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Antioxidant effect of onion peel extracts (*Allium cepa* L.) on the stability of soybean oil under thermo-oxidative degradationo

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ABSTRACT: Onion peels have considerable amounts of bioactive compounds with high antioxidant capacity. This study aimed to assess the antioxidant capacity of yellow, white, and purple onion peel extracts and to analyze their antioxidant effects on the thermo-oxidative stability of soybean oil. The extracts were assessed regarding the total phenolic compounds and antioxidant activities. The oil was supplemented with extracts of onion peel, tocopherol, ascorbyl palmitate, and tert-butylhydroquinone, whether isolated and combined. The treatments were subjected to thermo-oxidation and the samples were analyzed for oxidative stability, total polar compounds, and tocopherols content. The purple onion peel extract showed the highest efficiency in phenolic compounds and antioxidant activity. In the oxidative stability analysis, OAP, OTBHQ and OPE+OTBHQ (synergistic effect) stood out. Total polar compounds were elevated in SO, OTOC, and OTOC+OAP at 8 hours, and all treatments exceeded the 25% limit at 16 hours. δ-tocopherol showed greater retention at the end of 16 hours in the OPE treatment with 51.54%. Therefore, the use of purple onion peel extract can delay oxidation and contribute to the retention of tocopherols, enabling the use of lower concentrations of synthetic antioxidants.

Keywords: DPPH; FRAP; natural antioxidant; tocopherols; total phenolic compounds.

Efeito antioxidante dos extratos de casca de cebola (Allium cepa L.) na estabilidade do óleo de soja sob degradação termo-oxidativa

RESUMO: *As cascas de cebola possuem quantidades consideráveis de compostos bioativos com alta capacidade antioxidante. Este estudo teve como objetivo avaliar a capacidade antioxidante dos extratos de cascas de cebola amarela,*

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branca e roxa e analisar seus efeitos antioxidantes quanto à estabilidade termo-oxidativa do óleo de soja. Os extratos foram avaliados quanto aos compostos fenólicos totais e à atividade antioxidante. O óleo foi adicionado de extratos de casca de cebola, tocoferol, palmitato de ascorbila e terc-butil-hidroquinona, isolados e combinados. Os tratamentos foram submetidos à termo-oxidação, e as amostras foram analisadas quanto à estabilidade oxidativa, aos compostos polares totais e ao teor de tocoferóis. O extrato de casca de cebola roxa apresentou a maior eficiência em compostos fenólicos e atividade antioxidante. Na análise da estabilidade oxidativa, o OAP, OTBHQ e OPE+OTBHQ (efeito sinérgico) se destacaram. Os compostos polares totais foram elevados em SO, OTOC e OTOC+OAP em 8 horas, e todos os tratamentos excederam o limite de 25% em 16 horas. O δ-tocoferol apresentou maior retenção ao final de 16 horas no tratamento OPE com 51,54%. Portanto, o uso de extrato de casca de cebola roxa pode retardar a oxidação e contribuir para a retenção de tocoferóis, permitindo o uso de concentrações mais baixas de antioxidantes sintéticos.

Palavras-chave: *antioxidante natural; compostos fenólicos totais; DPPH; FRAP; tocoferóis.*

1 Introduction

Lipid oxidation is the main deterioration reaction that can occur during the processing and storage of fat-containing foods. In addition to the reduced nutritional quality, it is responsible for the development of unpleasant flavors and tastes of the products, becoming unfit for consumption (XIE *et al*., 2019).

The addition of antioxidants as free radical scavengers can neutralize lipid autoxidation and delay the production of volatile compounds that are markers of oxidative rancidity (JOHNSON; DECKER, 2015).

However, it has been reported that long-term ingestion of synthetic antioxidants can be toxic and carcinogenic (YANG *et al*., 2018). Thus, in order to replace synthetic antioxidants with natural ones, industries are looking for safer alternatives for implementing them in foods (GUO *et al*., 2016).

According to the Food and Agriculture Organization of the United Nations, Brazil is the largest producer of soybean in the world, reaching a production of 114.26 million tons in the 2019/2020 harvest (FAO, 2019). In addition, according to the United States Department of Agriculture, Brazil produced 128.50 million tons in 2019/2020 (USDA, 2021). According to the Brazilian Association of Vegetable Oil Industries (ABIOVE, 2021), the production of soy oil in Brazil in 2020 was 9.56 million tons, with domestic consumption of 8.53 million tons.

The demand for natural products and the willingness of consumers to invest more in foods that do not contain synthetic substances and are increasingly similar to natural ones have driven the food industries to seek alternative solutions in order to minimize problems such as oxidation in foods. The use of natural ingredients for this purpose is growing and is a subject of interest in scientific research using these natural compounds mainly in food processing (KARRE; LOPEZ; GETTY, 2013).

Onion (*Allium cepa* L.) is considered a functional food due to the presence of bioactive compounds such as anthocyanins and quercetins that have antioxidant attributes and anticancer agents (RODRIGUES *et al*., 2011). In the 2019 harvest, Brazil produced 1.56 million tons with a harvested area of 48.146 hectares. Within the national territory,

Santa Catarina is the largest producer with 457,221 tons and in the state of São Paulo, there was a production of 171,309 tons (IBGE, 2021).

Brazil has an economy based on agribusiness; therefore, there are food processing industries that generate agricultural byproducts without any use. In this waste material, there are significant amounts of phytochemicals, sources of valuable natural antioxidants that may be applied as food ingredients (GAWLIK-DZIKI *et al*., 2013).

Considering the high production and consumption of soybean oil, combined with the large production of onions in Brazil and its derivatives containing bioactive compounds, it is necessary to study the antioxidant potential of onion peel extract applied to soy oil to prevent thermo-oxidative degradation.

This work includes a literature review of the main theoretical references necessary for the study. Then, the entire methodology used is explained, showing the entire development of the analysis and the parameters used. Subsequently, the results obtained from the simulations and statistical analysis are presented and discussed, followed by the final considerations of the work performed.

2 Theoretical reference

The following subsections contain information on onion production, benefits, and waste. Subsequently, about lipid stability in relation to thermo-oxidation and antioxidants.

2.1 Agro-industrial production

Soybean production for the 2020/2021 crop is estimated at 135.41 million tons, an 8.5% higher volume. The planting area should also increase, estimated at 4.2%, with 38.5 million hectares (CONAB, 2021).

According to Jiang (2014), 85% of the total lipids found in soybean oil are composed of unsaturated fatty acids and about 60% of this percentage are essential fatty acids (linoleic and α-linolenic).

Onions have many health benefits and are the main sources of biologically active phytomolecules, including phenolic acids, flavonoids, thiosulfinates and anthocyanins (SLIMESTAD; FOSSEN; VÁGEN, 2007).

