppm PRPLS and BHT added SFO. In our study, although spectra were obtained from the samples taken every two hours, in order to observe the changes more clearly only the spectra of the unheated and 6, 12, 18 and 24 h heated oils are presented in these figures. In the 3600–3250 cm^{-1} region, the infrared band at approximately 3482 cm^{-1} (band no: 1) is attributed to carbonyl absorptions of glyceride esters (Guillén and Cabo 2002). This region also contains the infrared band at approximately 3444 cm^{-1}, which is assigned to the –OH stretching vibrations in hydroperoxides and the band at approximately 3530 cm^{-1} which is assigned to secondary oxidation products (Tena et al. 2014; van de Voort et al. 1994). As can be seen from Fig. 2, there are no bands at 3444 and 3530 cm^{-1} in the unheated SFO spectra. This result showed that there were no hydroperoxides and secondary oxidation products in the unheated SFO. As the oxidation process continues, the concentration of hydroperoxide increases in the sample, hence their absorption at 3444 cm^{-1} increases. However, it has been known that hydroperoxides are not stable and turn into secondary oxidation products during the lipid oxidation process. Therefore, it can also be expected that the absorption of secondary oxidation products increase in heated oils. As seen from Fig. 2, the absorption of the band at 3530 cm^{-1} increased during heating process and this increase was more noticeably than the increase observed in the band at 3444 cm^{-1}. This may be due to the rapid decomposition of primary oxidation products at high temperatures and conversion to secondary oxidation products. Since the 3444 and 3530 cm^{-1} bands overlap with the glyceride ester band appearing at 3482 cm^{-1}, they cause an increment in its absorbance/area (Guillén and Cabo 2002). Thus, in infrared spectroscopy studies, intensity/area analysis of the 3482 cm^{-1} band could be exploited to gain information about the amount of hydroperoxides and secondary oxidation products during oxidation (Cakmak-Arslan 2022). As seen from Fig. 2A, the intensity/area of this band in the control SFO increased after heating and this increase becomes more dramatic with increased heating time. It can be seen from Fig. 2B that the changes in the spectra acquired from the heated SFO after adding 1500 ppm PRPLS were similar to the spectra obtained from the control. When Fig. 2C and D are examined, it is seen that there are very small differences between the unheated and heated spectra of 2000 ppm PRPLS and BHT added SFO. This result showed that 2000 ppm PRPLS reduced the rate of heat-induced oxidation product formation in SFO and it was as effective as BHT which was used as positive control in this study. Figure 2E shows the correlations between the alterations in the area values of the 3482 cm^{-1} band versus heating time. As seen from this figure the correlation coefficients (R), which represent a quantitative measurement describing the linear relationship strength, between the changes in the area of the 3482 cm^{-1} band and the heating time are very high (above 0.91). The regression curves in the figure clearly reveal that the area under this band increases as the heating time

