SUITABILITY OF SOME FOOD GRADE ANTIOXIDANTS FOR SUNFLOWER OIL

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Abstract

Antioxidants are substances which interfere with the normal oxidation process forming a stable compound that will not propagate further oxidation. Different food-grade antioxidants were added to sunflower seed oil to follow up their suitability for oil oxidation stability at ambient and high temperatures.

The best antioxidant which showed the highest effect in increasing the shelf life and the oxidation stability of sunfolower oil was propyl gallate (PG). It increased the shelf life from 8 months for the control to 14 months. The second effective antioxidants were BHT and BHA (12.5 and 11.5 months), respectively.

Rosemary, α - Tocopherol and GT-2 were the lowest effective (11, 10 and 9.6 months), respectively.

The obtained results showed the susceptibility of antioxidants when used in heating the oil at 180 ± 5°C for up to 12 hours. They had the least increase in oil viscosity, refractive index, acid and peroxide values for up to 6 hours, followed by a sharp increase in the oil deterioration for up to 12 hours. Therefore, antioxidants are suitable for oil oxidation stability at ambient temperature, and may act as pro-oxidants at high temperatures for long periods of heating.

Key words: Antioxidants effect, oil stability, heating deterioration.

INTRODUCTION

Antioxidants are substances which interfere with the normal oxidation process forming a stable compound that will not propagate further oxidation of the glyceride. They are usually thought to function as free radical acceptors, thus terminating the oxidation at the initiation step. In the absence of an antioxidant, a hydrogen atom is lost from the allylic carbon in the fatty acid group with the formation of a fatty free radical. The latter is readily susceptible to be attacked by atmospheric oxygen, resulting in the formation of peroxides and hydroperoxides. When antioxidant is present, it functions as a free radical acceptor forming a stable compound that will not propagate further oxidation of the glyceride. Normally, there is a balance between the amount of free radicals generated in the body and antioxidants to protect against them. However, an additional burden of free radicals, or lack of antioxidant protection, can shift this balance. Free radicals are formed constantly by the body's normal use of oxygen, such as respiration and some cell-mediated immune functions. They are also found or generated from environmental pollutants, cigarette smoke, car exhaust fumes, radiation or ultraviolet, pesticides and certain industrial solvents. Free radicals can damage cell membrances and other vital cell components, such as genetic material in the cell nucleus and can inactivate enzymes. Damage to body cells and molecules by oxygen containing free radicals has been implicated in a wide variety of diseases. The unsaturated fatty acids of lipids and lipoproteins are especially susceptible to free radical mediated oxidation, and oxidative modification of low-density lipoportein (LDL) particles in the blood is believed to be an important part of the atherosclerotic process. Free radical damage to DNA is believed to play a role in initiation of carcinogenesis. Oxyradicals also can attack proteins, thereby changing their structure and ability to function (Jacob, 1994). For all these mentioned, reasons scientists current opinion is the supplementation of human diets with antioxidant and vitamins, especially vitamin E and C which have proved to be effective for protection against Low Density lipoprarein (LDL) oxidation (Jialal, 1993; Block, 1993 and Lachance, 1994).

This investigation was carried out to evaluate the effect of some food-grade antioxidants upon increasing the shelf life of sunflour oil and to determine their protective effect in the heated oil.

MATERIALS AND METHODS

Materials

Sunflower seed oil, pure and refined, was selected from edible oils for its instability due to its high unsaturated fatty acids (20% oleic and 65% linoleic acid. Robbelen, *et al.*, 1989). It was purchased from Silla Company at El Fayoum.b) Food grade antioxidants of BHA, P.G and Alpha - tocopherol (Vit. E) were obtained from Sigma Chemical Co., St. Louis, MO, USA. Rosemary was obtained from SKW Chemicals Georgia, U.S.A. Tenox GT2, was obtained from Estman Chemical Co., Tennesee, USA. It is composed of 70% total tocopherols (9% alphatocopherol; 46% Gamma - tocopherol; 17% delta-tocopherol) and 30% vegetable oil.