Due to high production and commercialization, the onion contributes to the increase of agro-industrial residues. Much of this waste is generated during industrial processing: the peel (including the top layer and the two posterior layers), roots, and malformed bulbs due to mechanical damage, biological origin, or malformation (BENÍTEZ *et al*., 2011).

Waste generated from industrially processed onions contains a significant amount of dietary and phenolic compounds, being rich in two types of phytochemicals: flavonoids and alc(en)yl-cysteine sulfoxides, both of which are beneficial to human health (NILE *et al*., 2017).

According to Souza (2008), the subgroups of compounds that make up the flavonoids are the anthocyanins (they give a reddish or purple color) and quercetins, together with derivatives (they give a yellowish color).

2.2 Lipid stability

In foods, the oxidative degradation of unsaturated fatty acids can occur in several ways, depending on the environment and catalyst agents. The hydrolytic reactions are catalyzed by lipase enzymes, present in oilseeds, or by the action of heat and moisture, with the formation of free fatty acids, which increase the rancidity of the oil and, to a lesser extent, the formation of methyl ketones and lactones, which may produce unpleasant aromas (O'BRIEN, 2008).

The evaluation of the condition of the lipid oxidation state is a way of controlling and guaranteeing the quality of the products to be commercialized. There are several ways to assess the stability of oils and fats. For this reason, the aim is to analyze under standardized conditions, depending on a given reaction induction time, that is, the essential period to reach the critical induction point (HORUZ; MASKAN, 2015).

The thermo-oxidation process is widely used to simulate the frying process that consists of subjecting oils and fats to high temperatures without the presence of food. In the absence of moisture and other food-borne compounds, air temperature and oxygen are the main variables to be considered. The compounds produced during thermo-oxidation are representative of those from frying oils and can be formed under better-controlled conditions (GORDON, 2003).

The oxidation rate of a product containing oil or fat depends mainly on the number of double bonds and their arrangement; however, oxidative stability is also influenced by the presence or addition of antioxidants (O'BRIEN, 2008). During lipid oxidation, antioxidants can act in different ways, such as forming bonds with metal ions, scavenging free radicals, and decomposing peroxides, preventing the triggering of oxidative reactions (MOURE *et al*., 2001).

Antioxidants can be classified according to their mode of action and, in addition, can be described as natural or synthetic. There is not enough demand for natural antioxidants to meet the total need (GUNSTONE, 2011).

Synthetic antioxidants are commonly applied to foods to prevent oxidation so that their shelf life can be extended (SASSE; COLINDRES; BREWER, 2009). Due to toxicity and carcinogenesis, the use of these antioxidants in food is restricted. In countries such as Japan, Canada and some European countries (England, Denmark, Norway and Switzerland), the use of TBHQ (tert-butylhydroquinone) in food is prohibited (CHONG *et al*., 2015; IQBAL; BHANGER, 2007).

The current trend is to replace synthetic antioxidants with natural ones. In this context, research has been carried out with natural extracts based on spices, seeds and peels, that is, agro-industrial residues, with the interest of analyzing the antioxidant activity and the possibility of application in food (GUO *et al*., 2016).

3 Research method

The following subsections will focus on onion peels regarding origin and transport to the analyses. Then the production of natural extracts, soybean oil, synthetic antioxidants used will be detailed. Next, analyses on the extracts, thermo-oxidation process with the combination of antioxidants, analyses on the oils, and statistical analysis will be presented.

3.1 Onion peels

Peels of yellow, white, and purple onions were collected in the city of Monte Alto, state of São Paulo, Brazil, in the 2018/2019 harvest season. The yellow peel was acquired from the SW Camassuti ME agroindustry (latitude -21.217714 S, longitude -48.44881 W), the white ones from the Fugita company (latitude -21.273628 S, -48.520489 W), and the purple ones from agroindustry Onions Hori (latitude -21.325152 S, longitude -48.553334 W).

Three batches of yellow, white and purple onion peels were collected right after the peeling step. The peels were packed in raffia bags (30 cm x 30 cm) with approximately 500 g and transported to the UNESP (São Paulo State University "Júlio de Mesquita Filho") in São José do Rio Preto-SP, Brazil, where they were dried in a forced air circulation oven at 40 °C for 48 hours for removal of residual moisture and stored in hermetically sealed packages under vacuum at -18 °C until the moment of analysis.

3.2 Natural extract production

The peels were previously crushed in a knife mill (Marconi, mod. MA340, Piracicaba, Brazil). The extracts were obtained following the method proposed by Ifesan, Fadipe, and Ifesan (2014). According to the methodology, 5 g of peels together with 50 ml of hydroalcoholic solvent (water: ethanol, 20:80, v/v) were added in a 250 ml erlenmeyer flask. Then, always under light protection, the mixture was submitted to agitation in an orbital shaker table (Tecnal, TE-141, Piracicaba, Brazil) at 120 rpm for 24 hours, at 25 °C. Afterwards, the mixture was vacuum filtered using Whatman 125 mm filter paper (No 1). Afterwards, it was rotoevaporated at 40 °C and lyophilized at a temperature of -44 °C and 400 mmHg pressure). The extracts were stored in amber flasks and inertized with gaseous nitrogen and conditioned at -18 °C.

3.3 Soybean oil and synthetic antioxidants

In order to carry out this work, refined soy oil, purchased from the local market (São José do Rio Preto-SP, Brazil), in sealed packages, whose label did not declare the addition of antioxidants in the list of ingredients, was used.

Antioxidants were kindly provided by Danisco™ Dupont®: tocopherol from Guardian® Toco 70 Ip (46% γ-tocopherol + β-tocopherol, 21% δ-tocopherol, 7% α-tocopherol and vegetable oil used as shipping agent); ascorbyl palmitate from Grindox® with purity 98%; and tert-butylhydroquinone (TBHQ) from EMBANOX™ with purity 99%.

3.4 Analysis in extracts

Yield calculation was expressed as a percentage;

$$\text{yield (\%)} = (\text{dry extract weight} / \text{weight of the dry peels}) \times 100 \quad (1)$$

Analysis of total phenolic compounds was performed by spectrophotometry according to Singleton and Rossi (1965). An aliquot of 0.1 mL of the hydroalcoholic extract was mixed with 0.5 mL of Folin Ciocalteu reagent, 1.5 mL of saturated sodium carbonate solution (20%), and 6.0 mL of distilled water. After two hours of reaction

at room temperature, the absorbance of the mixture was measured at 765 nm in a spectrophotometer (Shimadzu, mod. UV mini 1240, Kyoto, Japan), and used to calculate the content of total phenolic compounds in the lipid fractions. For quantification, a calibration curve was plotted using gallic acid as a standard (0 mg/L to 500 mg/L). The content of total phenolic compounds was expressed as milligrams of gallic acid equivalent per g dry extract (mg GAE/g dry extract).

