The Influence of Antioxidants on the Oxidation Stability of Biodiesel

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ABSTRACT: Oxidation stability of biodiesel is an important issue because FA derivatives are more sensitive to oxidative degradation than mineral fuel. Therefore, in the most recent European Specifications for biodiesel, a minimum value of 6 h for the induction period at 110°C, measured with a Rancimat instrument, is specified. To guarantee this value at the filling station, the use of additional antioxidants will be necessary. In this paper we show the influence of different synthetic and natural antioxidants on the oxidation stability, using the specified test method. Biodiesel produced from rapeseed oil, sunflower oil, used frying oil, and beef tallow, both undistilled and distilled, was investigated. The four synthetic antioxidants pyrogallol (PY), propylgallate (PG), TBHQ, and BHA produced the greatest enhancement of the induction period. These four compounds and the widely used BHT were selected for further studies at concentrations from 100 to 1000 mg/kg. The induction periods of methyl esters from rapeseed oil, used frying oil, and tallow could be improved significantly with PY, PG, and TBHQ, whereas BHT was not very effective. A good correlation was found between the improvement of the oxidation stability and the FA composition.

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KEY WORDS: Antioxidants, biodiesel, fatty acid methyl esters, induction period, oxidation stability, Rancimat.

The use of FAME as biodiesel is well established in Europe and in the United States. In 2001 the European Commission (EC) released a draft proposal for a directive to the European parliament on the promotion of biofuels, which came into force in 2003. For all member states a minimum share of 2% biofuels is proposed for 2005, which should be increased to 5.75% in 2010. For this reason the European Committee for Standardization (CEN) has developed unified European standards for the quality of FAME used as biodiesel (1).

In the final version of the European specifications (2), the parameter of oxidation stability also was incorporated to define a specific stability against oxidation during storage and thermal influence.

A research project named BIOSTAB, supported by the EC, was initiated in March 2001 to establish clear criteria and analytical methods to measure biodiesel fuel stability. The project is coordinated by the Bundesanstalt für Landtechnik, Wieselburg (BLT), Austria, with the participation of different research institutes, biodiesel producers, and petroleum products suppliers. Within the BIOSTAB project, our institute is in charge of the coordination of a project part dealing with evaluating the effect of synthetic and natural antioxidants on the oxidation stability of biodiesel.

Du Plessis *et al.* (3) carried out stability studies on methyl and ethyl FA esters of sunflower oil, measuring different physical and chemical parameters during storage under different conditions. A 2-yr storage study was reported for rapeseed oil esters, measuring the increase of PV, acid value, viscosity, and density (4). For the measurement of oxidation stability of fats and oils as well as FAME, the Rancimat method was used very successfully (5,6). Bondioli *et al.* (7) measured the induction period during storage of rapeseed oil methyl esters and found a rapid decrease after 30 d of storage. Mittelbach and Gangl (8) studied the stability of undistilled and distilled samples of rapeseed oil and used frying oil methyl esters and found a similar decrease in induction period except for distilled samples, which already had low values at the start.

Although there are numerous publications on the effect of natural and synthetic antioxidants on the stability of oils and fats used as food and feed, little is available on the effect of antioxidants on the behavior of FAME used as biodiesel. Simkovsky and Ecker (9) studied the effect of different antioxidants on the induction period of rapeseed oil methyl esters at different temperatures but did not find significant improvements. Canakci *et al.* (10) tested the influence of the antioxidant TBHQ on the PV of soybean oil methyl esters during storage and found good improvement of stability. Most recently, Dunn (11) described the effect of the antioxidants TBHQ and α-tocopherol on fuel properties of methyl soyate and found beneficial effects on retarding oxidative degradation of the sample.

In this paper we describe the influence of a series of commercial natural and synthetic antioxidants on the oxidation stability of FAME, prepared from different types of feedstocks. The influence of type and amount of antioxidants on undistilled and distilled biodiesel samples are studied to fulfill the requirements of current specifications for biodiesel.