The food additive regulation in USA has a limitation of 200 ppm of synthetic antioxidants and 300 ppm for tocopherol antioxidants; while others of natural antioxidants have 400 ppm as a recommended usage level (Eastman Chemical, 1993).

Methods

The antioxidants used were at the recommended usage levels as previously mentioned. Antioxidants were dissolved in 100 ml sunflower seed oil in duplicates and kept in brown bottles for the following:

a) Determination of shelf life or the oxidation stability of the samples using Rancimat Metrohm 679 as described in Hasenhuettle and Wan (1992).

b) Determination of viscosity using Viscometer Brookfield RVDV-I cone plate and connected with the water bath Brookfield TC 500 as described in Howard (1991).

c) Determination of refractive index, acid value and peroxide number as described by the AOCS (1985).

- All the sunflower seed oil samples (100 ml) were heated at 180±5oC for 12 hours at intervals of 3 hours heating for 4 consecutive days. The heated oils were sampled every day after heating in brown bottles and kept at 5oC for analytical experiments. The remainder of oil samples were heated the next day for another 3 hours and then sampled as previously until the forth day and the total of 12 hours heating.

- The heated oil samples without antioxidant (control) and with the added antioxidants were subjected to the some previously mentioned treatments for the determination of viscosity, refractive index, acid and peroxide values to follow the effect of the added antioxidants at high temperature compared to the control.

RESULTS AND DISCUSSION

The susceptibility of an oil or fat to auto-oxidation can generally be assessed in terms of oxidation stability. In the food industry, the oxidation stability of fats play an important part in ensuring the quality of their products. The quality assessment of fats with regard to freshness, keeping properties, and storageability can be carried out by either static or dynamic methods. In the static method, analytical determinations are made of various characteristics (such as the peroxide umber, acid value and the refractive index) related to the degree of auto-oxidation which has already taken place. Dynamic methods (such as oxidation stability) enable a better forecast of the future response of a fat to oxidative influences, (Frank *et al.*, 1982).

Few years ago, Brinkman Instruments introduced the Rancimat. It is based on the conductimetric method developed for fat and oil analysis (Hadorn and Zurcher, 1974) to determine the effectiveness of an antioxidant in an oil. The results, tabulated in Table 1, show the potential use of antioxidants to increase the shelf life of sunflower seed oil at ambient temperature. The oil samples were tested using the Rancimat at 100°C and the results were calculated at 25°C using the temperature coefficient of 2.2 for each 10 degree increase in temperature (Hadorn and Zurcher, 1974) and the coefficient of 2.5 as established by Pardun and Kroll (1972) for the autoxidation reaction for organic reaction rates.

The best antioxidant which showed the highest effect in increasing the shelf life and the oxidation stability of sunflower seed oil was PG. It increased the shelf life from 8 months for the control to about 14 months. The latter effective antioxidants in rank were BHT and BHA. They had comparaable sheef lives of 12.5 and 11 month respactivly equal shelf lives of (12.5 and 11 months) respectively. Rosemary, α-tocopherol and GT-2 were the lowest effective (11,10 and 9.6 months), respectively.

Data in Table (1) show the time of shelf life in average (mean) for each treatment with different antioxidants. This means the time of induction period of the initiation of deterioration till reaching the highest level which is the date of expiration. These results could be used in applications for determining trade standards for the processed oil in the quality control laboratory during production as mentioned before by Hill, (1994).

Figure 1 shows the relationship of viscosity and time and Figure 2 shows the relationship of refractive index and time. These two graphs are in agreement and express the true correlation between viscosity and refractive index. This correlation was known by Johnson and Kummerow (1957) who mentioned that the refractive index increased almost linearly with the increase in heating time and this is generally was attributed to the formation of high molecular weight materials.