The Ferric Reducing Antioxidant Power assay (FRAP) was performed according to the methodology described by Szydłowska-Czerniak *et al*. (2008); in the absence of light, an aliquot of 90 µL of the sample was transferred to test tubes and 270 µL of distilled water and 2.7 mL of FRAP reagent (25 mL of 0.3 M acetate buffer, 2.5 mL of 10 mmol TPTZ and 2.5 mL of 20 mmol ferric chloride) were added. The mixture was homogenized and kept in a heating bath (Fisatom, mod. 550, São Paulo, Brazil) at 37 ºC for 30 minutes. The coefficient of determination of the curve using trolox solutions (Sigma Aldrich®, USA) was R2 = 0.9922. Absorbance was measured in a spectrophotometer (Shimadzu, mod. UV mini 1240, Kyoto, Japan) at 595 nm. The results were expressed in micromol equivalente de Trolox per dry extract (µmol Trolox/g. dry extract).

For the DPPH• free radical method proposed by Brand-Williams, Cuvelier and Berset (1995), an ethanolic solution of DPPH• (2,2-diphenyl-1-picryhydracyl) at 6×10^{-5} M and ethanolic solutions of Trolox (6-hydroxy-2,5,7,8-tetramethyl-chromane-2-carboxylic acid) was prepared and used for the standard curve at concentrations from 0.19 mM to 0.93 mM. For the analysis, 100 µL of sample diluted in 2.9 mL of DPPH• solution was pipetted into an amber test tube. The absorbance of the samples was read at 515 nm in a spectrophotometer (Shimadzu, mod. UV mini 1240, Kyoto, Japan) after 25 minutes of reaction. The coefficient of determination using the Trolox solutions was $R^2 = 0.9996$ and the antioxidant activity was expressed in micromol equivalente de Trolox per dry extract (µmol Trolox/g. dry extract).

3.5 Thermal oxidation

For the thermo-oxidation process, the extract of purple onion peels was selected to be added to soybean oil. In addition to the onion peel extract, soybean oil was combined with tocopherol, ascorbyl palmitate and tert-butylhydroquinone, isolated (200 mg/kg) and combined with each other (100 mg/kg of each antioxidant) with the complete dissolution of the added antioxidants. The following treatments were subjected to thermo-oxidation: SO (soybean oil), OPE (soybean oil + 200 mg/kg of onion peel extract), OTOC (soybean oil + 200 mg/kg tocopherol), OAP (soybean oil + 200 mg/kg ascorbyl palmitate), OTBHQ (soybean oil + 200 mg/kg tert-butylhydroquinone), OPE+OTOC (soybean oil + 100 mg/kg onion peel extract + 100 mg/kg tocopherol), OPE+OAP (soybean oil + 100 mg/kg onion peel extract + 100 mg/kg ascorbyl palmitate) OPE+OTBHQ (soy oil + 100 mg/kg onion peel extract + 100 mg/kg tert-butylhydroquinone), OTOC+OAP (soybean oil + 100 mg/kg tocopherol + 100 mg/kg ascorbyl palmitate), OTOC+OTBHQ (soybean oil + 100 mg/kg tocopherol + 100 mg/kg tert-butylhydroquinone) and OAP+OTBHQ (soybean oil + 100 mg/kg ascorbyl palmitate + 100 mg/kg tert-butylhydroquinone).

The treatments, in duplicate, were subjected to discontinuous heating (10 hours on the first day and 6 hours on the following day) at 180 °C ± 5 °C on a heating plate (Lucadema, mod. Luca-43/01, São José do Rio Preto, Brazil), using a glass thermometer (Incoterm, mod. ASTM E-1, Porto Alegre, Brazil). For this, 50 mL of each treatment and times were laid out in 100 mL beakers with a surface/volume ratio of 0.4/cm. Samples were taken at different time intervals (0, 2, 4, 8, and 16 hours), stored in amber glass bottles, inerted

with nitrogen gas, and, thus, stored at -18 °C for further analysis of oxidative stability, total polar compounds, and tocopherol content.

3.6 Analysis in soybean oil

The oxidative stability index was measured according to the Cd 12b-92 method proposed by the American Oil Chemists' Society (AOCS, 2009) by determining the electrical conductivity of the volatile degradation products using Rancimat (model 743, Metrohm, Herissau, Switzerland). The determination was carried out at 110 ºC, with airflow of 20 L/h, where 3 g of the sample and 60 mL of distilled water were inserted into the flasks containing the electrodes. An electrical conductivity vs. time curve was automatically recorded during the reaction. The induction period derived from this curve was determined in hours.

Total polar compounds were determined by inserting the sensor of the Testo instrument (270, Testo, Campinas, Brazil) into the oil samples previously heated to (90 ± 50)°C. The reading of the total polar compounds content was made on the instrument's display as a light indicator appeared, 30 seconds after the immersion, with a result expressed in percentage (OSAWA; GONÇALVES; MENDES, 2010). The sensor was calibrated with oil supplied by the instrument manufacturer before analyzing the samples.

Tocopherol analysis was performed according to the AOCS Ce 8-89 (AOCS, 2017) method, using high-efficiency liquid chromatography (Varian brand, mod. 210-263, Walnut Creek, USA), equipped with a fluorescence detector. The following conditions were used: 250 mm x 4.6 mm silica column with 5 µm pores, 1.2 mL/min flow, excitation and emission wavelength at 290 nm and 330 nm, respectively, a mixture of 99.5% of n-hexane and 0.5% of isopropanol as mobile phase, all with purity grade for high-performance liquid chromatography (Varian, mod. 210-263, Walnut Creek, USA). The identification of tocopherols was carried out by comparing with the retention time of the 95% pure α-, β-, γ- e δ-tocopherol standards (Sigma-Aldrich, St. Louis, MO) The coefficient of determination was $R^2 = 0.9997$. These were quantified by external standardization and the tocopherol contents were expressed in terms of mg/kg.

3.7 Statistical analysis

The results obtained from the analytical determinations, in duplicate, were subjected to analysis of variance, and the differences between means were tested at 5% probability by the Tukey test using the ESTAT program version 2.0.

4 Search results

In the upcoming subsections, the results and discussions of the analyses of the extracts and analyses of the soybean oils will be presented.

4.1 Analysis in extracts

The results of yield, total phenolic compounds and antioxidant activity of onion peel extracts are shown in Table 1.