MATERIALS AND METHODS

Four biodiesel samples prepared from four different feedstocks, both undistilled and distilled, were used. Undistilled rapeseed oil methyl ester (RU) was purchased from Novaol-Austria (Bruck/Leitha, Austria). Starting material for the transesterifi-

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TABLE 1
Composition of Tocopherol-Type Antioxidants

Antioxidant[a]	α-Tocopherol (%)	β-Tocopherol (%)	γ-Tocopherol (%)	δ-Tocopherol (%)	Carrier oil (%)	Others (%)
CoviOx-T50	6.5	1	29	13.5	50	
CoviOx-T70	9.1	1.4	40.6	18.9	30	
Copherol F1300	87.2				12.8	
Controx VP	>17					<83[b]
DADEX TRC		33.6% mixed tocopherols				66.4[c]
BIOCAPS ER		12% mixed tocopherols			31	57[d]
BIOCAPS LT		31% mixed tocopherols			37	32[e]
BIOCAPS PA		28% mixed tocopherols			52	20[f]
BIOCAPS A-70	6		47	15	31	
BIOCAPS GP			30% mixed tocopherols			70[g]

[a]CoviOx-T50, CoviOx-T70, Copherol F1300, and Controx VP were manufactured by Cognis GmbH & Co. KG (Düsseldorf, Germany); DADEX TRC was from Daminco Inc. (New York, NY); BIOCAPS compounds were from Biocaps S.A. (Madrid, Spain).
[b]20–40% lecithin, 20–40% 6-*O*-palmitoyl-L-ascorbic acid (AP), and 5–10% citric acid esters of palm oil glycerides.
[c]2% AP, distilled MG, propylene glycol, citric acid, rosemary extract.
[d]17% AP, 25% rosemary extract, 15% lecithin.
[e]17% AP, 15% lecithin.
[f]AP.
[g]5% AP, 5% lecithin, 30% *n*-propyl gallate (PG), 30% excipient.

cation process was unrefined rapeseed oil. Undistilled used frying oil methyl ester (UU) was purchased from SEEG (Südsteirische Energie- und Eiweissgenossenschaft, Mureck, Austria). The frying oil was collected from households and restaurants. Two hundred liters of RU and of UU were distilled under reduced pressure at OMV (Vienna, Austria). Refined sunflower oil was purchased from a local supermarket and transesterified following a standard procedure (12). Distilled sunflower oil methyl ester was donated by Cognis (Boussens, France). Edible-grade tallow was purchased from a local slaughterhouse and was transesterified and distilled in the laboratory (see Table 3 for abbreviations of biodiesel samples). The biodiesel samples were analyzed according to the European draft specifications valid for FAME (2). FA composition was determined by GC using standard methods (13).

Antioxidants. TBHQ, BHT, BHA, pyrogallol (PY), *n*-propyl gallate (PG), 2-*tert*-butyl-4-methylphenol, and ethoxyquin were purchased from Sigma-Aldrich Handels GmbH (Vienna, Austria). 6-*O*-Palmitoyl-L-ascorbic acid was purchased from Merck GmbH (Vienna, Austria). Tenox 20 (mixture of 70% propylene glycol, 20% TBHQ, and 10% citric acid) was from Eastman-Kodak Co. (Köln, Germany), and Rendox ACP (mixture of propylene glycol, PG, BHA, and citric acid) was from Kemin Industries, Inc. (Des Moines, IA). Copherol F1300, Controx VP, CoviOx-T50, and CoviOx-T70 were gifts from Cognis GmbH & Co. KG (Düsseldorf, Germany). BIOCAPS ER, BIOCAPS LT, BIOCAPS PA, BIOCAPS A-70, and BIOCAPS GP were donated by Biocaps S.A. (Madrid, Spain). Characteristics of tocopherol-type antioxidants are listed in Table 1. Biodiesel samples were supplemented with 1000 ppm of antioxidant. For the most effective antioxidants, experiments at lower antioxidant concentrations (500, 250, and 100 ppm) were carried out. All chemicals and solvents used were of analytical grade unless otherwise specified.