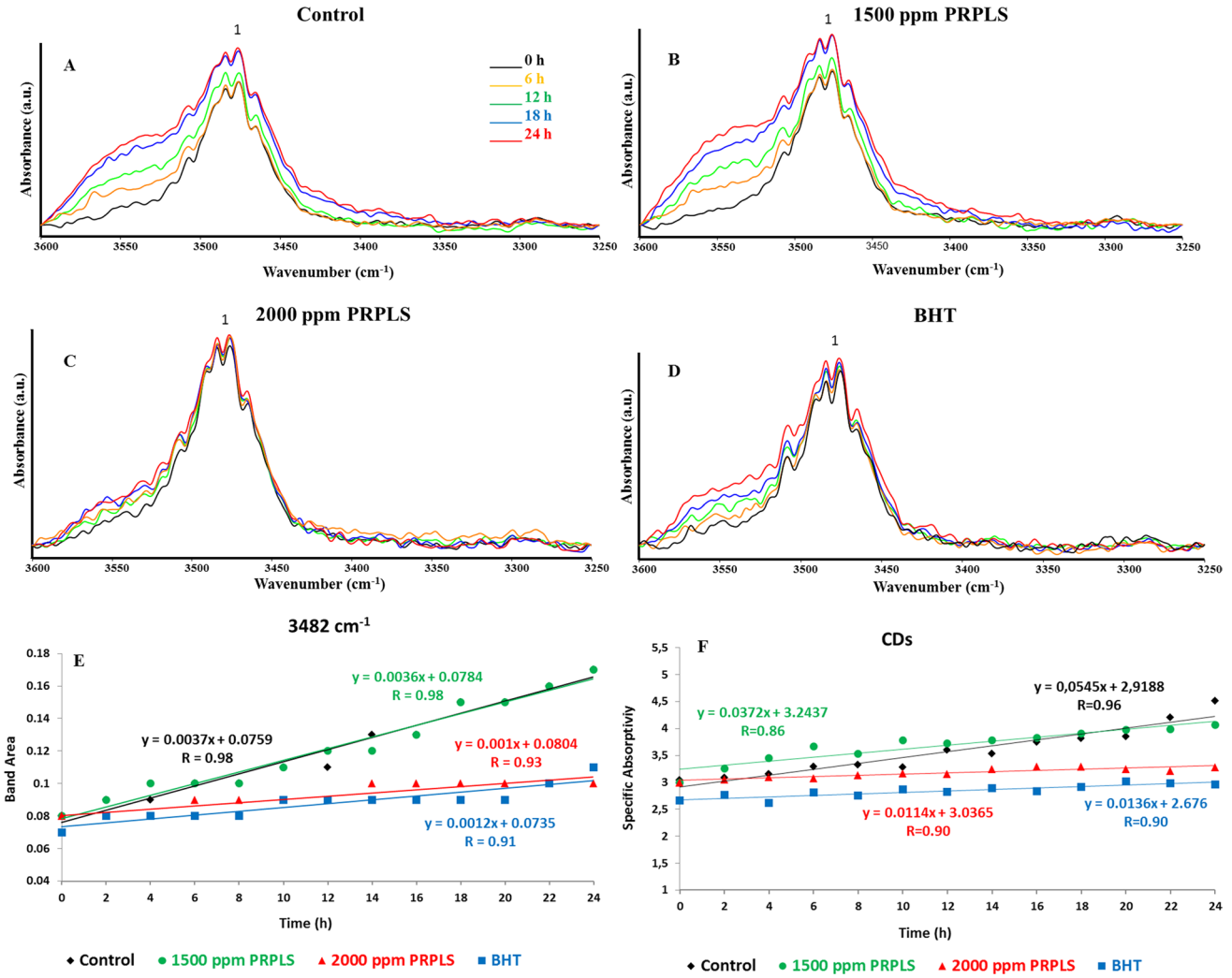


Fig. 2 Infrared spectra of unheated and 6, 12, 18, 24 h heated SFO in the 3600–3250 cm^{-1} spectral region for control (**A**), 1500 ppm PRPLS (**B**), 2000 ppm PRPLS (**C**), BHT (**D**) added SFO; and linear regression analysis of the changes in the area of the 3482 cm^{-1} band (**E**), in the specific absorptivity values of CDs (**F**) obtained from control, 1500 and 2000 ppm PRPLS and BHT added SFO with respect to heating time

increases and this increase becomes more pronounced as the heating time increases. This result confirms that the amount of primary and secondary oxidation products increased in SFO exposed to heat. In addition, as seen from this figure, the slope values of the control and 1500 ppm PRPLS added SFO are very close to each other (control: 0.0037; 1500 ppm PRPLS: 0.0036), while the slope value of 2000 ppm PRPLS added SFO is much lower (0.0010) than them. As also seen from the figure, the curve of 2000 ppm PRPLS added SFO almost overlaps with that of BHT added SFO with very close slope values (0.0012). This result confirmed that the addition of 2000 ppm PRPLS reduced the rate of the oxidation product formation in SFO as in BHT added oil.

In this study, to confirm the findings obtained from MIR data about the oxidation products, the specific absorptivity of conjugated dienes (CDs) and conjugated trienes (CTs) were detected. As argued above, the primary oxidation products are allylic hydroperoxides, in which the double bonds maintain but have altered configuration and/or position from their original form in the fatty acyl chains. Thus, the generation of hydroperoxides is concurrent with the conjugation of double bonds in unsaturated fatty acids. Hydroperoxides indicates diene and triene conjugated double bonds coming from 1,4-pentadiene or 1,4,7 octatriene components exist in linoleic or linolenic acids, respectively (Guillén and Cabo 2002). These CDs and CTs can be determined by UV–visible spectroscopy. In the UV–visible spectrum, the hydroperoxides (primary stage of oxidation) and CDs show strong absorption at 232 nm while the carbonylic compounds (secondary stage of oxidation) and CTs show strong absorption at 270 nm (Valasi et al. 2020). Therefore, the specific absorptivity values of CDs and CTs can be used to have

information about the amount of primary and secondary oxidation products in oils, respectively. Figure 2F depicts the correlations between the alterations in the specific absorptivity values of CDs with heating time in control, 1500 and 2000 ppm PRPLS and BHT added SFO. As seen from this figure, the specific absorptivity values of CDs increased linearly with heating time in the oils with high correlation coefficients (above 0.86) and the slope value of control curve (0.0545) was higher than those of other curves. This finding indicates that heating process caused an increase in the amount of hydoperoxides in SFO and this increase was more dramatic in control SFO, which has also been obtained from the MIR studies. Although it is expected that the amount of hydroperoxides in oils undergoing thermoxidation to be low due to the breakdown of these compounds at high temperatures, these results showed that there are hydroperoxides in the heated oils. In this study, the oils were heated at 180 °C for a total time of 24 h over 3 consecutive days (8 h per day) and samples were taken from these oils every 2 h until the end of the heating procedure. After each sample was taken into an amber glass, they were cooled at room temperature then they were closed and stored in the refrigerator. It is important to note that hydroperoxides may be formed shortly after taking each sample as they are cooled at room temperature before putting them in the refrigerator. Furthermore, the thermoxidation process was carried out emulating a common discontinued frying process, where the oil is kept at room temperature between frying cycles and hydroperoxides might be accumulated before the next frying session. In accordance with our results, in many previous studies, it has been shown that the peroxide value increases at high temperatures (Gharby et al. 2016; Moharam and Abbas 2010; Rohman and Che Man 2013). When the regression curves of the oils given in Fig. 2F are compared, it can be seen that the slope value of 1500 ppm PRPLS added SFO (0.0372) was close to the control, the 2000 ppm PRPLS added oil had the lowest slope value (0.0114) and the slope value of BHT added oil (0.0136) was slightly higher than the 2000 ppm PRPLS added oil. This result confirmed that 2000 ppm PRPLS reduced the hydroperoxide formation in SFO even better than BHT.