Table 1 ▶
Yield, total phenolic compounds, and antioxidant activity of onion peel extracts.
Source: research data

Onion peels		
Yellow	**White**	**Purple**
Analysis		
Yield (%)		
11,79 ± 0,02[b]	0,99 ± 0,08[c]	12,06 ± 0,06[a]
Total phenolic compounds (mg GAE/g)		
496,54 ± 1,98[b]	1,38 ± 1,78[c]	576,76 ± 2,12[a]
FRAP (µmol trolox/g dry extract)		
69,10 ± 1,30[b]	34,53 ± 1,29[c]	267,90 ± 0,28[a]
DPPH$^{\cdot}$ (µmol trolox/g dry extract)		
23,62 ± 0,74[b]	11,49 ± 0,59[c]	44,16 ± 0,90[a]

Means ± standard deviations followed by the same letters in the lines do not differ by Tukey's test ($p > 0,05$)

Different yields were found in obtaining the extracts using the 80:20 ethanol:water (v:v) ratio. The highest yield was obtained for purple onion peels (12.06%), followed by 11.79% and 0.99% for yellow and white onion peels extracts, respectively.

Kuriakose, Teenu and Stephen (2017) tested the extraction with ethanol at 80 °C, vacuum assisted and by the Soxhlet method and found 12% and 15% yield, respectively. Munir *et al*. (2018) studied the antioxidant potential of various types of plant residues, including onion, and reported a yield of 16% in the ratio of 80:20 ethanol:water.

Several studies in the literature have shown that the efficiency of extraction of antioxidant compounds can be influenced by the conditions under which the extraction process is carried out, including the type of solvent, temperature, and extraction time (SINDI; MARSHALL; MORGAN, 2014).

As for the total phenolic compounds, there was a variation between 1.39 to 576.76 mg GAE/g dry extract of onion peels. The yellow and purple peels reached higher values and differed statistically; however, the extract of the white onion peel had the lowest concentration of total phenolic compounds. It is assumed that the high content of phenolic compounds in onion peels extracts is due to the presence of quercetin (SLIMESTAD; FOSSEN; VÁGEN, 2007).

Albishi *et al*. (2013) used an ultrasonic method with a methanol-acetone-water mixture and analyzed some varieties of onion peels and obtained values of total phenolic compounds of 23.67, 22.71 and 0.54 mg GAE/g of extract dry for red, yellow and white onion extracts respectively, values lower than the present study. Vaucher *et al*. (2017), in a research carried out with purple onion peel extracts obtained by stirring, microwave, and ultrasound, obtained values between 91.9 and 839.3 mg GAE/g dry extract, with the ratio of cereal alcohol:water at 80:20 and variation in agitation.

Regarding the antioxidant activity by the FRAP method, values of 69.10, 34.53, and 267.90 µmol trolox/g of dry extract were obtained for the yellow, white, and purple onion peels, respectively. Thus, as for the total phenolic compounds, the purple onion peels showed higher content, followed by yellow and white onion peels. The value found in the present work was higher than those obtained by Vaucher *et al*. (2017) since the authors obtained 97.60 µmol trolox/g in purple onion peels. This lower value is due to different cultivars, methods, and extraction time.

Regarding the antioxidant activity by the DPPH• assay, 23.62, 11.49 and 44.16 µmol trolox/g of dry extract were found for yellow, white and purple onion peels, respectively.

The high antioxidant activity exhibited by onion peels results from the concentration of compounds, mainly phenolics, present in onion peels (ALBISHI *et al*., 2013). Similarly, Santana (2015), in a study with powdered extracts, found 28.47, 9.79 and 32.90 mol trolox/g of dry extract of yellow, white and purple onion peels, respectively.

The results with the highest amount of phenolic compounds and antioxidant activity were found, in order, in purple, yellow and white onion peels. This could be due to the coloring of the peels. According to Benedet, Umeda and Shibamoto (2007), the intensity of this color is strongly correlated with the flavonoid content. The subgroups of compounds that make up the flavonoids are the anthocyanins (they give a reddish or purple color) and quercetins, together with derivatives (they give a yellowish color).

Since the results of this study demonstrated that the purple onion peel extract was the most efficient in terms of phenolic compounds content and antioxidant activity, this extract was added to soybean oil for thermo-oxidation at 180 °C.

4.2 Analysis in soybean oil

The oxidative stability index of samples under thermal oxidation at 180 °C for 16 hours, (Table 2) showed a sharp reduction in the stability of soybean oil over time, especially after 2 hours of heating, for all treatments. At the same time, it can be observed that there was no statistical difference between treatments.

Table 2 ▼
Means of the oxidative stability index (h) for the interaction treatments x heating times at 180 °C.
Source: research data

Treatments	Heating time (hours)				
	0	2	4	8	16
SO	6,86 ± 0,59^{aC}	4,14 ± 0,12^{bA}	3,64 ± 0,02^{bBC}	2,02 ± 0,01^{cEF}	1,02 ± 0,01^{cBCD}
OPE	6,60 ± 0,35^{aC}	4,43 ± 0,04^{bA}	3,73 ± 0,21^{bBC}	2,23 ± 0,08^{cDE}	1,07 ± 0,02^{dBC}
OTOC	6,24 ± 0,54^{aC}	4,63 ± 0,16^{bA}	3,54 ± 0,02^{cC}	2,75 ± 0,00^{cA}	0,77 ± 0,09^{dEF}
OAP	8,78 ± 0,15^{aC}	4,49 ± 0,13^{bA}	4,04 ± 0,02^{bcCB}	2,30 ± 0,05^{bcCD}	1,42 ± 0,11^{dA}
OTBHQ	16,19 ± 0,20^{aA}	4,39 ± 0,43^{bA}	4,25 ± 0,35^{bAB}	2,53 ± 0,02^{cB}	1,38 ± 0,01^{dA}
OPE+OTOC	7,00 ± 0,33^{aC}	3,97 ± 0,01^{bA}	3,58 ± 0,02^{bBC}	2,57 ± 0,08^{cAB}	0,92 ± 0,10^{dCDE}
OPE+OAP	8,40 ± 0,06^{aC}	4,07 ± 0,36^{bA}	3,90 ± 0,14^{bABC}	2,24 ± 0,08^{cD}	1,06 ± 0,01^{dBC}
OPE+OTBHQ	13,55 ± 0,62^{aB}	4,40 ± 0,00^{bA}	3,98 ± 0,04^{bABC}	1,90 ± 0,10^{cF}	1,22 ± 0,01^{cAB}
OTOC+OAP	8,63 ± 0,21^{aC}	4,55 ± 0,14^{bA}	3,85 ± 0,16^{cABC}	2,51 ± 0,08^{dBC}	1,05 ± 0,02^{eBCD}
OTOC+OTBHQ	14,16 ± 0,79^{aAB}	4,73 ± 0,28^{bA}	3,88 ± 0,17^{bABC}	1,91 ± 0,02^{cF}	0,66 ± 0,04^{cF}
OAP+OTBHQ	16,16 ± 0,01^{aA}	4,36 ± 0,09^{bA}	3,58 ± 0,04^{bBC}	2,47 ± 0,02^{cBC}	0,83 ± 0,00^{dDEF}

