JAP&T
TPA-Timişoara

Available online at http://journal-of-agroalimentary.ro

Journal of Agroalimentary Processes and Technologies 2019, *25* (2), 111-116

Journal of Agroalimentary Processes and Technologies

Exploiting the potential of dried tomatoes and their processing by-product to enhance the thermo-oxidative stability of rapeseed oil

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Abstract

The goal of this study was to improve the thermo-oxidative stability of rapeseed oil used in various high-temperature food applications. At the same time, consideration was given to valorize the bioactive potential of a by-product resulting in large amounts from industrial tomatoes processing. For this purpose, the dried tomatoes powder and their processing by-product powder have been added at a level of 200, 500 and 1000 ppm in rapeseed oil subjected to convective heating for 240 min at 185±5°C. Further, the thermo-oxidative degradation of heat-treated oil samples was monitored. The results of this research showed that the tomatoes processing by-product has a high content of bioactive compounds. The tomatoes powder as well as their processing by-product powder added in the oil samples at a level of 500 ppm has an inhibitory effect on the thermo-oxidative degradation of rapeseed oil similar to butylhydroxytoluene (BHT) applied to a level of 200 ppm. Thus, the tomatoes powder and their processing by-product are recommended as natural antioxidants for edible oil used in high-temperature food applications.

Keywords: thermo-oxidative stability of rapeseed oil, tomatoes and their processing by-product, antioxidant properties.

1. Introduction

Lipid oxidation is one of the main potential causes of food degradation. Lipid oxidation occurs especially in the case of raw materials and products rich in polyunsaturated fatty acids, in the case of foods subjected to high-temperature heat treatments with a large surface in contact with the air. As a consequence of this phenomenon, it may be the appearance of a rancid odor, the change of food color and texture, which negatively impacts the sensory qualities of food producs. The nutritional value of foods subjected to thermo-oxidative degradation of the lipid fraction can also be severely affected [1].

During high-temperature processing of vegetable oils, oxidation, polymerization and hydrolysis simultaneously occur, causing the alteration of edible oils chemical composition [2].

The primary products of lipid oxidation, hydroperoxides, did not smell. The secondary products of oxidative degradation of lipid fraction of foods, being largely volatile, are responsible for aroma changes. Rancid odor perception limit may vary, and in the case of advancing the oxidation process, it may induce unacceptable flavor changes by consumers [3].

Rapeseed oil is a very popular edible oil and it may represent an excellent source of oil-soluble vitamins, polyunsaturated fatty acids and antioxidants for human diet. Vegetable oils oxidative stability is mainly related to phenolic compounds [4]. Rapeseed oil, in comparison with other oils, contains the highest amount of linolenic acid (10-13%)

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Although rapeseed oil retains its natural antioxidants and it has a good nutritional profile due to the high content of unsaturated fatty acids, this oil is susceptible to lipid oxidation, especially during high-temperature applications, specific to food industry [5, 6].

Enhancing oxidative stability and shelf life of vegetable oils for high-temperature food applications with antioxidants can be challenging. Both synthetic and natural antioxidants are suitable for stabilizing frying oils against thermal lipid oxidation. Usually, the synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and propyl gallate (PC) are added in vegetable oils to retard oxidative degradation but their using has been limited due to toxicology issues [7]

However, in response to consumer demands for clean products with no synthetic ingredients, the food industry has been continuous seeking new sources of green or naturally derived antioxidants. Thus, the exploiting the potential of natural sources of antioxidants became a great opportunity for food sector [8, 9]. Moreover, there is an continuous interest for recycling by-products from the processing of vegetable raw materials to obtain natural antioxidants, further used in food, pharmaceutical and cosmetically purposes [10, 11].

Tomatoes represent a rich source of bioactive compounds with proven terapeutic properties such as lycopene, beta-carotene, potassium, ascorbic acid, chlorogenic acid, flavonoids, phenolic compounds tocopherol and xanthophylls [12-14].

Although the tomatoes processing by-products are annualy obtained in considerable quantities, until now they are incompletely recovered and underused in order to exploit their antioxidant potential [15, 16]. The literature studies on this topic, reveal that tomatoes processing by-product represent a valuable source of bioactive compounds and dietary fiber [17].

In this concern, the goal of this study was to investigate the inhibitory potential of dried tomatoes powder and their processing by-product incorporated in rapeseed oil at a level of 200, 500 and 1000 ppm, on thermo-oxidative stability of oil samples subjected to high-temperature (185±5°C) heating. A control oil sample without any additions as well as an oil samples with BHT addition was also prepared. The oxidative deterioration of oil samples was monitored by specific chemical indices such as peroxide value, para-anisidine value and total oxidation value.