To have information about the secondary oxidation products, the band at 1745 cm^{-1} (band no: 7), which is the fundamental band of the carboxylic acid vibrations of triglycerides, was also analyzed (Guillén and Cabo 2000). Figure 3 shows the 1770–1710 cm^{-1} region of spectra obtained from control, 1500 and 2000 ppm PRPLS and BHT added SFO samples. As seen from Fig. 3A–D, there is an increment in the area of the 1745 cm^{-1} band in control and 1500 ppm PRPLS added SFO after heating but there were very small changes in the 2000 ppm PRPLS and BHT added SFO samples. When the slope values in the regression graph given in Fig. 3E are compared, it can be seen that the slope value of the control SFO was quite high (0.0132), the slope value of the 1500 ppm PRPLS added SFO was slightly lower (0.0127) than the control, the slope value of 2000 ppm PRPLS added SFO was quite low (0.0043) and was closer to BHT added SFO (0.0029). As argued above, with the breakdown of hydroperoxides formed during the first step of oxidation, many secondary oxidation products such as alcohols, free fatty acids, esters, ketones and aldehydes are formed (Choe and Min 2006). These new compounds also cause some alterations in the properties of the 1745 cm^{-1} band. In the previous studies, it has been shown that the changes in the 1745 cm^{-1} band are due to the band formed at 1728 cm^{-1} arising from those secondary oxidation products which all contain carbonyl groups (Guillén and Cabo 2000; Poiana et al. 2015). The 1728 cm^{-1} band is so close to the 1745 cm^{-1} band that it might overlap with it and cause broadening and an increase in its area (Cakmak-Arslan 2022). Therefore, the increments in the area values of this band noted in the control and 1500 ppm PRPLS added oils showed that the concentration of secondary oxidation products increased with the heating process. Although the PRPLS concentration of 1500 ppm was not successful to reduce the formation of secondary oxidation products, the addition of 2000 ppm PRPLS reduced the rate of the formation of secondary oxidation products after thermal treatment, like in BHT added oil. As can be seen from Fig. 3F, the specific absorptivity values of CTs, which also provide information about the amount of secondary oxidation products, increased with heating time in all oil samples. If the slope values of the regression curves are compared, it is seen that the control had the highest slope value (0.051), the slope value of 1500 ppm PRPLS added oil (0.0378) was lower than the control, BHT added oil had the lowest slope value (0.0286) and the slope value of 2000 ppm PRPLS added oil (0.0294) was very close to BHT added oil. These findings confirmed that the amount of secondary oxidation products increased in the oils during heat treatment and 2000 ppm PRPLS reduced the rate of the formation of secondary oxidation products in the oils in a similar manner to BHT.

Figure 4A–D shows the spectral alterations in the 3009 cm^{-1} band (band no: 2) obtained from control, 1500 and 2000 ppm PRPLS and BHT added SFO samples and Fig. 4E shows the correlations between the alterations in the area under this band with respect to heating time. The 3009 cm^{-1} band is due to the C–H stretching vibrations of the cis-olefinic double bonds of unsaturated fatty acids (Poiana et al. 2013). Therefore, by analyzing the area under this band, valuable information can be obtained about the alterations in the proportion of cis double bonds of unsaturated fatty acids during heat treatment. As can be seen from Fig. 4, the area under this band decreases as the heating time increases in all samples. As also seen from these figures, the rate of the decrease was very high in control and 1500 ppm