SO: soybean oil; OPE: soy oil + onion peel extract; OTOC: soybean oil + tocopherol; OAP: soybean oil + ascorbyl palmitate; OTBHQ: soybean oil + tert-butylhydroquinone; OPE+OTOC: soy oil + onion peel extract + tocopherol; OPE+OAP: soybean oil + onion peel extract + ascorbyl palmitate; OPE+OTBHQ: soybean oil + onion peel extract + tert-butylhydroquinone; OTOC+OAP: soybean oil + tocopherol + ascorbyl palmitate; OTOC+OTBHQ: soybean oil + tocopherol + tert-butylhydroquinone; OAP+OTBHQ: soybean oil + ascorbyl palmitate + tert-butylhydroquinone. Means ± standard deviation followed by the same lowercase letters in the lines do not differ by the Tukey test ($p > 0.05$). Means ± standard deviation followed by the same uppercase letters in the columns do not differ by the Tukey test ($p > 0.05$).

The differences observed may be related to the interactions of an antioxidant and pro-oxidant nature of the bioactive compounds present and/or added to soybean oil.

At time 0, OTBHQ and OAP+OTBHQ presented higher stability indices probably due to the synthetic antioxidant capacity. However, it was observed that the results in 2 hours of thermo-oxidation showed a reduction from 16.19 h and 16.16 h to 4.39 h and 4.36 h, respectively.

The OPE showed statistically similar behavior to the SO at all times. Jorge *et al*. (2018) evaluated the effect of extract of *Portulaca oleracea* L. in soybean oil and reported the induction time was 5.7 hours when they used the concentration of 100 mg/kg.

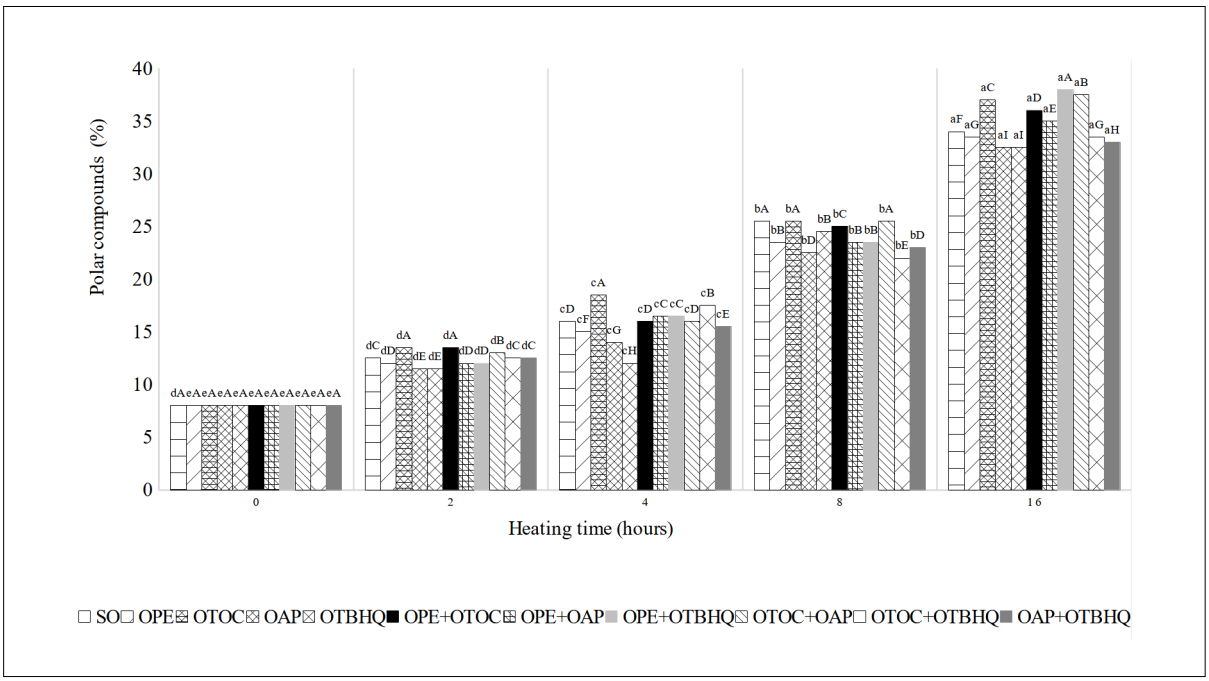
Barrera-Arellano *et al*. (2002), when evaluating the loss of tocopherols and the formation of degradation compounds in soybean oil subjected to heating under frying conditions, found 7.80 hours of induction time. This difference may have occurred due to the high concentration of tocopherols used by the authors, as they used 500 mg/kg of α-tocopherol compared to the 200 mg/kg used in the present study.

The OAP and OTBHQ treatments were the most efficient at the end of the entire thermo-oxidation period, with 1.42 and 1.38, respectively, of induction time. In the OPE+OTBHQ treatment, a synergistic effect was verified in 16 hours of thermo-oxidation.

The amount of total polar compounds is considered a reliable indicator to assess the quality of frying oil due to its accuracy and repeatability (CHEN *et al*., 2018). Hydrolysis, oxidation, or thermal degradation of fats and oils will produce non-volatile compounds, therefore, the quality of the edible oil will decrease as the polar compounds increase (GHARACHORLOO; GHAVAMI; MAHDIANI; AZIZINEZHAD, 2010).

Before the heat treatment, all treatments had polar compound values statistically equal to 8.0%, as shown in Figure 1.

Figure 1 ▼
Means of polar compounds (%) for different treatments and time of heating at 180 °C.
Source: research data



SO: soybean oil; OPE: soy oil + onion peel extract; OTOC: soybean oil + tocopherol; OAP: soybean oil + ascorbyl palmitate; OTBHQ: soybean oil + tert-butylhydroquinone; OPE+OTOC: soy oil + onion peel extract + tocopherol; OPE+OAP: soybean oil + onion peel extract + ascorbyl palmitate; OPE+OTBHQ: soybean oil + onion peel extract + tert-butylhydroquinone; OTOC+OAP: soybean oil + tocopherol + ascorbyl palmitate; OTOC+OTBHQ: soybean oil + tocopherol + tert-butylhydroquinone; OAP+OTBHQ: soybean oil + ascorbyl palmitate + tert-butylhydroquinone. Means ± standard deviation followed by the same lowercase letters in the lines do not differ by the Tukey test ($p > 0.05$). Means ± standard deviation followed by the same uppercase letters in the columns do not differ by the Tukey test ($p > 0.05$).