Determination of thermal oxidation stability. The Model 743 Rancimat (Metrohm AG, Herisau, Switzerland) was used for measurements of thermal oxidation stability. Air flow was set at 10 L/h, and the temperature of the heating block was set at

TABLE 2
FA Composition of Biodiesel Samples[a]

FA	RU (% m/m)	RD (% m/m)	SU (% m/m)	SD (% m/m)	UU (% m/m)	UD (% m/m)	TU (% m/m)	TD (% m/m)
14:0	0.09	ND	ND	ND	0.41	0.27	2.20	2.84
16:0	5.95	2.05	5.98	7.22	14.38	11.55	21.88	25.61
16:1	ND	ND	ND	ND	0.39	0.34	1.57	2.11
18:0	2.07	2.61	4.66	4.20	4.26	4.43	17.03	21.95
18:1	60.34	62.20	23.95	27.40	57.17	58.04	45.12	37.61
18:2	20.87	21.05	63.74	61.18	17.08	19.18	8.05	4.71
18:3	8.15	7.90	ND	ND	2.08	2.25	1.09	0.58
20:0	0.61	1.02	0.29	ND	0.53	0.50	ND	ND
20:1	1.27	2.10	0.23	ND	0.88	0.92	ND	ND
22:0	0.34	0.55	0.77	ND	0.67	0.42	ND	ND
22:1	0.19	0.39	ND	ND	ND	0.21	ND	ND
Not identified	0.12	0.13	0.38	—	2.15	1.89	3.06	4.59

[a]Abbreviations: RU, rapeseed oil methyl ester; RD, distilled RU; SU sunflowerseed oil methyl ester; SD, distilled SU; UU, used frying oil methyl ester; UD, distilled UU; TU, beef tallow methyl ester; TD, distilled TU; ND, not detectable.

TABLE 3
Data from Analyses of Biodiesel Samples[a]

Parameter	Method[b]	Units	RU	RD	SU	SD	UU	UD	TU	TD	prEN 14214
Density at 15°C	EN ISO 3675	kg/m^3	879.9	881.9	883.6	882.9	880.9	880.2	875.6	872.3	860–900
Viscosity at 40°C	EN ISO 3104	mm^2/s	4.24	4.22	3.93	3.88	4.63	4.27	4.57	4.45	3.50–5.00
Flash point	DIN EN 22719[c]	°C	164	165	145	146	166	169	167	168	≥120
Sulfur content	DIN EN ISO 14596	mg/kg	4	2	2	1	8	3	9	3	≤10
Carbon residue of 100%	DIN EN ISO 10370[c]	%m/m	0.01	0.01	0.02	0.01	0.04	<0.005	0.01	<0.005	≤0.3[d]
Sulfated ash	ISO 3987	%m/m	0.006	0.001	0.002	0.002	0.002	0.001	0.006	0.005	≤0.02
Water content	EN ISO 12937	mg/kg	300	200	200	100	400	100	200	200	≤500
Total contamination	EN 12662	mg/kg	6	6	8	3	7	15	11	2	≤24
Acid value	prEN 14104	mg KOH/g	0.37	0.57	0.41	0.2	0.36	0.28	0.26	0.26	≤0.50
Oxidation stability	prEN 14112	h	9.1	3.4	3.4	1.2	5.9	3.5	1.2	0.4	≥6
Methanol content	prEN 14110	%m/m	0.04	ND	ND	ND	0.03	ND	ND	ND	≤0.20
Ester content	prEN 14103	%m/m	98.2	99.0	99.6	99.9	95.4	98.7	93.5	94.2	≥96.5
MG	prEN 14105	%m/m	ND	ND	0.02	0.006	0.165	ND	ND	ND	≤0.80
DG	prEN 14105	%m/m	ND	ND	0.038	ND	ND	ND	ND	ND	≤0.20
TG	prEN 14105	%m/m	ND	ND	ND	ND	ND	ND	ND	ND	≤0.20
Free glycerol	prEN 14105	%m/m	ND	0.0025	0.003	0.011	0.003	ND	ND	ND	≤0.02
Total glycerol	prEN 14105	%m/m	ND	0.0025	0.014	0.013	0.046	ND	ND	ND	≤0.25
Iodine value	prEN 14111	g I_2/100 g	112.9	112.5	124.4	125.7	88.7	90.2	55.8	44.1	≤120
Phosphorus content	pr EN 14107	mg/kg	1	<1	<1	<1	<1	<1	<1	<1	≤10
Alkaline metals (Na + K)	pr EN 14108 (Na) pr EN 14109 (K)	mg/kg	0.1 + 1.2	0.6 + 0.05	0.1 + 0.7	0.5 + 0.1	0.2 + 1.5	0.3 + 0.1	0.1 + 0.5	0.4 + 0.6	≤5

[a]For abbreviations see Table 2. [b]Reference 2 unless otherwise modified. [c]Reference 15. [d]Out of 10% distillate residue.