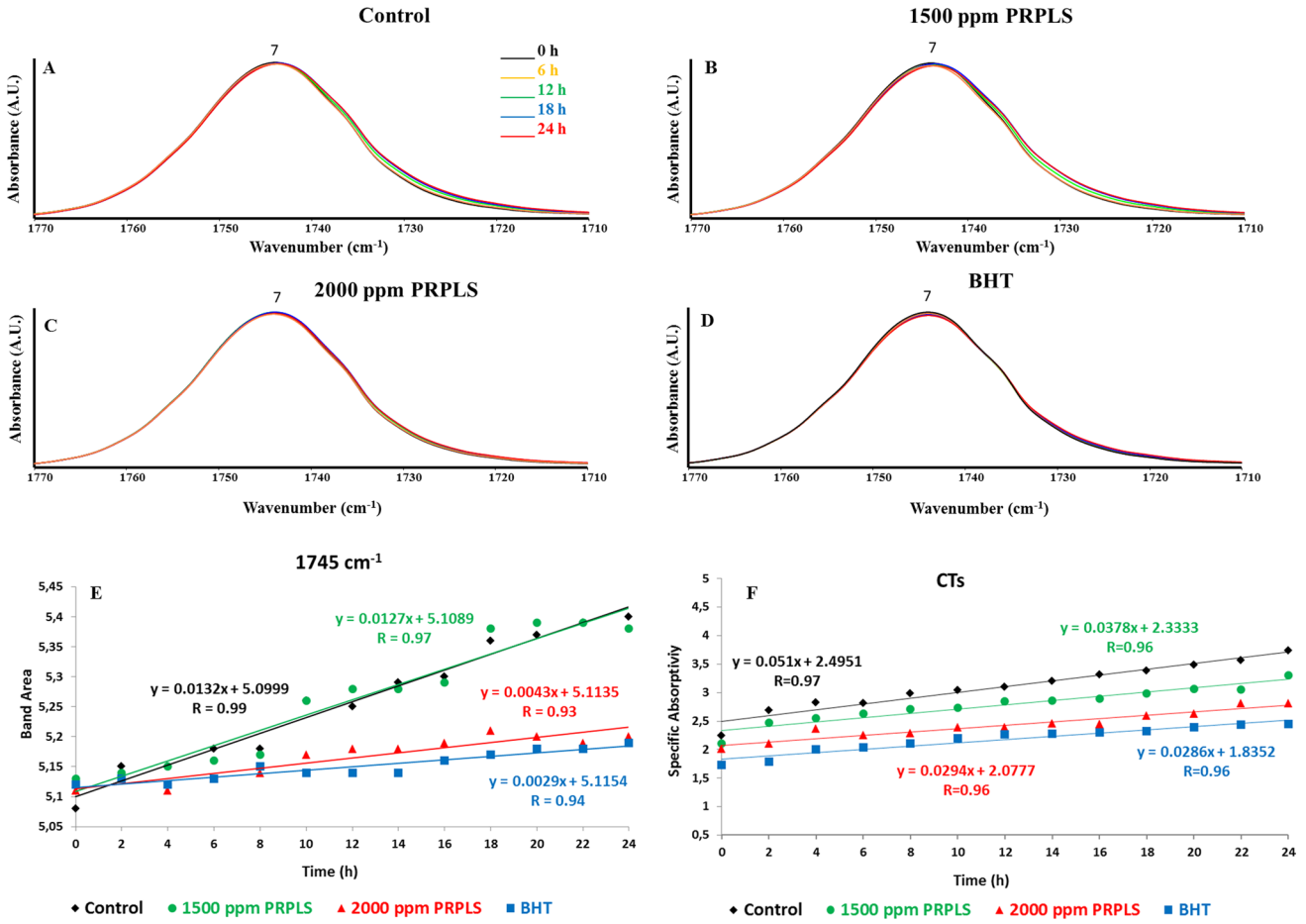


Fig. 3 Infrared spectra of unheated and 6, 12, 18, 24 h heated SFO in the 1770–1710 cm^{-1} spectral region for control (**A**), 1500 ppm PRPLS (**B**), 2000 ppm PRPLS (**C**), BHT (**D**) added SFO; and linear regression analysis of the changes in the area of the 1745 cm^{-1} band (**E**), in the specific absorptivity values of CTs (**F**) obtained from control, 1500 and 2000 ppm PRPLS and BHT added SFO with respect to heating time

PRPLS added oils but it was very low in 2000 ppm PRPLS added oil. When the slope values of the regression curves (Fig. 4E) are compared, it is seen that the slope values of the control and 1500 ppm PRPLS added oils are almost equal to each other (0.0027 and 0.0026, respectively), the slope value of BHT is lower than them (0.0020) and 2000 ppm PRPLS added oil has the lowest slope value (0.0012). This result shows that the concentration of cis double bonds of unsaturated fatty acids in SFO decreased after the heating process and the addition of 2000 ppm PRPLS reduced the rate of this decrease even better than the synthetic antioxidant BHT.

Figure 5A–D shows the 1000–630 cm^{-1} region of the infrared spectra of the control, 1500 and 2000 ppm PRPLS and BHT added SFO samples. In this region, the band at 987 cm^{-1} (band no: 17) is due to bending vibrations of the C-H trans-conjugated diene groups of hydroperoxides, the band at 965 cm^{-1} (band no: 18) is due to trans double bonds in secondary oxidation products, while the band at 722 cm^{-1} (band no: 19) is due to out-of-plane vibrations of cis-disubstituted olefins (Guillén and Cabo 2000; van de Voort et al. 1994). Therefore, by analyzing this region, information about both cis and trans isomers can be obtained. Figure 5E shows the correlations between the changes in the area under the 722 cm^{-1} band arising from cis fatty acids versus heating time. As seen from Fig. 5A–E, the area under this band decreased during the heating process in the control and 1500 ppm PRPLS added SFO samples, while there was no significant change in 2000 ppm PRPLS added oil although the heating time increased. As seen from the regression graph, the control had the highest slope value (0.0185), the slope value of 1500 ppm PRPLS added oil was slightly lower than the control (0.0176), the slope value of BHT added oil was lower (0.0147) than control and 1500 ppm PRPLS added oil; and lastly the 2000 ppm PRPLS added oil has the lowest slope value (0.0065). This result confirms the conclusion obtained from the 3009 cm^{-1} band implying that the heating process causes a decrease in the concentration of

