☘Stability Studies on Methyl and Ethyl Fatty Acid Esters of Sunflowerseed Oil

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ABSTRACT

Fatty acid esters, high in linoleic acid, were prepared and stored for long-term engine tests. Storage tests with these esters were undertaken to obtain more information on optimal storage requirements and general stability characteristics.

Samples were kept at three temperature levels (20 C, 30 C and fluctuating around 50 C) for a 90-day period and were removed at regular intervals for chemical and physical analysis. The influence of air, temperature, light, TBHQ and contact with mild steel was evaluated by comparing the free fatty acid, peroxide, anisidine, ultraviolet absorption, viscosity and induction periods. A statistical model was used to evaluate the data and to reduce the large number of data points to comparable curves.

Storage of esters in contact with air, especially at a temperature above 30 C, resulted in significant increases in peroxide, ultraviolet absorption, free fatty acid, viscosity and anisidine values. Exclusion of air retarded oxidation at all temperature levels.

A direct relationship between viscosity increases and oxidation parameters was evident. Exposure to light caused a small increase in the oxidation parameters of esters stored at the highest temperature level. Addition of TBHQ prevented oxidation of samples stored under moderate conditions. Under unfavorable storage conditions the anti-oxidant was no longer effective. Mild steel had very little effect on the oxidation parameters. Only the anisidine values of samples stored at the highest temperature level were slightly increased. Methyl esters performed slightly better than ethyl esters during the storage test.

The following practical guidelines for storage of fatty acid ester fuels are: (i) airtight containers should be used; (ii) the storage temperature should be <30 C; (iii) mild steel (rust free) containers may be used, and (iv) TBHQ has a beneficial effect on oxidation stability.

INTRODUCTION

Experimental fuels made from the fatty acid esters of sunflowerseed oils were used in long-term tests with diesel engines (1). The test fuels were prepared in batches of 1,000 l (2,3), and it was essential to store the ester fuels under favorable conditions preventing major chemical changes. It is known that linoleic acid, the main component of sunflowerseed oil, is relatively unstable, and it was suggested that storage requirements for fatty acid esters could be different from those used for plant oils (4,5). It was found that the induction period for sunflowerseed oil fatty acid esters was one-third that of the starting sunflowerseed oil (6). It also was shown that the induction periods of ethyl and methyl fatty acid esters differ (7), and that methyl esters were slightly more stable than ethyl esters. Similar differences in stabilities based on pyrolysis studies were reported (5). Treatment of the esters with tertiary butylhydroquinone (TBHQ) improved the induction periods significantly (7).

In the present investigation fuel esters were stored for a 90-day period under conditions likely to be experienced in practice. Three different temperature levels were selected and attempts were made to measure the influence of air, light, contact with mild steel (containers) and synthetic anti-oxidant (TBHQ).

EXPERIMENTAL PROCEDURES

Materials

Degummed sunflowerseed oil was used for the preparation of the esters. Containers were made of clear and amber glass, equipped with screw caps and seals. Mild steel (cold rolled commercial quality) strips, 75 × 20 × 0.5 mm, were cut to fit into the glass containers. Ethyl and methyl alcohols were of AR grade, and the sodium hydroxide was of CP grade (supplied by E. Merck, Darmstadt). TBHQ was of industrial grade and supplied by Eastman Chemical International, Zug, Switzerland.

Methods

Esters were prepared by alkali catalysis (0.5% sodium hydroxide based on oil). Details on the preparation and purification of the esters are published elsewhere (2,3).

The ester and alcohol contents of the original esters were determined by gas chromatography. A Perkin-Elmer Sigma 3 instrument, equipped with a glass column (2m × 2mm) packed with DEGS stationary phase (12.5% DEGS on Chromosorb W) was used. Moisture levels were determined with a Karl Fischer 652 Coulometer. Ashing of samples were conducted at a temperature of 520 C, and the minerals were determined by flame atomic absorption spectroscopy (Perkin-Elmer 305B instrument). Phosphorus was determined by a spectrophotometric procedure (8).

Free fatty acid values were determined by titration with dilute potassium hydroxide (9), peroxide values were determined according to the ISO method (10) and anisidine values as described (11). Ultraviolet absorption was recorded at 232 nm as described by Hadorn (12) and viscosity measured at 38.8 C with a Zeitfuchs capillary viscometer (centistokes).

Storage tests on the methyl and ethyl fatty acid esters were conducted for 90 days with six different experimental treatments at three different temperature levels (20 C, 30 C and fluctuating around 50 C) (~50 C). Quality measurements were done on ester samples at six intervals viz. 0, 10, 24, 38, 58 and 90 days. Details of the experimental treatments are given in Table I.

Statistical Analysis

The data were analyzed by means of time-response curves, and the significance of the effects of the various experimental factors was assessed on the basis of appropriate contrasts of these curves. A natural logarithmic transformation of response (y) of the form z = ln(y) was introduced in order to stabilize the error variance in the responses. In view of the vast number of different time-response curves involved

TABLE I

Experimental Treatments Used at Each Temperature Level

Code	Sample container	Exposed to:
B	amber glass	–
W	clear glass	light
S	amber glass	steel*
T	amber glass	steel + TBHQ**
O	amber glass	air + steel
OT	amber glass	air + steel + TBHQ

*Mild steel.

**Industrial grade TBHQ, 0.04%.

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(187 curves on 1122 observations), some form of data reduction was deemed necessary in order to obtain a comprehensible and concise representation of the results. Each combination of variable and storage temperature level involved 12 response-time curves on 72 data points (36 curves per variable), and it is obvious that graphic representation in this unreduced form will be virtually impossible to digest.