110°C. The temperature correction factor ΔT was set to 1.5°C as recommended by Metrohm. All determinations of induction period were performed in duplicate, and the mean value is reported. Variability of our determinations was ±2%. The effectiveness of all antioxidants was expressed as a stabilization factor,

$$F = IP_X / IP_0 \qquad [1]$$

where IP_X is the induction period in the presence of the antioxidant, and IP_0 is the induction period in the absence of the additive.

RESULTS AND DISCUSSION

For the studies of oxidation stability, 10 commercially available synthetic antioxidants and 10 mixtures of natural antioxidants were used. The natural products are mainly mixtures of different tocopherols dissolved in a carrier oil; the composition according to the producers is listed in Table 1. As biodiesel samples, four different products that will be widely used in Europe were tested. The feedstocks were rapeseed oil, sunflowerseed oil, used frying oil, and beef tallow. To investigate the effect of distillation, which should lead to the removal of natural antioxidants, all biodiesel samples were distilled. In Table 2 the FA composition of all biodiesel samples is listed. All eight biodiesel samples were analyzed according to the draft European specifications (Table 3). With a few exceptions, all biodiesel samples met the specifications. As expected, the sunflower oil samples have iodine values higher

TABLE 4
Influence of Antioxidants on Oxidation Stability of Undistilled Rapeseed Oil (RU) and of Undistilled Used Frying Oil Methyl Ester (UU)

Antioxidant[a,b]	RU induction period (h)	UU induction period (h)	F_{RU}	F_{UU}
Reference	9.15	5.92		
TBHQ	38.53	29.44	4.21	4.97
Propyl gallate	27.36	29.90	2.99	5.05
Pyrogallol	26.81	31.95	2.93	5.40
BHA	24.30	13.80	2.66	2.33
BIOCAPS GP	18.02	17.94	1.97	3.03
CoviOx-T50	10.88	11.48	1.19	1.94
Tenox 20	10.83	9.42	1.18	1.59
AP	10.61	4.91	1.16	0.83
2*t*-BHT	10.54	7.23	1.15	1.22
CoviOx-T70	10.46	12.46	1.14	2.10
Controx VP	10.32	10.81	1.13	1.83
BHT	9.85	10.84	1.08	1.83
Copherol 1300	9.82	6.77	1.07	1.14
Ethoxyquin	9.78	8.49	1.07	1.43
DADEX TRC	9.69	10.52	1.06	1.78
Rendox ACP	9.28	11.46	1.01	1.94
BIOCAPS A-70	8.54	10.16	0.93	1.72
BIOCAPS LT	8.42	6.42	0.92	1.08
BIOCAPS ER	8.38	6.17	0.92	1.04
BIOCAPS PA	7.40	6.51	0.81	1.10

[a]Antioxidant concentration was 1000 mg/kg for each assay.
[b]Tenox, Eastman-Kodak (Köln, Germany); for other manufacturers see Table 1. 2*t*-BHT, 2-*tert*-butyl-4-methylphenol; *F*, stabilization factor; for other abbreviation, see Table 1.

than 120. The ester contents of the undistilled used frying oil sample and the tallow samples were slightly under the limit, which can be explained by the content of polymers in the used frying oil sample. In the tallow samples there may have been higher amounts of unsaponifiables. Concerning the oxidation stability, which is limited with a minimum induction period of at least 6 h at 110°C, only the undistilled rapeseed oil sample has an induction period higher than the limit. Distillation of the sample lowered the induction period from 9.1 h to 3.4 h. All other samples showed induction periods lower than 6 h, so in the future it will be necessary to use antioxidants to meet the specifications.

In a first screening, all antioxidants were tested in biodiesel from RU and UU at a concentration of 1000 mg/kg to evaluate the most effective products. In Table 4 the values of the induction periods, as well as the calculated stabilization factors, *F,* are listed according to their effectiveness. In both biodiesel samples, PY, PG, and TBHQ were the most effective antioxidants, leading to *F* from 2.93 to 5.40, meaning that the induction period was increased by these factors. Among the natural antioxidants, BIOCAPS GP seems to be the most effective, but it should be noted that the product also contains about 30% PG.