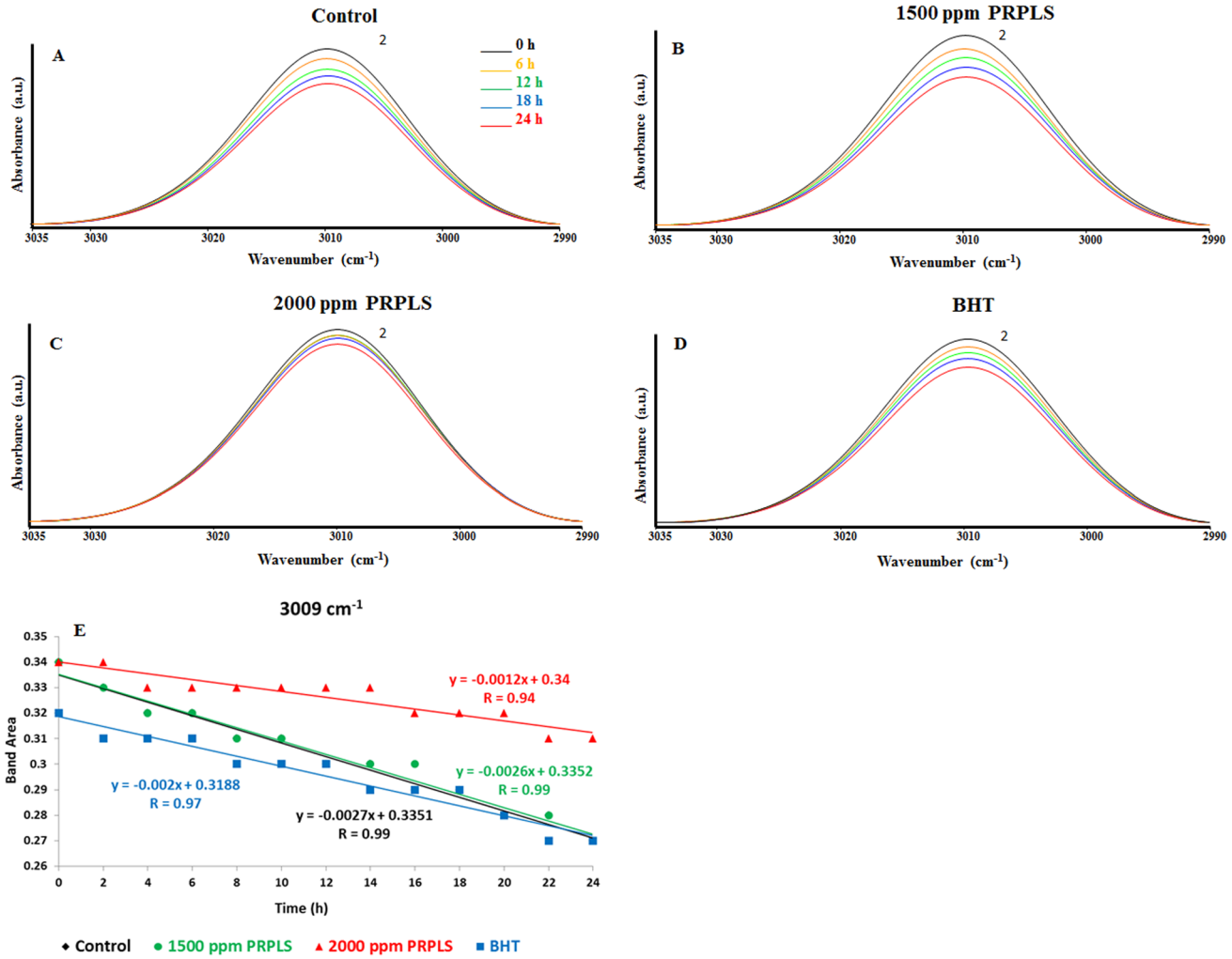


Fig. 4 Infrared spectra of unheated and 6, 12, 18, 24 h heated SFO in the 3035–2990 cm^{-1} spectral region for control (**A**), 1500 ppm PRPLS (**B**), 2000 ppm PRPLS (**C**), BHT (**D**) added SFO; and linear regression analysis of the changes in the area of the 3009 cm^{-1} band obtained from control, 1500 and 2000 ppm and BHT added SFO with respect to heating time (**E**)

cis fatty acid in SFO and the addition of 2000 ppm PRPLS reduces the rate of this decrease even better than BHT. This decrement in the proportion of cis double bonds of fatty acids might be interpreted to be a result of lipid oxidation. As argued above, in the initial stage of oxidation, H atoms are detached from fatty acids and lipid alkyl radicals are generated. The amount of energy required to detach this H atom changes depending on its position in the fatty acid. Since the energy required to remove H atoms attached to a carbon atom between two double bonds is less, these hydrogens are readily detached from the fatty acid and the double bond next to the carbon radical shifts to the next more stable carbon atom and alters its structure from the cis form to the trans form (Choe and Min 2006). Therefore, as the oxidation process continues, the amount of cis fatty acids in the system decreases and the amount of trans fatty acids increases in parallel. The decreases detected in the area values of the 3009 and 722 cm^{-1} bands may have appeared as a result of these changes.

The infrared bands at 987 and 965 cm^{-1} can be utilized to obtain information about the changes in the proportion of trans fatty acids in the system. As seen from Fig. 5A–D, the 987 cm^{-1} band, which originates from the trans-conjugated diene groups, gave a very weak signal in unheated oils. However, the area value of this band increased as the heating time increased. The rate of increase was lower in 2000 ppm PRPLS and BHT added oils. Looking at the regression graph for this band (Fig. 5F), it is seen that the slope values of the control and 1500 ppm PRPLS added SFOs are equal to each other (0.0020), the slope values of the 2000 ppm PRPLS and BHT added SFOs are half of the slope values of the others and almost equal to each other (~0.001). This result shows that as the heating time increases, the amount of trans fatty acids in control SFO increases. Moreover, although

