Influence of antioxidants addition on the oxidative stability of a mixture of sunflower and corn oils

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INFLUENCE OF ANTIOXIDANTS ADDITION ON THE OXIDATIVE STABILITY OF A MIXTURE OF SUNFLOWER AND CORN OILS

UDC 665.3 : 66.094.3

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ABSTRACT

Oxidative stability is an important parameter in evaluation the quality of oils and fats, as it gives a good estimation of their susceptibility to oxidative deterioration. It is generally accepted that natural antioxidants are more potent, more efficient and safer than synthetic antioxidants. The aim of this study was to investigate the oxidative stability of sunflower oil, corn germ oil, and mixtures there of (50:50), and the effect of addition of rosemary extract (StabilEnhance ® OSR and OxyLess ® CS of 0.1% and 0.3%), and propyl gallate (0.01%) on the extension oxidative stability of the oil mixture (50:50). A determination of oxidation stability of oils and their combination, and the effect of antioxidants (rosemary extract and propyl gallate) was conducted by a test of rapid oxidation of oil (Schaal oven and Rancimat test). The result of oil oxidation was expressed by the induction period (IP), a protective factor (PF) and by antioxidant activity of antioxidants (AA). The stability of a mixture of oil is proportional to the induction period. From these results it can be concluded that an addition of corn germ oil (50%) in sunflower oil led to changes in the oxidation stability of oil blends expressed within the induction period. The addition of corn germ oil in sunflower oil prolongs the stability of blends of oil degradation by oxidation. The natural antioxidant rosemary extract OxyLess®CS significantly increases the oxidative stability of a mixture of sunflower and corn oils compared to StabilEnhance®OSR and propyl gallate.

Key words: vegetable oils, oxidative stability, rosemary extract, propyl gallate

INTRODUCTION

Knowledge of vegetable oils oxidation stability is important to determine in advance time to keep of oil from stronger oxidation, without significant changes in quality and to define the shelf life of oil. Oxidative deterioration rate of vegetable oils depends on the composition of oil, storage conditions, the presence of substances that speed up or slow down the oxidation [1]. The composition of oleic, linoleic and linolenic acids in oil affects the oxidative stability [2, 3]. Secondary products, created from the auto-oxidation process of oils (aldehydes, ketones) in small quantities affect to the sensory properties of oil [4, 5]. Methods for determination of the oxidation stability of vegetable oils were based on the accelerated oxidation of oils, these are Rancimat test, Schaal oven test and AOM test [6-8]. Farhoosha et al. (2008) were showed that the kinetic parameters of the oxidation of vegetable oils using the Rancimat test affected to the viability of the oil [9]. Vegetable oils stability may be improved by addition of antioxidants, substances that slow down the oxidative decay. Synthetic and natural antioxidants were applied for the vegetable oils stabilization [10, 11, 23]. Synthetic antioxidants are cheaper than natural, but some natural antioxidants are more effective and health safer. Bera et al. (2006.) were nvestigated the thermal stabilisation of synthetic antioxidants (BHT, TBHQ, EQ) and natural antioxidant extract ajowan, used for stabilization of linseed oil [12]. They found that TBHQ has a higher thermal stability, but natural antioxidants are often used due to the attractive spice flavors and fragrances. Today, they are used various extracts of herbs for protection of oxidative deterioration of peanut oil, high-oleic sunflower oil and other vegetable oils [13, 14]. Greedy et al., (2006) report that green tea ethanol extract has a higher antioxidant activity, measured as induction period, in relation to the activity of BHT and black tea extract in sunflower oil [15]. Corn germ oil has good oxidation stability, which increases the added antioxidants.

The aim of this study was to investigate the oxidative stability of sunflower oil (linoleic type), corn germ oil and their mixtures 50:50, and the influence of added natural antioxidants rosemary extract type Oxy'Less ® CS, type StabilEnhance ® OSR and synthetic antioxidants propyl gallate to change the oxidative stability of the oil mixture. Addition of corn germ oil (50%) in sunflower oil tends to be obtained the mixture of oils that will provide the greater oxidative stability compared to the stability of the pure sunflower oil.