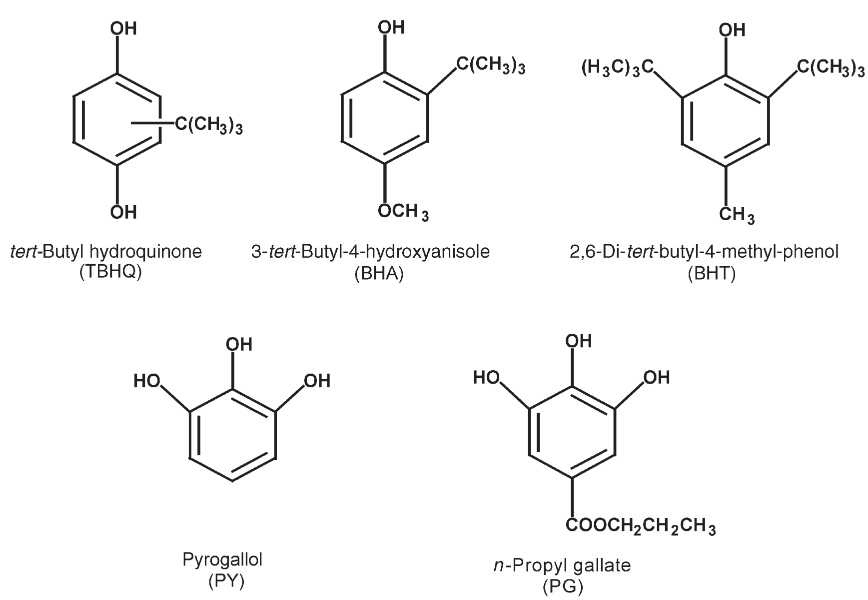
For further study of the dependence of antioxidant concentration on the other biodiesel samples, the four most effective antioxidants were selected. Furthermore, BHT was used because this antioxidant is easily available, is well known in the mineral oil industry, and is said to be used in biodiesel fleet tests in Germany. Scheme 1 shows the formulas and chemical names of these five compounds. The antioxidants were added to the biodiesel samples in concentrations between 100 and 1000 mg/kg, and the corresponding induction periods were measured with the Rancimat instrument. The goal of the measurements was to find the optimal antioxidant for each feedstock and to determine the corresponding antioxidant concentration that leads to an induction period of at least 10 h, which should be sufficient for meeting the specification for the oxidation stability for a longer storage time.

In Figure 1A,B the results of measurements with the rapeseed oil samples are shown. With the undistilled sample, PG and PY produced the best results; each one doubled the induction period when present at 250 mg/kg. In the distilled sample the best results were achieved with PY and BHA at lower concentrations, and there was an almost linear improvement with increasing PG concentration. BHT had almost no effect, whereas TBHQ showed good results only in the undistilled sample. The great difference between distilled and undistilled samples can be explained by the removal of natural antioxidants during distillation. This is in accordance with the observations of Mittelbach and Gangl (8), who observed very poor oxidation stability with distilled biodiesel samples.

Both used frying oil samples had a low oxidation stability without antioxidants. Significant improvement could be achieved with the addition of PY and PG, but TBHQ also was quite efficient (Fig. 2). Even at a concentration of 1000 mg/kg, BHT did not lead to values over 10 h. BHA had a slightly better effect than BHT.

The undistilled sunflower oil sample showed good effects with PY and PG at a concentration of 1000 mg/kg, whereas the other products were not sufficiently effective (Fig. 3A). The relatively poor improvement of oxidation stability with all antioxidants can be explained by the higher concentration of linoleic acid, which is less stable toward oxidation than oleic acid. These results are in accordance with findings from Niklová *et al.* (14), who studied the effect of natural and synthetic antioxidants on oxidation stability of sunflower and rapeseed oil. With the distilled sunflower oil sample, even antioxidant concentrations of 1000 ppm did not lead to an induction period of 10 h (Fig. 3B).