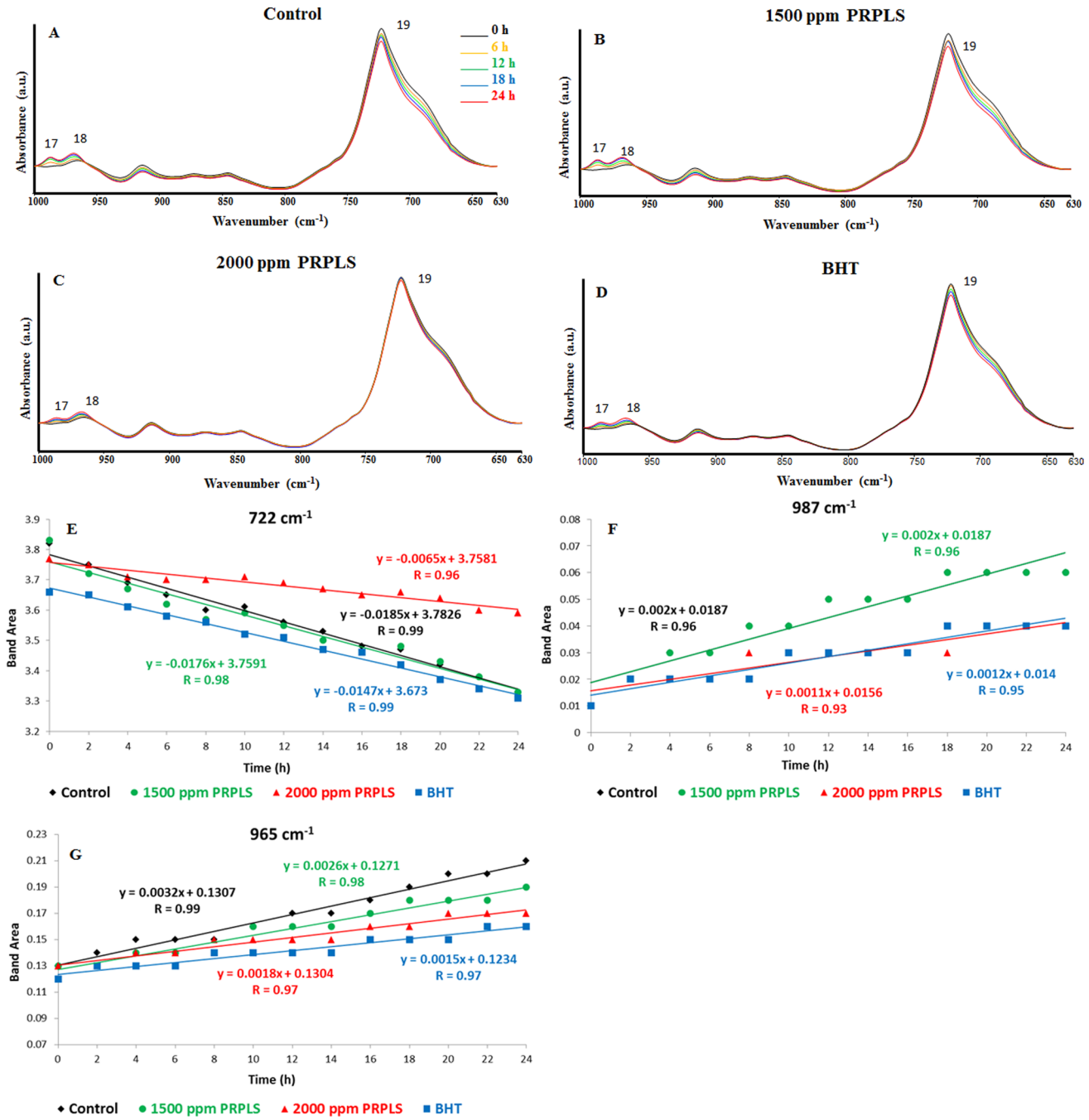


Fig. 5 Infrared spectra of unheated and 6, 12, 18, 24 h heated SFO in the 1000–630 cm^{-1} spectral region for A control (**A**), 1500 ppm PRPLS (**B**), 2000 ppm PRPLS (**C**), BHT added (**D**) SFO; and linear regression analysis of the changes in the area of the 722 cm^{-1} (**E**), 987 cm^{-1} (**F**), 965 cm^{-1} (**G**) bands obtained from control, 1500 and 2000 ppm PRPLS and BHT added SFO with respect to heating time

1500 ppm PRPLS was not successful in reducing trans fatty acid formation, 2000 ppm PRPLS reduced the rate of the formation of them successfully, alike with BHT. When the changes in the 965 cm^{-1} band, which results from trans double bonds in secondary oxidation products, was examined, it can be seen that this band is very weak in unheated oil samples. As seen from Figs. 5A–D and G, as the heating time increases, the area under this band increases in the control and 1500 ppm PRPLS added SFO and the rate of increase is very low in 2000 ppm PRPLS added SFO. If the slope values of the oil samples are compared, it is seen that the control has the highest slope value (0.0032), the slope value of the 1500 ppm PRPLS added SFO was slightly lower than the control (0.0026), the slope value of 2000 ppm PRPLS

added oil (0.0018) is very low compared to them and much closer to BHT added oil (0.0015). This result showed that 1500 ppm PRPLS was able to reduce trans fatty acid formation to a small extent but 2000 ppm PRPLS reduced trans fatty acid formation successfully. As mentioned above, the loss of cis double bonds and the appearance of trans fatty acids occur simultaneously during the oxidation process. Therefore, the decreases detected in the areas of the 3009 and 722 cm^{-1} bands and the increases in the areas of the 987 and 965 cm^{-1} bands indicate the conjugation and cis–trans isomerization of the double bonds that occur after heating and according to our results 2000 ppm PRPLS reduced this conjugation and isomerization successfully.

Chemometric analysis

In our study, PCA, which has been used in some previous oil studies, was used to evaluate the differences between and within the sample groups (Cakmak-Arslan 2022; Romano et al. 2021). PCA is a multivariate data analysis technique which is widely used with spectral data consisting of thousands of features that require data reduction. In this analysis, the original large multidimensional data is reduced to several PCs that best represent the data at low dimensions. The PCs are expressed in terms of percentage of variables explained. The first PC (PC1) has the highest % variables in the data followed by PC2, PC3 and so on (Berrueta et al. 2007). In the current study, since it has been determined that 2000 ppm PRPLS provided protection for all analyzed parameters, this analysis was applied to control and 2000 ppm PRPLS added oils. The results of PCA were interpreted by considering the score and loading plots. The score plot shows the projection of the data onto the span of the PCs while the loading plot indicates the relationship between the PCs and original variables (Rohman and Che Man 2012). Figure 6A and B shows the PCA score and loading plots of the spectra obtained from the control and 2000 ppm PRPLS added SFOs sampled every two hours during the heating process, respectively. The PCA results displayed the spectral variations between control and 2000 ppm PRPLS added SFO samples with different heating times and the changes related to the oxidation. As seen from Fig. 6A, maximum variation values are remarkable (PC1 + PC2 = 97%). As also seen from this figure, unheated (0 h) and shorter time (2, 4, 6, 8 h) heated control SFO samples are located on the positive side of PC1 and the longer time (10, 12, 14, 16, 18, 20, 22, 24 h) heated control SFO samples are located on the negative side of PC1. As also seen from this figure, the unheated control SFO located away from the 2, 4, 6, 8 h heated control SFO samples. This result indicated that there is a very clear separation between heated and unheated control oil samples, there are structural and compositional changes even after 2 h of heat exposure in control SFO and these changes reach much more dramatic dimensions after 8 h of heat exposure. In addition, this figure also shows that all of the 2000 ppm PRPLS added SFO samples and the unheated and shorter time (2, 4, 6, 8 h) heated control SFO samples are clustered on the positive side of PC1 and the 2000 ppm PRPLS added SFO samples are located very close to the shorter time heated control SFO samples. This result revealed that the structure and composition of 2000 ppm PRPLS added SFO changed slightly during 24 h, indicating that PRPLS was successful in reducing the rate of oxidative damage in the oil. These results confirmed the spectroscopic findings, where heat treatment induced important alterations in the structure, content and composition of the control SFO and the addition of 2000 ppm PRPLS showed a strong protective effect against lipid oxidation.