MATERIALS AND METHODS

Examination of oxidation stability will be carried with refined sunflower oil (linoleic type) and rapeseed oil. Examined refined oils were purchased in the store. The share of the major fatty acids of the oils is: sunflower oil (21-23% oleic, linoleic 62-67%); corn germ oil (24-32% oleic, linoleic 55-62%); [16]. Mixture of these two types of oil in a ratio of 50:50 (100 mL) was prepared by mechanical mixing. The study of the impact of individual antioxidants addition on the stability of these oil mixtures was carried out with synthetic antioxidant propyl gallate (0.01%), natural antioxidants rosemary extract type Oxy'Less ® CS and type StabilEnhance ® OSR in shares of 0.1% and 0.3%.

Oxy'Less ® CS - powdered rosemary extract, obtained from Rosmarinus officinalis L., carnosol acid 18-22%, dry extract 92-98%, Naturex, France. StabilEnhance ® OSR - liquid rosemary extract, obtained from Rosmarinus officinalis L., carnosol acid min. 5%, Naturex, France. Propyl gallate -synthetic antioxidant, Danisco, Denmark.

Each antioxidant is added directly to the oil mixture and homogenized mechanically at a temperature of 70 °C for 30 minutes. Examination of the initial chemical characteristics (quality parameters) of vegetable oils was carried out using standard methods.

Determination of free fatty acids

Free fatty acids (FFA) were determined by the standard method (ISO 660:1996) which is based on the principle of the titration with sodium hydroxide solution c (NaOH)=0.1 mol/L. The result is expressed as a percentage (%) of free fatty acid (FFA), as oleic acid.

Determination of peroxide value

Peroxide value (PV) is an indicator of the degree of oxidative deterioration of vegetable oils. Peroxide value of oil is determined by the standard method (ISO 3960:1998). The result is expressed as mmol of active oxygen derived from the resulting peroxide present in 1 kg of oil (mmol/kg).

Determination of anisidine value

The calculated value of anisidine (AV) gives us an insight into the share of non-volatile carbonyl compounds, which are secondary products of oxidation of vegetable oils that have a negative impact on sensory properties and oxidative stability. It is believed that a good quality vegetable oil has the anisidine value less than 10 (no limitation in legislation). Anisidine value is determined by the standard method (ISO 6885). The determination is based on the reaction of p-anisidine with higher unsaturated aldehydes (2, 4-dienal and 2-enal) in acidic medium, to form Schiff bases.

Determination of the number of Totox

Peroxide number in combination with anisidine value is used to determine the total value of the oxidation of vegetable oils or Totox number (TV) (ISO 6885:2006). Totox number is calculated according to the formula: Totox number= 2 PV+AV Totox number is considered to be a very useful indicator of the quality and oxidative stability of the oil; from anisidine value we can get the information about history oil oxidation, and from the peroxide value about current oil oxidation state.

Oxidative stability of oil

Schaal oven test

Schaal oven test is one of the oldest tests for examining oxidation stability of vegetable oils. It is based on the accelerated oxidation of oils influenced by of heat that accelerated this process. To perform this test, the samples of examined vegetable oils were heated in a thermostat at a constant temperature of 63 °C and monitored changes of peroxide number or sensory changes caused by oxidative deterioration of the oil at regular intervals. The result of the oxidation stability of examined plant oils, using of this test, is shown as the value of peroxide number after a certain time of the implementation of the test (for 4 days).

Rancimat test

Oxidation stability of examined vegetable oils, their mixtures (50:50) with and without added antioxidants is determined by Rancimat test of accelerated oils oxidation (ISO 6886:1996). The test is based on the rapid spoilage of oil at constant temperature and constant air intake, and determines the induction period (IP). For oxidation stability determination was used the Rancimat device, model 743 (Metrohm, Switzerland). The effect of antioxidants (natural and synthetic) on the extension of the oil mixture oxidative stability was determined by the protection factor (PF) [10] according to the formula: PF = IPinh / IP0. IPinh - induction period of the oil sample with antioxidants addition (h), induction period IP0-oil samples without added antioxidant (h). The protection factor indicates how many times increase the stability or sustainability of vegetable oil by adding of antioxidants. Determination of the oil samples oxidation stability was performed in duplicate, and showed the average value of the induction period. Longer induction period indicates on greater activity of added antioxidants and protection factor higher than 1.0 indicates on better protection from oil oxidative deterioration [15].

RESULTS AND DISCUSSION

Initial chemical characteristics (free fatty acids, peroxide, anisidine value, Totox number) of the examined vegetable oils are shown in Table 1.