Obviously, because of low concentrations of natural



SCHEME 1

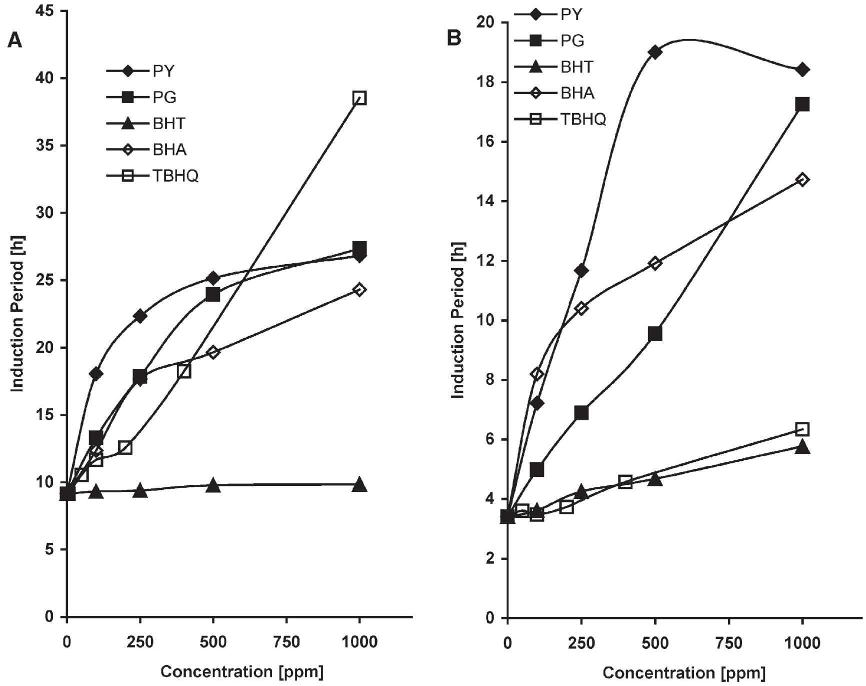


FIG. 1. Influence of antioxidant concentration on the oxidation stability of rapeseed oil methyl esters: (A) undistilled; (B) distilled. PY, pyrogallol; PG, *n*-propyl gallate.

antioxidants, both tallow methyl ester samples showed very poor oxidation stability (Fig. 4A,B). With the undistilled sample, PY showed the best improvement, leading to induction periods of over 20 h at a concentration over 500 mg/kg; the other antioxidants led to significantly lower induction periods, hardly reaching 10 h. Surprisingly, PG showed a far better effect on the distilled sample, leading to induction periods of over 50 h; BHA and BHT were not very effective. The relative ineffectiveness of BHT in most of the experiments was surprising, because this substance is commonly used for many types of food and nonfood products. In prior investigations it was found that BHT may disappear during measurements due to its relatively high volatility, especially at a measuring temperature of 110°C.

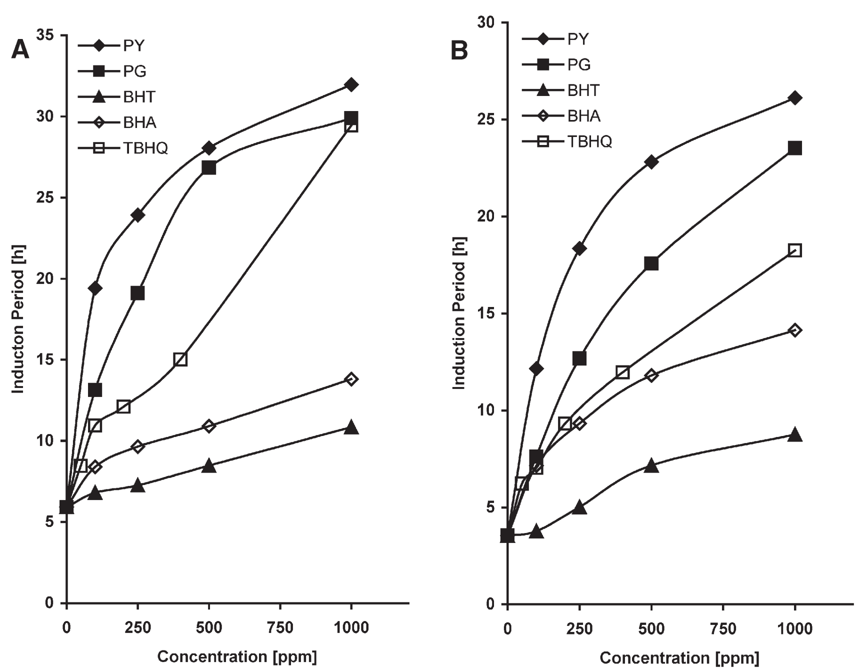


FIG. 2. Influence of antioxidant concentration on the oxidation stability of used frying oil methyl esters: (A) undistilled; (B) distilled. For abbreviations see Figure 1.