Moreover, Figures (1) and (2) classify the used antioxidants upon their effectiveness in lowering the viscosity and the refractive index of the heated oils with antioxidants at 180°C for 12 hrs. It is well observed that BHA and α-tocopherol

Table 1. Oxidation stability of sunflower oil treated with different food-grade antioxidants.

	Oxidation stability					
	Rancimat at 100°C		Calculated * at ambient temp.			
Sunflower oil + antioxidant	Mean (Hours).	± S.D. (Hours)	Induction (Months)	Expired (Months)	Mean (Months)	± S.D. (Months)
Control	8.03	0.31	4.45	11.91	8.18	3.73
BHA	11.00	0.20	6.10	16.32	11.51	5.36
BHT	12.27	0.23	6.80	18.20	12.50	5.70
PG	14.10	1.00	7.82	20.92	14.37	6.55
α-Tocopherol	10.03	0.37	5.56	14.88	10.22	4.66
GT-2	9.66	0.20	5.10	14.12	9.60	4.11
Rosemary	11.85	1.05	4.52	17.58	11.05	6.53

* The oxidation stability conducted with Rancimat at 100°C were calculated at 25°C using the temperature coefficient of 2.2 for induction period (Hadorn and Zurcher, 1974) and 2.5 for expired period (Pardun and Kroll, 1972).

have close results to the control, while all the other antioxidants showed no effect in prventing the heated oils from increasing their viscosity and their refractive index, which lead to their increase in formation of high molecular weight materials up to 12 hours. Thus, a conclusion could be mentioned that the selected food grade antioxidants except BHA showed the problem of carry-over in the heated oils for up to 12 hours as cited before by Sherwing and Thompson (1967). Also, these graphs show that the effect of antioxidants (except GT 2) in the heated oils are in moderate function up to 6 hourse of heating and then a sharp increase of viscosity and refractive index was observed. These data could conclude that the used antioxidant are not suitable for heated oils for up to 6 hours. Meanwhile, they are of good benefit to human health in nutrition with salad oils treated with antioxidants which prohibit the cell internal body oxidation as mentioned by Jacob (1994), in case of being used without heating at high temperatures for such long time.

For assessing the suitability of the added antioxidants to sunflower seed oil samples, analytical determinations are made for various characteristics. The data tabulated in Table 2 show the effect of each added antioxidant on the heated oil upon the heating time. Acid value reflects the degree of oil hydrolysis and the amount of free fatty acid involved in the heated oil samples. From these data, it can be observed that the oil sample treated with BHA had the least amount of free fatty acids (1.04) after heating for up to 12 hrs. On the other hand, BHT and Rosemary have the highest acid value (2.4 and 2.55), respectively. These results are in good correlation with the viscosity values shown in Figure (1).

Peroxide value monitor the degree of oil oxidation and the amounts of peroxides and hydroperoxides built up in the heated oil. Due to the high sensitivity of the hydroperoxides to high temperatures and their breakdown to aldehydes and ketones (Kopp, 1973) causing the different smell of the heated oils, therefore, the low peroxide value could deal with the highest oxidation and the time of their breakdown. From Table 3 BHA is ranked the best antioxidant which protected the oil samples from oxidation up to 12 hours. The oil samples treated with the antioxidants BHT and Rosemary had a sensitive effect upon peroxides causing their breakdown into aldehydes and ketones, which may be observed in Table 3. It shows the gradual increase in peroxides and then their decrease due to their breakdown as aforementioned by Kopp (1973). Moreover, BHA showed a moderate carry-over among the other antioxidants in its suitability at high temperature for 3 hours only. These results are in agreement with those of Shermin and Thompson, (1967).

To make a conclusion across all the obtained physical and chemical analyses,

Table 2. Changes in acid value of sunflower oil treated with different food grade antioxidants.