After 2 hours of thermo-oxidation, the treatments showed a slight increase in the number of polar compounds with values between 12% and 13.5%. After 4 hours, the OTBHQ, OAP, and OPE treatments reported the lowest amounts of polar compounds, such as 12%, 14%, and 15%, respectively. After 8 hours of thermo-oxidation, SO, OTOC, and OTOC+OPA treatments extrapolated values established by some authors as recommendation limits for total polar compounds.

Values between 20% and 25% of polar compounds were suggested by Gertz (2000) for rejection or replacement of cooking oil due to negative effects on the quality of the frying oil, on the flavor, and the nutritional value of fried foods. However, Xu (2000) states that when the amounts of total polar compounds reach levels of 24%, the oil is considered degraded and must be replaced by new oil. Thus, it was noted that after 8 hours of heating, the OPE presented 23.5% of total polar compounds, a result that suggests the onion peel extract as a promising natural antioxidant agent. In addition to the other treatments: OPA (22.5%), OPE+OTOC (23.5%), OPE+OTOC (23.5%), OPE+OPA (23.5%) and OTOC+OTBHQ (22.0%).

Delfanian, Kenari and Sahari (2016) found 18.63% of total polar compounds in soybean oil added with 400 mg/kg of loquat peel extract (*Eriobotrya japonica*) heated for 12 hours at 180 ºC.

In 16 hours, the treatments in the current work presented values above 32.5%. Considering 25% to 27% as maximum limits established by the legislation of some countries for polar compounds, such all treatments were already unusable after 16 hours of heating by thermo-oxidation. This increase is likely to be related to time, temperature, and type of food (ZHANG *et al*., 2020).

Some countries such as Belgium, Germany, Holland and the United States have legislation for limits on total polar compounds in oils and fats, which are 24% and 27% (OSAWA, GONÇALVES; MENDES, 2010). In Brazil, the recommended value establishes a maximum of 25% of total polar compounds (ANVISA, 2004).

Table 3 and Figure 2 show the retentions of tocopherols. Tocopherols are important from an industrial and technological point of view, as they are powerful antioxidants capable of minimizing the negative consequences of lipid oxidation (SHAHIDI; ZHONG, 2010).

According to Codex Alimentarius Commission (2015), there are standard values for tocopherols and their isomers in soybean oil, that is, 9-352 mg/kg for α-tocopherol; 0-6 mg/kg for β-tocopherol; 89-2307 mg/kg for γ-tocopherol; 154-932 mg/kg for δ-tocopherol; and 600-3,370 mg/kg for total tocopherols.

There was a significant reduction in tocopherol levels over the heating time. The decrease in the number of tocopherols over time may be related to the antioxidant, pro-antioxidant, and radical scavenging functions that these compounds have (SAINI; KEUM, 2016).

Among the treatments evaluated, OTOC had the highest amount of α-tocopherol at time 0, with 61.36 mg/kg. This fact is due to the addition of 200 mg/kg of the natural antioxidant.

From 8 hours onwards, SO was the only treatment in which the α-tocopherol content was null showing no protection as it was not added with antioxidants. Likewise, the absence of this isomer was reported at the end of the 16 hours thermo-oxidation time for all treatments.

Table 3 ▼
Means of tocopherols (mg/kg) for the interaction treatments x heating times at 180 °C.
Source: research data

Regarding the γ-tocopherol isomer, the treatments OAP+OTBHQ and OTOC+OAP had the highest concentrations after 16 hours of thermo-oxidation, with 4.35 mg/kg and 4.16 mg/kg, respectively.

Tocopherols/ Treatments	Heating time (hours)			
	0	4	8	16
		α-tocopherol		
SO	55,22 ± 0,30^{aE}	23,68 ± 0,33^{bC}	0	0
OPE	54,47 ± 0,15^{aE}	22,87 ± 0,20^{bC}	5,39 ± 0,15^{cE}	0
OTOC	61,36 ± 0,23^{aA}	20,59 ± 0,11^{bDE}	7,42 ± 0,46^{cC}	0
OAP	55,41± 0,42^{aE}	29,25 ± 0,13^{aB}	5,96 ± 0,04^{cDE}	0
OTBHQ	55,40 ± 0,18^{aE}	35,94 ± 0,29^{bA}	6,92 ± 0,11^{cC}	0
OPE+OTOC	60,01 ± 0,33^{aB}	7,96 ± 0,31^{bH}	6,76 ± 0,32^{bCD}	0
OPE+OAP	56,76 ± 0,24^{aD}	16,19 ± 0,32^{bG}	7,53 ± 0,06^{cC}	0
OPE+OTBHQ	56,84 ±0,18^{aD}	18,59 ± 0,35^{bF}	5,23 ± 0,18^{cE}	0
OTOC+OAP	54,58 ± 0,14^{aE}	19,83 ± 0,07^{bE}	10,40 ± 0,11^{cA}	0
OTOC+OTBHQ	59,47 ± 0,16^{aB}	20,97 ± 0,12^{bD}	6,84 ± 0,02^{cC}	0
OAP+OTBHQ	57,86 ± 0,30^{aC}	16,10± 0,07^{bG}	9,50 ± 0,33^{cB}	0
		γ-tocopherol		
SO	130,63 ± 0,67^{aFG}	53,48 ± 0,42^{bE}	7,14 ± 0,29^{cH}	1,13 ± 0,04^{dF}
OPE	134,20 ± 0,20^{aE}	55,92 ± 0,01^{bD}	16,08 ± 0,13^{cD}	2,68 ± 0,13^{dD}
OTOC	165,92 ± 0,25^{aA}	48,10 ± 0,11^{bF}	21,80 ± 0,26^{cB}	0
OAP	130,86 ± 0,21^{aFG}	60,91 ± 0,09^{bC}	16,57 ± 0,21^{cD}	1,65 ± 0,02^{dE}
OTBHQ	132,11 ± 0,42^{aF}	84,47 ± 0,62^{bA}	12,39 ± 0,14^{cF}	3,91 ± 0,08^{dB}
OPE+OTOC	146,43 ± 0,44^{aB}	28,53 ± 0,27^{bH}	13,63 ± 0,30^{cE}	0,88 ± 0,01^{dF}
OPE+OAP	130,93 ± 0,27^{aFG}	48,79 ± 0,17^{bF}	16,00 ± 0,09^{cD}	3,28 ± 0,05^{dC}
OPE+OTBHQ	130,49 ± 0,59^{aG}	52,37 ± 0,13^{bE}	9,20 ± 0,28^{cG}	2,51 ± 0,08^{dD}
OTOC+OAP	137,56 ± 0,28^{aD}	63,66 ± 0,21^{bB}	23,77 ± 0,28^{cA}	4,16 ± 0,04^{dAB}
OTOC+OTBHQ	140,97 ± 0,35^{aC}	61,58 ± 0,20^{bC}	9,68 ± 0,13^{cG}	0
OAP+OTBHQ	134,26 ± 0,43^{aE}	45,46 ± 0,37^{bG}	18,29 ± 0,18^{cC}	4,35 ± 0,21^{dA}