2. Material and methods

2.1.Tomatoes processing

Fresh tomatoes (*Solanum lycopersicum*) have been purchased from local supermarkets (Timisoara, Timis County, Romania). A portion of tomatoes (1.5 kg) was cut into slices, and another part (1.5 kg) was processed for tomatoes juice obtaining. The tomatoes, cut into slices, and their processing by-products were subjected to drying in a forced air oven (Froilabo AC60/France, 1000 W) for 16 h at 60°C, two days in a row for 8 hours for avoiding the bioactive compounds degradation. The moisture content of tomatoes decreased by drying from 93.17 to 4.69%, while for tomatoes processing by-product, the moisture content decreased from 65.28 to 4.06%. The dried samples were grounded until they became a fine powder.

2.2.Preparation of rapeseed oil samples with addition of dried tomatoes and their processing by-product powder

Both tomatoes powder (T) as well as tomatoes processing by-product powder (TB) at a level of 200, 500 and 1000 ppm were incorporated in rapeseed oil (R) and the obtained samples were labeled as follows: R+200 ppm T, R+500 ppm T, R+1000 ppm T, respectively R+200 ppm TB, R+500 ppm TB, R+1000 ppm TB. Also, a control rapeseed oil sample (C) and an oil sample with butylhydroxytoluene (BHT) applied to a level of 200 ppm were prepared.

2.3.Heat treatment of oil samples

The refined rapeseed oil samples (20.0±0.5 g) were weighed into Pyrex Petri dishes with an inner diameter of 11 cm and heated without lids at 185±5°C for 4 h in an electric convection oven (Esmach/Italy, 1200W). The temperature of oil samples has been monitored with a calibrated chromel-alumel thermocouple (HI 935009, Hanna Instruments). After heating, the samples were cooled at ambient temperature (25°C), stored in glass bottles and placed under refrigeration conditions, at 4-6ºC until analysis.

2.4.Analytical determinations

The moisture or water content of samples (fresh and dried tomatoes and their processing by-product) was determined using the Official Methods of Analysis [18].

The lipid oxidation was monitored by measuring of chemical indices such as peroxide value (PV), para-anisidine value (p-AV), the inhibition of oil oxidation (IO) and total oxidation value (TOTOX).

PV (meq O_2/kg oil) has been iodometric evaluated in accordance with the standard methods for oils analysis [19].

p-AV has been investigated according to Official Methods of Analysis using the UV-VIS spectrophotometer (Analytic Jena Specord 205) [19]. This index is a measure of the carbonyl content in the investigated oil samples. p-AV measures the secondary lipid oxidation products (aldehyde and ketone, etc.) generated during oxidative degradation of oils, which are usually estimated by using isooctane as the solvent at a specific wavelength of 350 nm.

The inhibition of oil oxidation (IO) was calculated according to the formula (1) [20]:

$$IO\ (\%) = \left(1 - \frac{\text{increase in PV for sample}}{\text{increase in PV for control}}\right) \times 100 \quad (1)$$

The TOTOX value is used to estimate the oxidative damage of the lipids, being calculated on the base of both PV and p-AV, using the equation (2) [21]:

$$\text{TOTOX value} = 2 \times PV + \text{p-AV} \quad (2)$$

3. Results and discussions

3.1.Primary oxidation products of rapeseed oil oxidation

PV and IO have been used as reliable indicators to highlight the primary lipid oxidation of rapeseed oil sample. Determination of hydroperoxides, the primary products of lipid oxidation, can be used as an oxidation index for the first stages of lipid oxidation [22].

Hydroperoxides, are labile chemical species undergoing further degradation reactions to produce a complex range of oxidation secondary products. PV value helps to monitoring the propagation step of free radical chain mechanism and the hydroperoxides accumulation in the oil sample. However, it is not possible to use the PV to judge the quality of oil samples, because hydroperoxides decompose during secondary lipid oxidation step. Therefore, the measuring of hydroperoxides content is limited due to their transitory nature [23].

It can be say that the presence of these compounds may represent a potential for later formation of undesirable sensorial attributes of the food products. PV increases can be recorded only when the rate of hydroperoxides formation is more than that of their degradation.

Data from Table 1 express the changes of PV recorded in rapeseed oil samples subjected to high-temperature processing, in response to oil supplementation with BHT, T and TB. According to these results it can be observed that the highest value of PV was recorded in the control sample.