Table 1. Initial chemical characteristics of vegetable oils

Vegetable oils	FFA (% olein)	PV (mmol /kg)	AV	TV
Sunflower oil	0.12±0.03	0.43±0.11	6.15±0.09	7.01
Corn germ oil	0.22±0.02	0.89±0.08	3.84±0.02	5.62

FFA - free fatty acid, % oleic acid; PV- peroxide value, mmol /kg; AV- anisidine value; TV- Totox value

Values, obtained for free fatty acid (FFA) and peroxide value (PV) have shown that the examined vegetable oils had good quality and in accordance with the Rules of edible oils and fats [17]. Calculate anisidine value (AV) and Totox number (TV) also point to the satisfactory quality of oil.

Oxidative stability of sunflower oil and corn oil was determined with the Schaal oven test (63 °C) in period of 4 days by peroxide number every 12 hours (Table 2.). Changes caused by oil oxidation method of accelerated deterioration from heat resulted in the formation of primary oxidation products expressed as peroxide value (PV). The results in the table were showed that sunflower oil had a lower stability, after 4 days of the testing was achieved higher PV value of 11.29 mmol/kg of oil. This oil, after 60 hours of the testing, was exceeded the max. PV according to the Regulations. The results were showed that corn seed oil had a better stability, greater resistance to the oxidative spoilage and reached a low value of PV 2:38 mmol/kg after 4 days of the test. Good oxidation stability of this oil was attributed to the high content of total tocopherols, 70-80% in the form of γ-tocopherol and ubiquinone (200 mg/kg).

Table 2. Oxidative stability of vegetable oils determined by the Schaal oven test during 4 days follow of peroxide values each 12 hours

Sample	PV (mmol /kg)								
	0	12	24	36	48	60	72	84	96
Sunflower oil	0.43	0.68	1.48	1.93	3.33	5.81	6.62	8.79	11.29
Corn germ oil	0.89	1.14	1.22	1.67	1.72	1.79	1.84	1.89	2.38

Table 3. Oxidative stability of vegetable oils determined by the Rancimat test

Sample	IP (h)	Increase IP (%)
Sunflower oil	2.38	--
Corn germ oil	4.96	--
Sunflower oil + corn germ oil (50:50)	3.19	34.03

IP – induction period, (h); Increase IP compared to sunflower oil, (%)

Oxidative stability of the oils and their mixtures (50:50) was determined and expressed by Rancimat test induction period (IP) showed that corn germ oil had a greater stability and resistance to oxidative decay (Table 3). The result of this test was showed that sunflower oil had IP of 2.38 (h), and corn germ oil 4.96 (h). The addition of maize germ oil (50%) in sunflower oil, we wanted to increase the resistance of sunflower oil to oxidative spoilage. In this mixture the oil reached the composition of fatty acids and natural antioxidants that extended induction period of 19.3 (h) and a higher stability compared to pure sunflower oil.

Research results of oxidation stability mixture of sunflower oil and maize germ oil (50:50) and the impact of the addition of synthetic antioxidants propyl gallate (0.01%), natural antioxidant extracts of rosemary type Oxy'Less ® CS and type StabilEnhance ® OSR, in 0.1% and 0.3% at longer oxidation stability were shown in Tables 4-5.

Control sample is a mixture of sunflower oil and maize germ (50:50) with no added antioxidant was showed the value of the induction period of 3.19 (h). The value of the induction period (IP) showed the resistance of oil mixtures to oxidation spoilage, higher IP means better oxidation stability. Addition of natural antioxidant extracts of rosemary type OSR StabilEnhance ® (0.1%) in this oil mixture slightly increased the stability of the oil to 17.87%. Greater increase in stability of the oil is observed by the addition of synthetic antioxidants propyl gallate (0.01%), it was increased stability of 45.14% (IP is 4.63 h). Addition of rosemary extract type Oxy'Less ® CS (0.1%) significantly increased the time of the induction period (5.81 h) of oils mixture. Stability of the oil mixture was increased to 82.13% in relation to the stability of the control sample (Table 4). Chu and Hsu (1999) were investigated the effect of rosemary extract, ascorbyl palmitate and tocopherols on the stability of peanut oil by OSI test [18]. They pointed out that all of three added antioxidants were increased the value of the OSI index, the greatest impact on increasing the sustainability of oil had rosemary extract. Frankel et al. (1996) were founded that the additions of rosemary extract, carnosol and rosmarinic acid effectively protected corn germ oil from oxidative deterioration in compared to the application of carnosol [19].