In PCA, loading plot can be used to indicate how the original variables relate to the PCs. The loading plot describes the significance of the independent variables and gives information about which variables provide the highest contribution to the components. Thus, loadings can be thought as the weights of each original variable when calculating the principle components and information about which variations in the functional groups between the samples bring about the difference could be obtained from loadings plot (Rohman et al. 2021). In this study, the PC1 and PC2 explained 94% and 3% of the total variability, respectively, accounting for the oxidation changes. According to the loadings plot given in Fig. 6B, prominent alterations were detected particularly in the 3600–3250, 3025–2800, 1800–1600, 1000–600 cm^{-1} regions. As can be clearly seen from Fig. 6B, the loading of PC1 has the strongest contribution in the bands associated with the primary and secondary oxidation products (3485 and 1745 cm^{-1}), cis double bonds (3009 and 722 cm^{-1}) and trans fatty acids (987 and 965 cm^{-1}). This result showed the importance of these particular spectral bands for the arrangement of the samples with different heating times shown in Fig. 6A and supported the findings obtained from the analyses of the spectral bands.

In this study, valuable information about the thermal oxidation of SFO was acquired by analyzing the changes in the areas of certain MIR bands. Upon a heating process, the increase observed in the area values of the 3482 cm^{-1} and 1745 cm^{-1} bands indicate an increased amount of primary and secondary oxidation products; the decrease detected in the area values of the 3009 cm^{-1} and 722 cm^{-1} bands indicate a decreased proportion of cis-unsaturated fatty acids; the increase in the area values of the 965 cm^{-1} and 987 cm^{-1} bands indicate an increased proportion of trans-unsaturated fatty acids in the control SFO spectrum. The increases in primary and secondary oxidation products were also confirmed by measuring the specific absorptivity values of CDs and CTs. These results show that SFO is very sensitive to thermal oxidation. It has been reported that the major factor

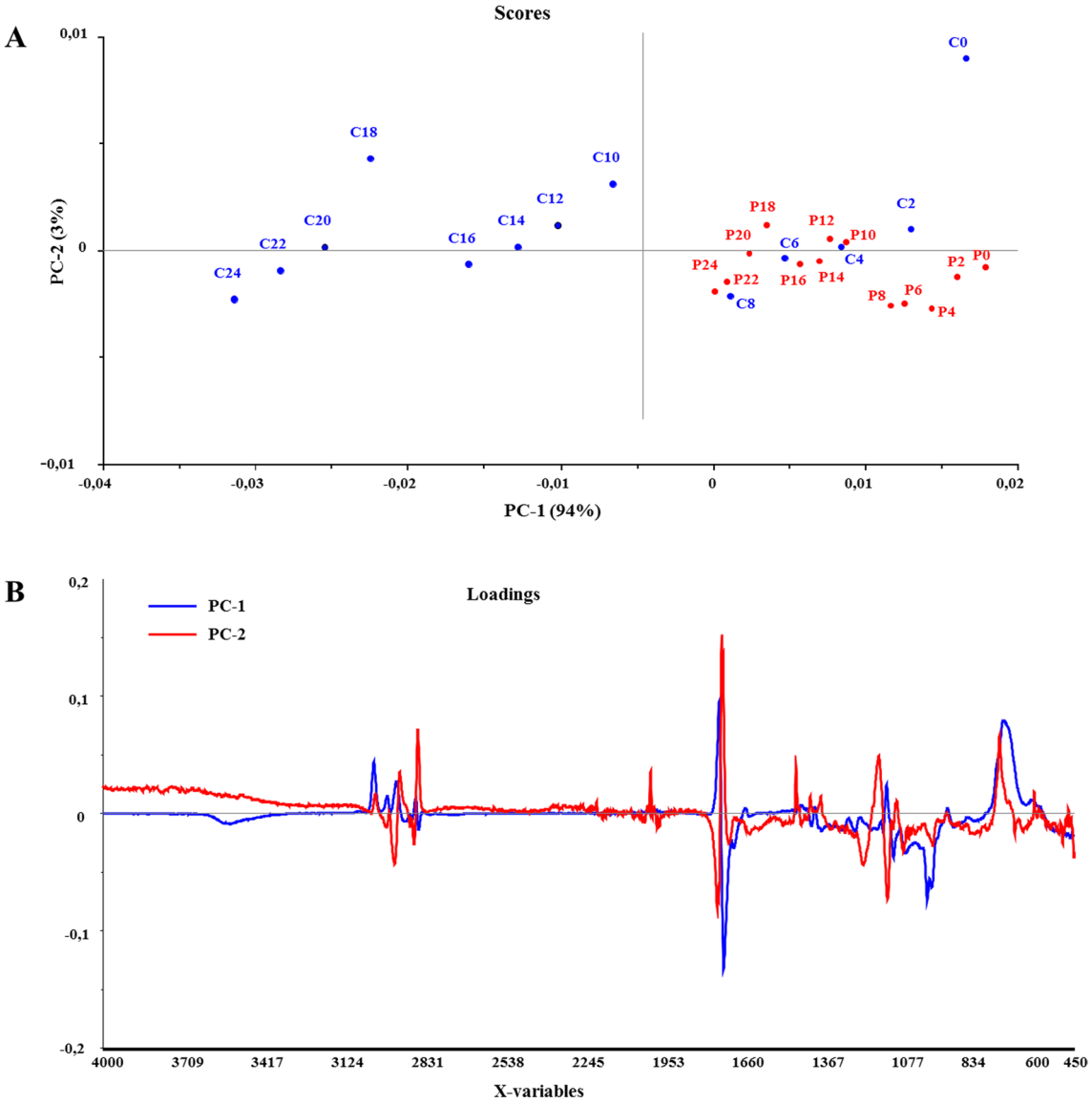


Fig. 6 PCA scores (**A**) and loadings (**B**) plots of the 4000–450 cm^{-1} spectral region of the ATR- MIR spectra obtained from control and 2000 ppm PRPLS added SFOs sampled every two hours during a 24-h heating process