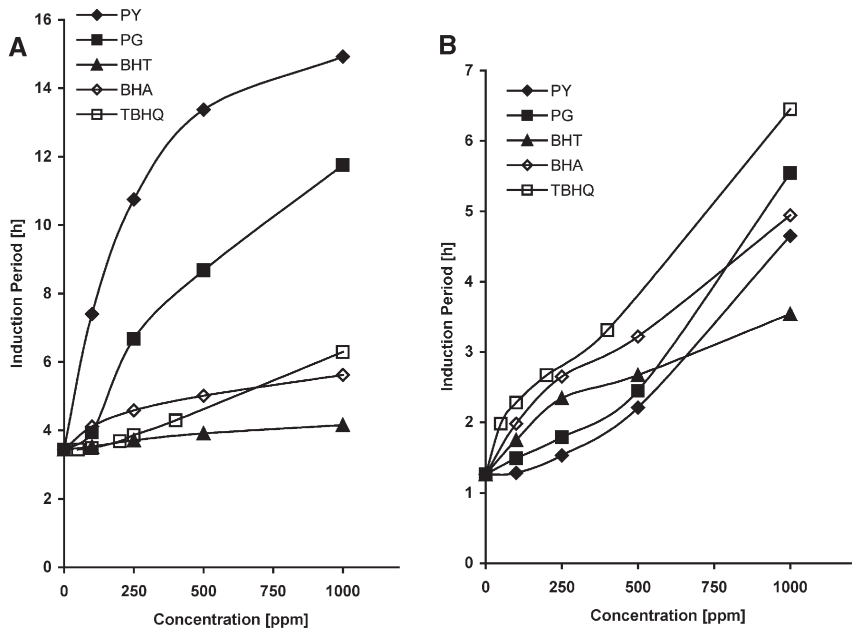


FIG. 3. Influence of antioxidant concentration on the oxidation stability of sunflowerseed oil methyl esters: (A) undistilled; (B) distilled.

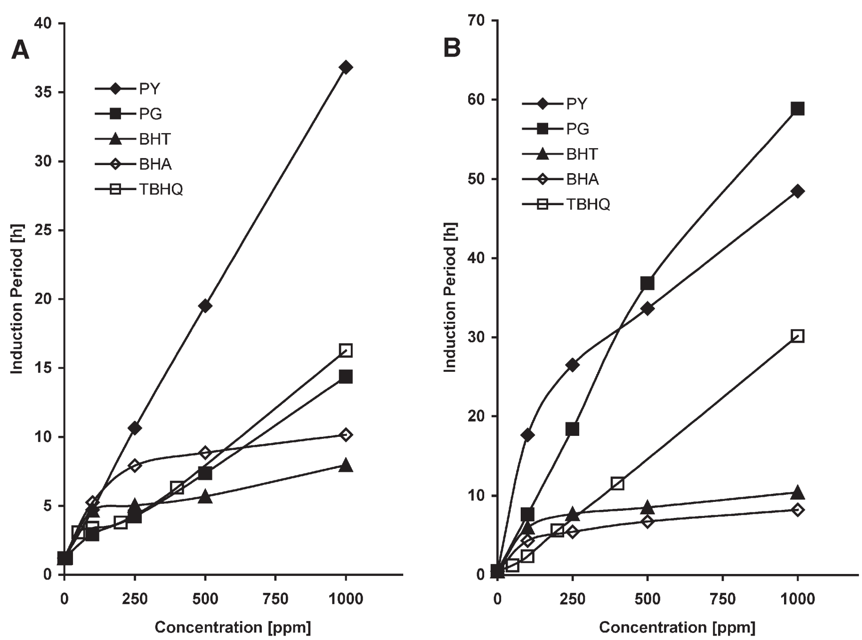


FIG. 4. Influence of antioxidant concentration on the oxidation stability of tallow methyl esters: (A) undistilled; (B) distilled.

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