Table 1. Changes in PV of high-temperature heated rapeseed oil samples in response to addition of BHT, T and TB

Sample	PV (meq O_2/kg oil)
C	40.28±1.21
R+200 ppm BHT	27.82±0.81
R+200 ppm T	34.29±1.07
R+500 ppm T	28.06±0.84
R+1000 ppm T	21.48±0.70
R+200 ppm TB	37.15±1.15
R+500 ppm TB	30.27±0.97
R+1000 ppm TB	24.12±0.81

The addition of BHT in rapeseed oil samples at a level of 200 ppm induced a decrease in PV from 40.28 to 27.82.

The addition of tomatoes powder at a level of e 500 ppm showed an inhibitory effect towards primary lipid oxidation approximately similar to that provided by addition of BHT at a level of 200 ppm.

The incorporation of tomato powder in rapeseed oil samples at a level of 200 ppm had a lower inhibitory effect than BHT, and a dose of 1000 ppm T induces an inhibitory effect stronger than BHT.

The incorporation of TB in rapeseed oil samples resulted in the decreasing of PV value, overall, the antioxidant effect of TB was less that that displayed by addition of tomatoes powder.

Table 2 provides information about the inhibitory potential of BHT, T and TB on primary lipid oxidation of rapeseed oil samples in the heating time. IO was expressed as a percentage, taking into account the increase in the PV value for oil samples with addition of BHT, T and TB in response to high-temperature heating and the increase in the PV value for the control sample heat treated in the same conditions. At the initial moment, the PV value for the thermally processed oil samples was 1.81 meq O_2/kg oil.

Table 2. Inhibitory effect of BHT, T and TB on primary lipid oxidation during rapeseed oil heating

Sample	IO (%)
R+200 ppm BHT	32.39±0.73
R+200 ppm T	15.57±0.33
R+500 ppm T	31.77±0.70
R+1000 ppm T	48.87±1.06
R+200 ppm TB	8.14±0.18
R+500 ppm TB	26.02±0.50
R+1000 ppm TB	42.01±0.79

It could be concluded that the addition of T and TB at a level of 1000 ppm in rapeseed oil samples showed an inhibition of primary lipid oxidation higher than the addition of BHT, while the addition of T and TB at a level of 200 ppm provided an inhibitory action lower that BHT. The results indicated that T applied at a level of 500 ppm displayed an inhibitory power approximately as BHT during rapeseed oil samples heating.

T and TB did not show pro-oxidative effect during high temperature heating of rapeseed oil samples up to 4 h. As it was reporded by Shaker *et al.* [24], the pro-oxidative effect has been found by increasing the content of of oxidized products with prolonged heating process, when additives were incorporated in the vegetable oil samples.

3.2.Secondary oxidation products of rapeseed oil oxidation

Unsaturated fatty acids from edible oil samples represent the primary targets of thermo-oxidation and autoxidation reactions, leading to secondary oxidation products generation [25]. p-AV is a reliable indicator of oxidative rancidity in edible oils subjected to thermal treatments at a high-temperature.

In Table 3 are shown the changes of p-AV recorded in rapeseed oil samples subjected to high-temperature processing as effect of supplementation with BHT, T and TB.

Table 3. Changes in p-AV of high-temperature heated rapeseed oil samples in response to addition of BHT, T and TB

Sample	p-AV
C	12.91±0.43
R+200 ppm BHT	10.16±0.25
R+200 ppm T	11.43±0.33
R+500 ppm T	10.41±0.27
R+1000 ppm T	9.02±0.21
R+200 ppm TB	12.77±0.40
R+500 ppm TB	11.83±0.35
R+1000 ppm TB	10.49±0.29

It can be noticed that the thermal treatment promoted the transformation of hydroperoxides to secondary products which induced off-flavors in rapeseed oil. The addition of BHT, T and TB in oil samples resulted in important decreases in p-AV relative to the control sample.

The highest level of tomatoes powder provides the highest protection against secondary oxidation of rapeseed oil samples subjected to high-temperature heating. These data are in agreement with the results reported by Poiana [26], which revealed that the natural antioxidants induce a significant inhibition of thermo-oxidation occurring in vegetable oils heated at a high-temperature.

The addition of BHT in oil samples at a level of 200 ppm induced a decrease in PV from 12.91, recorded for C sample, to 10.16. Also, the addition of T and TB at a level of 200, 500 and 1000 ppm showed inhibitory effect towards secondary lipid oxidation.

The incorporation of tomatoes powder in rapeseed oil samples to a level of 500 ppm provides protection against secondary lipid oxidation in a similar manner as BHT.