Cont. on next page

Table 3 continued

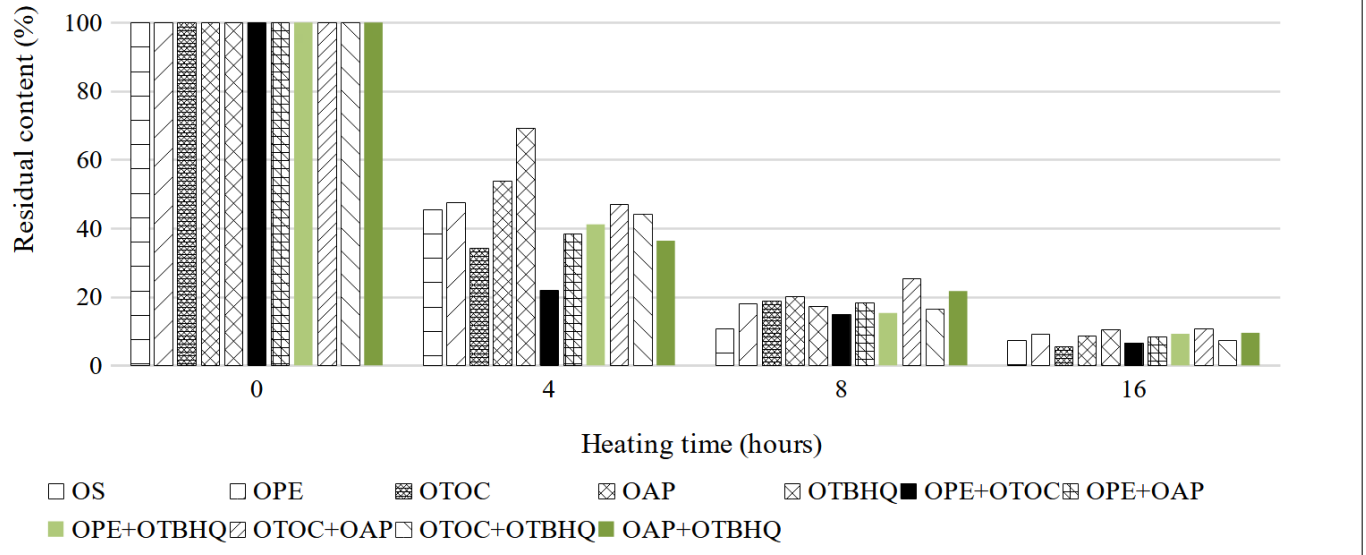
		δ-tocopherol		
SO	35,81 ± 0,16^{aG}	23,80 ± 0,21^{bF}	16,78 ± 0,16^{cI}	15,48 ± 0,17^{cD}
OPE	34,22 ± 0,18^{aH}	27,39 ± 0,23^{bC}	18,85 ± 0,28^{cEF}	17,64 ± 0,19^{cC}
OTOC	49,65 ± 0,01^{aA}	26,23 ± 0,13^{bD}	23,37 ± 0,50^{cB}	15,48 ± 0,12^{dD}
OAP	36,83 ± 0,21^{aFG}	29,68 ± 0,01^{bB}	22,28 ± 0,09^{cC}	17,69 ± 0,30^{dC}
OTBHQ	38,04 ± 0,04^{aEF}	35,59 ± 0,25^{bA}	19,68 ± 0,13^{cDE}	19,57 ± 0,30^{cB}
OPE+OTOC	45,48 ± 0,44^{aB}	18,69 ± 0,36^{bH}	17,06 ± 0,27^{cH}	15,73 ± 0,30^{dD}
OPE+OAP	38,52 ± 0,64^{aE}	22,07 ± 0,17^{bG}	18,02 ± 0,07^{cG}	16,00 ± 0,24^{dD}
OPE+OTBHQ	38,65 ± 0,36^{aE}	21,86 ± 0,19^{bG}	20,02 ± 0,15^{bD}	18,29 ± 0,12^{cC}
OTOC+OAP	41,89 ± 0,27^{aCD}	26,81 ± 0,14^{bCD}	25,06 ± 0,13^{bA}	20,80 ± 0,04^{cA}
OTOC+OTBHQ	42,70 ± 0,24^{aC}	25,07 ± 0,02^{bE}	23,52 ± 0,26^{cB}	17,73 ± 0,13^{dC}
OAP+OTBHQ	41,17 ± 0,25^{aD}	23,29 ± 0,18^{bF}	22,76 ± 0,15^{bBC}	17,79 ± 0,27^{cC}
		Total		
SO	221,65 ± 1,13^{aH}	100,96 ± 0,97^{bE}	23,91 ± 0,45^{cH}	16,61 ± 0,21^{dG}
OPE	222,88 ± 0,23^{aGH}	106,17 ± 0,42^{bD}	40,31 ± 0,26^{cDE}	20,31 ± 0,33^{dDE}
OTOC	276,92 ± 0,48^{aA}	94,92 ± 0,09^{bF}	52,58 ± 1,22^{cB}	15,48 ± 0,12^{dH}
OAP	223,09 ± 0,41^{aFGH}	119,83 ± 0,03^{bB}	44,80 ± 0,27^{cC}	19,34 ± 0,32^{dE}
OTBHQ	225,54 ± 0,28^{aEFG}	155,99 ± 1,16^{bA}	38,99 ± 0,39^{cEF}	23,48 ± 0,37^{dB}
OPE+OTOC	251,92 ± 1,21^{aB}	55,18 ± 0,32^{bH}	37,44 ± 0,89^{cF}	16,61 ± 0,30^{dG}
OPE+OAP	226,21 ± 1,15^{aE}	87,05 ± 0,66^{bG}	41,55 ± 0,22^{cD}	19,28 ± 0,19^{dE}
OPE+OTBHQ	225,98 ± 0,42^{aEF}	92,82 ± 0,67^{bF}	34,44 ± 0,24^{cG}	20,79 ± 0,20^{dD}
OTOC+OAP	234,03 ± 0,41^{aD}	110,30 ± 0,28^{bC}	59,22 ± 0,04^{cA}	24,96 ± 0,01^{dA}
OTOC+OTBHQ	243,14 ± 0,74^{aC}	107,61 ± 0,06^{bD}	40,03 ± 0,41^{cDE}	17,73 ± 0,13^{dF}
OAP+OTBHQ	233,28 ± 0,98^{aD}	84,85 ± 0,12^{bG}	50,55 ± 0,66^{cB}	22,14 ± 0,48^{dC}

SO: soybean oil; OPE: soy oil + onion peel extract; OTOC: soybean oil + tocopherol; OAP: soybean oil + ascorbyl palmitate; OTBHQ: soybean oil + tert-butylhydroquinone; OPE+OTOC: soy oil + onion peel extract + tocopherol; OPE+OAP: soybean oil + onion peel extract + ascorbyl palmitate; OPE+OTBHQ: soybean oil + onion peel extract + tert-butylhydroquinone; OTOC+OAP: soybean oil + tocopherol + ascorbyl palmitate; OTOC+OTBHQ: soybean oil + tocopherol + tert-butylhydroquinone; OAP+OTBHQ: soybean oil + ascorbyl palmitate + tert-butylhydroquinone. Means ± standard deviation followed by the same lowercase letters in the lines do not differ by the Tukey test ($p > 0.05$). Means ± standard deviation followed by the same uppercase letters in the columns do not differ by the Tukey test ($p > 0.05$).