		Heating at 180 ± 5°C			
Sunflower oil + antioxidant	Zero	3 hrs	6 hrs	9 hrs	12 hrs
Control	0.48	1.20	1.48	1.74	1.46
BHA	0.42	0.69	0.86	0.97	1.04
BHT	0.42	0.62	0.79	1.92	2.41
PG	0.40	0.75	0.98	1.57	1.70
α-Tocopherol	0.47	0.56	0.92	1.09	1.53
GT-2	0.42	0.83	1.26	2.19	1.12
Rosemary	0.73	0.85	1.42	1.98	2.55

Table 3. Chages in peroxide value of sunflower oil treated with food grade antioxidant.

		Heating at 180 ± 5°C			
Sunflower oil + antioxidant	Zero	3 hrs	6 hrs	9 hrs	12 hrs
Control	4.30	6.18	10.73	14.53	39.37
BHA	4.38	7.48	11.98	16.67	21.83
BHT	3.51	6.92	15.07	22.36	17.79
PG	4.33	7.64	10.82	13.97	35.50
α-Tocopherol	3.88	7.92	11.36	14.29	28.93
GT-2	4.42	8.16	10.11	11.11	37.42
Rosemary	4.85	7.08	10.42	16.79	11.49

we could conclude that the antioxidants are suitable in their function for increasing oxidative stability at ambient temperature only, while they could act as pro-oxidants or they could breakedown into other substances, which could act as pro-oxidants.

The obtained results are in good agreement with the Swiss Public Office regulations, which offered a list of permitted additives in foods including antioxidants in edible fats and oils. They recommended that antioxidants in edible fats and oils. are additives that do not improve frying performance and are not used in products sold as frying oils (Firestone *et al.*, 1991). Moreover, Dutta and Savage (1998), did not observe any influence of tocopherols on the stability of the extracted Walnut oil.

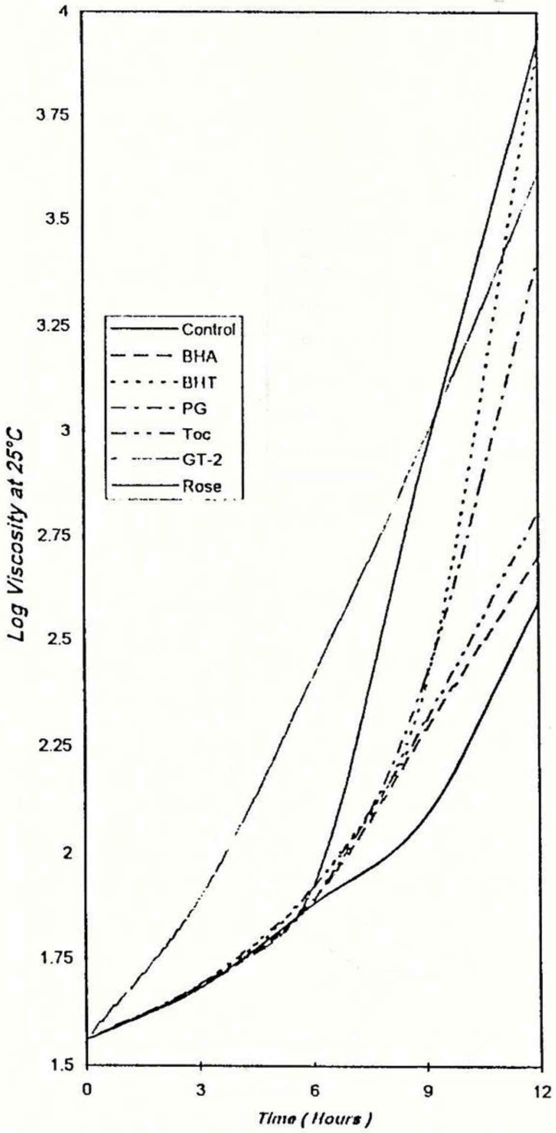

Figure 1. Viscosity of heated sunflower oil at 185 ± 5°C treated with food-grade antioxidants.