affecting the rate of oxidation reactions is the concentration of unsaturated fatty acids in oils. The C=C double bonds of fatty acids in lipids function as active sites of various oxidation reactions (Choe and Min 2006). It has been known that 2 double bonds in fatty acids can induce oxidation 10–40 times faster than the existence of a single double bond (Szterk et al. 2010). For this reason, oxidation reactions take place more and faster in oils with high unsaturated fatty acids. In other words, as the proportion of unsaturated fatty acids and the degree of unsaturation of the fatty acids increase, it becomes more vulnerable to oxidation. Consistent with the literature, we determined that the fatty acid with the highest percentage in the composition of SFO was linoleic acid (55.44%), which is a type of polyunsaturated fatty acid (Aleena et al. 2020). As a result, the main reason for the lipid oxidation observed in the control SFO, the magnitude of which increases as the heating time increases, is the high amount of polyunsaturated fatty acids in it. The high amount of unsaturated fatty acids in SFO, particularly linoleic acid, made it very vulnerable to the oxidation reactions. In consistent with our results, in the previous studies, the fatty acid contents of the SFO was analyzed before and after heating process and it has been reported that a significant decrease was observed in the amount of linoleic acid after frying procedure (Sadoudi et al. 2014; Al Amin et al. 2023; Aşkın and Kaya 2020).

All the results described above clearly show that the supplementation with 2000 ppm PRPLS and BHT prior to

heating reduced lipid oxidation in SFO. It has been known that the antioxidant activity of PRPLS is mainly due to the polyphenols in it and there is a strong positive correlation between the polyphenol content of PRPLS and its antioxidant activity (Andrade et al. 2017; Mouhoubi-Tafinine et al. 2016). The polyphenols in PRPLS are mainly phenolic acids such as gallic acid, caffeic acid, pinocembrin, pinobanksin, p-coumaric acid, chrysin, galangin, hesperetin, kaempferol, naringenin and flavonoids such as catechin, quercetin, cyanidin. In this study, it was determined that the contents of quercetin, kaempferol, CAPE, total phenolic and flavonoid compounds of PRPLS were very high. The antioxidant potential of polyphenols could be attributed to the hydroxyl groups in their structures and their structural properties that help to form free radical scavenging functions (Villaño et al. 2007). These compounds may act as hydrogen donors, reducing agents, scavengers of reactive oxygen species, metal chelators and they can prevent lipid peroxidation by inhibiting the generation of reactive oxygen species, capturing superoxide and peroxy radicals, reducing transition metal ions, breaking free radical chain reactions (Socha et al. 2015). Although the principal mechanisms behind the ability of polyphenols to inhibit or delay oxidation are related to inactivating free radicals or metals, their antioxidant activity in foods is largely due to their effective location in active oxidation sites (Pazos et al. 2010). Polyphenols, which are the hydrophilic compounds, have a surfactant-like character to form hydrophilic or hydrophobic interactions depending on their medium and this feature allows them to accumulate at certain interfaces (Thaipong et al. 2006). In previous studies it has been shown that in lipid systems hydrophilic antioxidants show protection against oxidation more effectively than lipophilic antioxidants (Frankel and Meyer 2000). This is explained by the fact that while lipophilic antioxidants are soluble in oil, hydrophilic antioxidants like polyphenols locate at the air-oil interface and form a protective film that prevents oxygen access (Frankel 1996; Orozco-Solano et al. 2011). Thus, the protective effect of PRPLS on the oxidation of frying oils could be attributed to the generation of a protective film by the polyphenols in it at the air-oil interface that prevents oxygen access due to the hydrophilic properties of polyphenols. Orozco-Solano et al. (2011) reported that polyphenols showed higher antioxidant activity in heated oils than tocopherols which have lipophilic characteristics. In another study carried out to compare the impacts of avocado and olive leaf extracts on the thermal stability of canola and SFO, it was reported that olive leaf extract, which contains more polyphenol, showed higher protection in both oils (Jiménez et al. 2017). Similarly, Farag et al. (2007) showed that the addition of olive leaf juice in different concentrations stabilized the SFO and this protection was provided by the polyphenols in it. In addition, some previous studies have reported that vegetable extracts such as sage and rosemary (Che Man and Jaswir 2000), pomegranate peel (Iqbal et al. 2008), oregano (Houhoula et al. 2003), all of which are known to contain high amounts of polyphenols, were detected to increase the thermal stability of oils during deep frying.

Conclusion

This study represents the first report evaluating the antioxidant activity of PRPLS on edible oils during frying by using ATR-MIR spectroscopy. The results show that heating induces lipid oxidation in SFO, causing the generation of primary, secondary oxidation products and trans fatty acids and a decrease in the amount of cis fatty acids and thus important changes in its structure and composition. The addition of 2000 ppm PRPLS prior to heating reduces the rates of all these structural and compositional changes in SFO in a similar manner to BHT and promotes control of the oxidation reactions. These results prove that PRPLS has a strong protective effect against lipid oxidation during frying in SFO, which can be difficult to stabilize due to its high polyunsaturated fatty acid content.

In conclusion, PRPLS is a successful inhibitor of lipid oxidation in practices that need the oil to be heated at high temperatures and it can be suggested as an effective natural antioxidant that can be used in the edible oil industry as a healthier alternative to synthetic antioxidants. The use of PRPLS in edible oils as an antioxidant will provide not only a good protection against the oxidation, but also many positive health effects due to its high content of phenolic compounds. However, the use of PRPLS extracts as additives in oils may cause some changes in the properties of oils, such as appearance, texture, odor/aroma and taste/flavor. Therefore, additional studies on sensory properties and consumer acceptability of PRPLS added oils should be performed. In addition, precautions should be taken regarding the use of PRPLS in order to avoid some problems and risks in people who are allergic to the compounds in PRPLS. This study also indicated that ATR-MIR spectroscopy could be used as a fast and efficient technique to evaluate the oxidative stability of edible oils and antioxidant activity of natural and synthetic antioxidants in the oils.

Funding This work was supported by the Duzce University-Research Fund, BAP (2021.05.01.1249).

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

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