On the other hand, OTOC and OTOC+OTBHQ presented null contents in this same period. For δ-tocopherol, at the end of 16 hours, higher levels were found in the OTOC+OAP treatment, with 20.80 mg/kg, followed by OTBHQ (19.57 mg/kg). However, the highest retentions of this isomer were found in OPE and OTBHQ, with 51.54% and 51.45%, respectively, concerning time 0. Thus, it can be concluded that the peel extract

Figure 2 ▼
Residual content (%) of total tocopherols in soybean oil added to antioxidants.
Source: research data

provided oxidative protection to the δ-tocopherol isomer at 180 °C in soybean oil due to its high antioxidant activity.



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In total tocopherols, it was found that OPE presented small retention, with 9.11%, in relation to the other treatments, such as OTOC+OAP, OTBHQ, and OAP+OTBHQ. However, the OPE+OTBHQ demonstrates the synergism between the onion peel extract and the antioxidant TBHQ.

It can be seen that δ-tocopherol was more stable than γ-tocopherol, followed by α-tocopherol. According to Kamal-Eldin (1996), the stability sequence suggested in several references for different fractions of tocopherols is: δ- > γ- > β- > α-tocopherol.

In relation to total tocopherols, at the beginning of thermo-oxidation, OTOC stood out from the other treatments with 276.92 mg/kg. In 4 hours, the OTBHQ with 155.99 mg/kg can be highlighted. At the end of the thermo-oxidation time, 16 hours, there is greater amounts of total tocopherols for OTOC+OPA, TBHQ and OPA+OTBHQ with 24.96, 23.48 and 22.14 mg/kg, corresponding to retentions of 10%, 66%, 10.41% and 9.49%, respectively.

However, it is worth emphasizing the OPE+OPA, OPE+OTBHQ and OPE treatments, which obtained 20.79, 20.31 and 19.28 mg/kg, respectively, and retentions between 8.52% and 9.20%. The amounts and retention of total tocopherols of OPE+OTBHQ, OPE and OPE+PA demonstrate a small protective effect of OPE and the synergism between onion extract and the antioxidants OTBHQ and OPA in lipid oxidation.

Veronezi, Costa and Jorge (2014) evaluated the effect of adding 3,000 mg/kg of basil extract on the retention of tocopherols in soybean oil subjected to 10 hours

of thermo-oxidation at 180 °C and found 460.35 mg/kg of tocopherols total value higher than the present study.

On the other hand, Freitas *et al*. (2020) in a research carried out with soybean oil added with 100 mg/kg of residual tomato extract verified 88% of total tocopherol retention after 5 hours of heating at 180 °C. There is evidence of decreasing total tocopherol content during frying or heating (NAYAK *et al*., 2016).

There was a significant reduction in tocopherol levels over the heating time. The decrease in the number of tocopherols over time may be related to the antioxidant, pro-antioxidant, and radical scavenging functions that these compounds have (SAINI; KEUM, 2016).

Among the treatments evaluated, OTOC had the highest amount of α-tocopherol at time 0, with 61.36 mg/kg. This fact is due to the addition of 200 mg/kg of the natural antioxidant. From 8 hours onwards, SO was the only treatment in which the α-tocopherol content was null showing no protection as it was not added with antioxidants. Likewise, the absence of this isomer was reported at the end of the 16 hours thermo-oxidation time for all treatments.

Regarding the γ-tocopherol isomer, the treatments OAP+OTBHQ and OTOC+OAP had the highest concentrations after 16 hours of thermo-oxidation, with 4.35 mg/kg and 4.16 mg/kg, respectively. On the other hand, OTOC and OTOC+OTBHQ presented null contents in this same period. For δ-tocopherol, at the end of 16 hours, higher levels were found in the OTOC+OAP treatment, with 20.80 mg/kg, followed by OTBHQ (19.57 mg/kg).

However, the highest retentions of this isomer were found in OPE and OTBHQ, with 51.54% and 51.45%, respectively, concerning time 0. Thus, it can be concluded that the peel extract provided oxidative protection to the δ-tocopherol isomer at 180 °C in soybean oil due to its high antioxidant activity.

In total tocopherols, Figure 2 it was found that OPE presented small retention, with 9.11%, in relation to the other treatments, such as OTOC+OAP, OTBHQ, and OAP+OTBHQ. However, the OPE+OTBHQ demonstrates the synergism between the onion peel extract and the antioxidant TBHQ.

It can be seen that δ-tocopherol was more stable than γ-tocopherol, followed by α-tocopherol. According to Kamal-Eldin (1996), the stability sequence suggested in several references for different fractions of tocopherols is: δ- > γ- > β- > α-tocopherol.

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However, it is worth emphasizing the OPE+OPA, OPE+OTBHQ and OPE treatments, which obtained 20.79, 20.31 and 19.28 mg/kg, respectively, and retentions between 8.52% and 9.20%. The amounts and retention of total tocopherols of OPE+OTBHQ, OPE and OPE+PA demonstrate a small protective effect of OPE and the synergism between onion extract and the antioxidants OTBHQ and OPA in lipid oxidation.

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5 Conclusion

The highest values of yield, total phenolic compounds, and antioxidant activity were found in purple onion peel extract. Regarding oxidative stability of the soybean oil, the OPE+OTBHQ, OAP, and OTBHQ were the most efficient treatments at the end of the entire heating period. For total polar compounds, the treatments with a time of 8 hours stood out, except for SO, OTOC and OTOC+OAP. Concerning tocopherols, δ-tocopherol had higher retention at the end of 16 hours in OPE and OTBHQ treatments, with 51.54% and 51.45%, respectively. Thus, it can be concluded that OPE presented a small protection against lipid oxidation. In addition, the synergistic effect between the OPE and OTBHQ may allow the reduction of the concentration of TBHQ to be applied to soybean oil, contributing to better health safety.

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Conflict of interest

The authors declare that there is no conflict of interest.

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