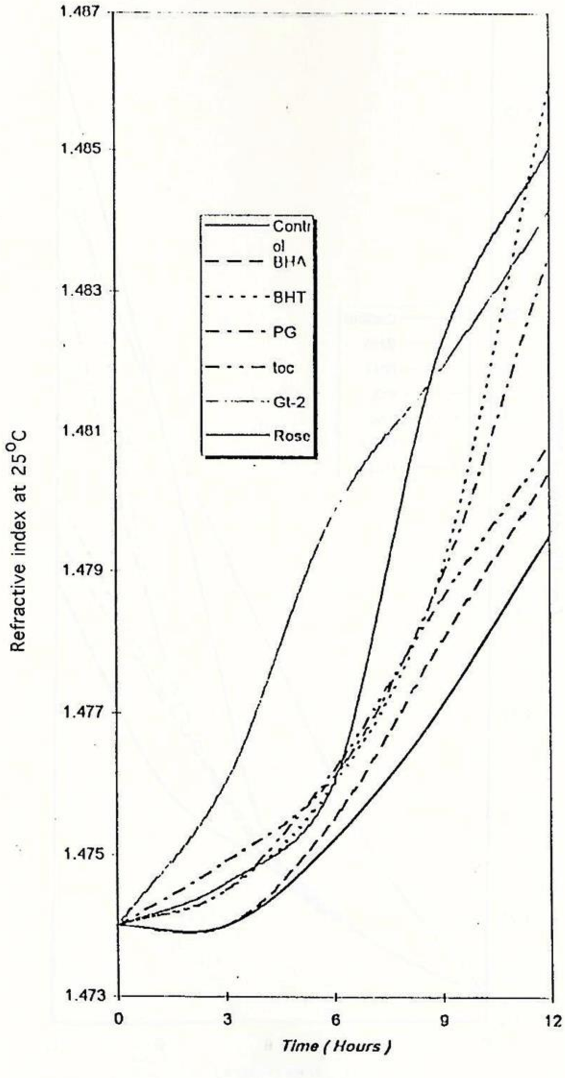

Figure 2. Refractive index of heated sunflower oil treated with food-grade antioxidants.

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ملائمة بعض مضادات الأكسدة الغذائية علي ثبات زيت عباد الشمس

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تعتبر مضادات الأكسدة مركبات تتدخل في عملية الأكسدة الطبيعية مكونة مركب ثابت يمنع حدوث الأكسدة الذاتية. وقد تم إضافة مضادات الأكسدة الغذائية لزيت عباد الشمس لتتبع ملاءمتها في زيادة ثبات الزيت ضد الأكسدة علي درجة حرارة الغرفة. وأظهرت النتائج أن بروبيل جالول كان أفضلهم حيث أعطي تأثير في زيادة فترة الصلاحية من ثمانية شهور للكنترول إلي أربعة عشر شهراً. ويليه في المرتبه الثانية كل من BHT,BHAحيث كانت فترة الثبات ١٢,٥ ، ١١,٥ شهر بالترتيب وأقلهم تأثيراً هو حصي اللبان والفا توكوفيرول ومركب GT-2 حيث أعطي ثبات للزيت بمقدار ١١, ١٠, ٦, ٩ شهر علي التوالي.

ولقد أظهرت النتائج أيضا حساسية مضادات الأكسدة العالية عند استخدامها في تسخين الزيوت علي ١٨٠ه م ± ٥ ه م لمدة ١٢ ساعة وكانت الزيادة بمعدل منخفض لكل من لزوجة الزيت ومعامل الانكسار ورقم البيوكسيد وللحموضة حتي ستة ساعات تسخين يليها زيادة حادة في تدهور صفات الزيت المستخدمة حتي اثني عشر ساعة. لذلك فإن مضادات الأكسدة تعتبر ملائمة لثبات الزيت علي درجة حرارة الفرفة بينما قد تكون مساعدة علي سرعة أكسدة الزيت علي درجات الحرارة العالية (١٨٠° م) وبزيادة وطول مدة التسخين إلي اثني عشر ساعة.