Table 4. Induction period (IP) and protection factors (PF) determined by the Rancimat test

Antioxidant	Share (%)	sunflower oil + corn germ oil (50:50)			
		IP (h)	Increase IP (%)	PF	AA
Control sample	0	3.19	--	1.00	--
PG	0.01%	4.63	45.14	1.45	1.00
StabilEnhance OSR	0.1%	3.76	17.87	1.18	0.39
OxyLess CS	0.1%	5.81	82.13	1.83	1.80

Control sample: mixture of sunflower oil + corn germ oil (50:50)
PG-propyl gallate; StabilEnhance®OSR-rosemary extract; Oxy´Less®CS- rosemary extract; AA - antioxidant activity compared to propyl gallate

Merrillet et al. (2008) reported about the oxidation stability of conventional and high oleic vegetable oils and impact of the antioxidants addition (rosemary extract, ascorbyl palmitate, TBHQ and mixture of tocopherols) on the oil stability by OSI test. They noted that corn germ oil showed the good stability; added antioxidants successfully increased resistance to oxidative spoilage.

By increasing the content of added natural antioxidant rosemary extract (Oxy'Less ® CS and StabilEnhance ® OSR) from 0.1% to 0.3%, it significantly prolong the induction period (IP) in oil mixture compared to the control (Table 5). Addition of 0.3% StabilEnhance ® OSR was achieved the increase in IP 14.5 (h); with the addition of a 0.3% of Oxy'Less ® CS IP is considerably higher 2.9 (h). It is evident from the obtained results that two types of rosemary extracts extend the stability of oil mixture in 61.13% and 182.76%.

Table 5. Induction period (IP) and protection factors (PF) determined by the Rancimat test

Antioxidant	Share (%)	sunflower oil + corn germ oil (50:50)			
		IP (h)	Increase IP (%)	PF	AA
Control sample	0	3.19	--	1.00	--
PG	0.01%	4.63	45.14	1.45	1.00
StabilEnhance OSR	0.3%	5.14	61.13	1.61	1.35
OxyLess CS	0.3%	9.02	182.76	2.83	4.05

Control sample: mixture of sunflower oil + corn germ oil (50:50)
PG-propyl gallate; StabilEnhance®OSR-rosemary extract; Oxy´Less®CS- rosemary extract; AA - antioxidant activity compared to propyl gallate

The calculated values of the protective factor (PF) in all tested samples showed that oil rosemary extract Oxy'Less ® CS (0.1% and 0.3%) had a better efficiency of oil mixture protection from oxidative deterioration becaose of the higher antioxidant activity. Oxy'Less ® CS was increased the stability of the mixture of sunflower and corn oil; protection factors were 1.83 and 2.83. Erkan et al. (2008) were reported that rosemary extract had a high antioxidant activity because of the high proportion of phenolic compounds [20]. Martinez-Tome et al. (2001) were founded that rosemary extract was more effective in refined olive oil protection in comparison to the synthetic antioxidants (propyl gallate, BHA, BHT) [21]. Synthetic antioxidant, propyl gallate, was showed a greater protection of tested oil mixture from oxidation (PF 1:45) compared to rosemary extract type OSR StabilEnhance ® (0.1%) wherein the PF 1.18. However, the addition of

0.3% StabilEnhance ® OSR was increased protection of oil mixture from PG. Silva et al. (2001) were reported that application of propyl gallate was more efficient in protecting from oxidation of refined sunflower oil in relation to the application of natural antioxidant tocopherol [22].

CONCLUSIONS

Based on results of oxidation stability of a sunflower oil and corn oil mixture (50:50), without the addition of antioxidants, may be performed the following conclusions:

- The corn germ oil, due to a larger share of oleic acid has a greater stability to oxidative spoilage compared to sunflower oil (Schaal oven test and the Rancimat test).
- Addition of corn germ oil (50%) in sunflower oil increases the stability to oxidative spoilage.
- Application of examined antioxidants increases the oxidative stability of sunflower oil and corn oil mixture (50:50).
- Addition of rosemary extract type Oxy'Less ® CS (0.1% and 0.3%) efficiently protects examined oil mixture (50:50) in relation to the use of rosemary extract type OSR StabilEnhance ® (0.1% and 0.3%) and propyl gallate (0, 01%).
- Use of StabilEnhance ® OSR (0.1%) rosemary extract slightly increases the stability of oil mixture compared to oil sample without the antioxidants addition.
- StabilEnhance ® OSR (0.3%) gives a better protection of oil mixture compared to the propyl gallate.

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