The addition of tomatoes powder to a level of 1000 ppm displayed an inhibitory effect higher than BHT, while the incorporation of tomatoes powder at a level of 200 ppm showed a lower inhibitory action than BHT. As regards the addition of TB in rapeseed oil samples, the doses of 200 and 500 ppm showed a lower action than BHT, while at a level of 1000 ppm the inhibitory effect was approximately similar to that of BHT applied at a level of 200 ppm.

3.3.TOTOX value

The TOTOX value provides an overview on oxidation process occurring in rapeseed oil samples subjected to high-temperatures heating. TOTOX value for oil samples underwent to thermal treatment markedly dropped by addition of BHT, T and TB, as is depicted in Figures 1 and 2.

The TOTOX value sharply decreased from 96.47 to 65.8 by addition of BHT. Also, the addition of T in rapeseed oil samples led to decrease in TOTOX value in the range 14-44% related to the control sample, while the incorporation of TB at a level of 200, 5200 and 1000 ppm led to decrease in TOTOX value in the range 7-37% related to the control sample.

The inhibitory effect of T and TB on lipid oxidation was dose-dependent so, the extent of lipid oxidation was inversely related to T and TB level.

Therefore, the oxidative stability of the analyzed oils probably depends on the different content of antioxidant compounds provided by T and TB added in rapeseed oil samples.

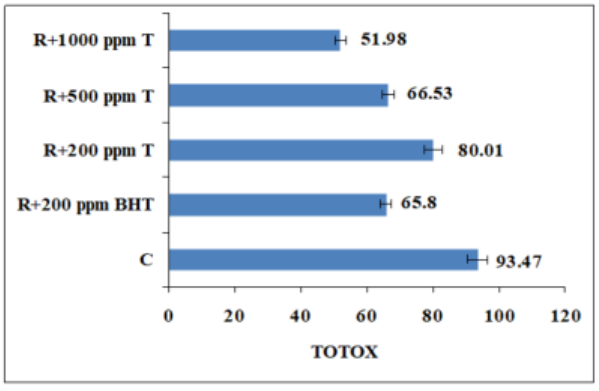

Figure 1. Changes in TOTOX value of high-temperature heated rapeseed oil samples in response to addition of BHT and T

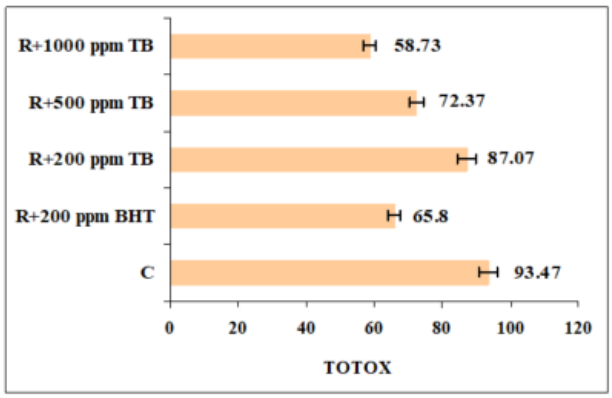

Figure 2. Changes in TOTOX value of high-temperature heated rapeseed oil samples in response to addition of BHT and TB

The natural antioxidants incorporated in vegetable oils must be cost-effective, safe, easy available, stable, effective at low dose, without any undesirable flavor, odor or color attributes. They should remain stable when the oils are exposed to high-temperature and also provide protection to the foods fried in these oil. T and TB showed these qualities, being recommended as natural antioxidants for edible oils subjected to various food applications at a high temperature.

4. Conclusions

Exposing the rapeseed oil samples to hogh temperature heating led to formation of hydroperoxides and secondary oxidation products, negatively impacted on oil quality. The addition, of T and TB in oil samples enhanced the thermo-oxidative stability of rapeseed oil. The efficiency of T and TB to improve the oxidative stability of rapeseed oil during thermal treatment was dose-sependent in the studied range (200-1000 ppm). Oil supplementation with T to a level of 500 ppm inhibited the lipid oxidation in a similar manner to BHT, while a level of 1000 ppm provide better protection toward thermo-oxidative degradation than BHT. The standard chemical indices appear to be a reliable tool to assess the ability of natural antioxidants to inhibit lipid oxidation. Our data prove that T and TB are very effective inhibitors on lipid thermo-oxidation in high-temperature food applications. Therefore, T and TB can be recommended as potential natural antioxidants for edible oils. This study represents an attempt to re-use the tomatoes processing by-product as natural antioxidant efficient for limiting the oxidative degradation of edible oils subjected to high-temperature heating.

The information provided by this study are important both for the consumers and food industry.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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