For each ester × variable combination the desired simplification was achieved by:

1. Fitting a mathematical model which incorporates auxiliary ("dummy") variables to express the parameters of the basic time-response curve as functions of the treatment effects.
2. Applying a stepwise backward elimination process to the model in order to eliminate treatment terms that do not contribute significantly to the regression.

Graphic representation of the reduced model is feasible, because only those curves that display significant treatment effects feature in the model as different entities.

In terms of the transformed response z the model is of the form:

$$z_j = a + b_j t + c_j t^2 \qquad [1]$$

where t = storage time (days); j = 1, 2, 3 identifies the storage temperature, and the regression parameters b_j and c_j (j = 1, 2, 3) are functions of the experimental treatment effects. In terms of four auxiliary variables (W, S, T and O) we may express each of these parameters in the forms:

$$b_j = \beta_{1j} + \beta_{2j}W + \beta_{3j}S + \beta_{4j}T + \beta_{5j}O + \beta_{6j}O.T \qquad [2]$$

and $$c_j = \gamma_{1j} + \gamma_{2j}W + \gamma_{3j}S + \gamma_{4j}T + \gamma_{5j}O + \gamma_{6j}O.T \qquad [3]$$

where the auxiliary variables are all identically equal to zero unless:

i) The glass container is transparent, then W = 1.
ii) Steel has been added, then S = 1.
iii) TBHQ has been added, then T = 1.
iv) The contents are exposed to air, then O = 1.

The regression constant a in equation [1] represents the common initial value of z at time t = 0.

For any given level j of storage temperature, the parameter pairs (β_{ij}, γ_{ij}; i = 2,. . .6) represent the effects of treatments W, S, T, O and O × T on the regression constants pertaining to the control treatment B (β_{ij} and γ_{ij}).

The model defined in equations [1] to [3] applies to all variables monitored except induction period, where the initial value a may be affected by the addition of TBHQ. To make provision for this possibility the model is modified by introducing the relationship:

$$a = a_0 + a_1 T \qquad [4]$$

so that the initial values $a = a_0$ when TBHQ is absent and $a = a_0 + a_1$ when TBHQ is present.

A simultaneous 10% level of significance was maintained in the backward elimination process by employing Aitken's (13) criterion for a "R^2-minimal adequate model."

In each case the reduced ("minimal adequate") model is represented in graphic form on three adjacent axes (one for each level of storage temperature). The curves are plotted as $y = \exp(a + bt + ct^2)$ against t and the symbols B, W, S, T and OT are used to identify the various treatments at each level of storage temperature.

Curve B which corresponds to the amber glass control treatment is always represented. If $\beta_{ij} = \gamma_{ij} = 0$, at temperature level j, the curve runs parallel to the time axis, indicating that the values are not significantly affected by storage time per se. Curves W, S, T and O will be represented if the corresponding treatment effects $W' = W - B$, $S' = S - B$, $T' = T - S$ and $O' = O - S$ differ significantly from zero. (Symbolic representation - on a log scale O - S represents the vertical distance between curves O and S.)

This means that curves W and S are represented if they differ from B (β_{2j} and/or γ_{2j} as well as β_{3j} and/or γ_{3j} have not been constrained to zero during the elimination process). Similarly, curves T and/or O are represented if they differ from S. Curve OT is represented if it differs from both O and T (i.e., if there is a significant O × T interaction effect or if both O′ and T′ differ from zero. Symbolically $OT = S + O' + T' + OT'$).

Note that direct comparison of treatment B with O and T is made only in the absence of S effects ($S' = O'$). Similarly, direct comparison of OT with S is made only in the absence of both T and O curves. Therefore, curves that virtually coincide may both be represented if the effects of O and S are neutralized by TBHQ. For example, if we assume that the only significant effects are O′ and OT′, and that $O' \cong -OT'$ at every time point, then curve O as well as the coinciding B and OT curves will be represented.

RESULTS AND DISCUSSION

Effect of Storage on Acid Values

The changes in acid values of methyl and ethyl esters are

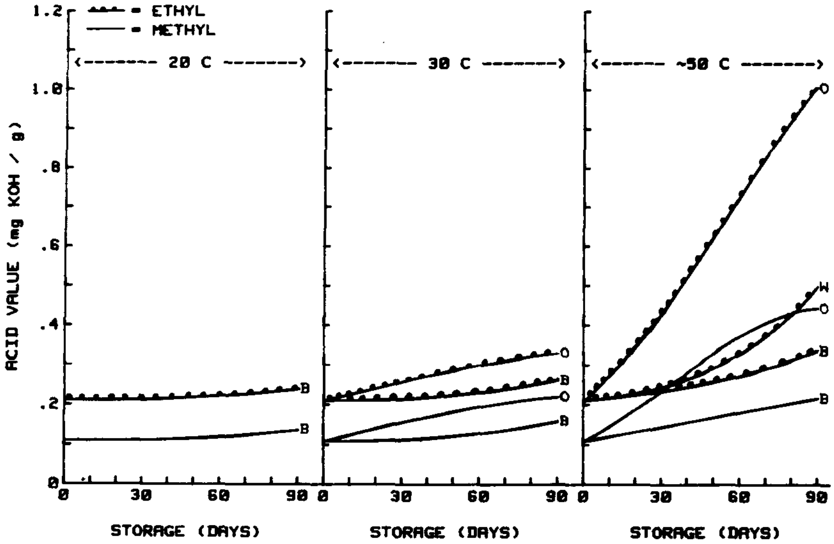

FIG. 1. The influence of storage on the acid values of fatty acid esters.

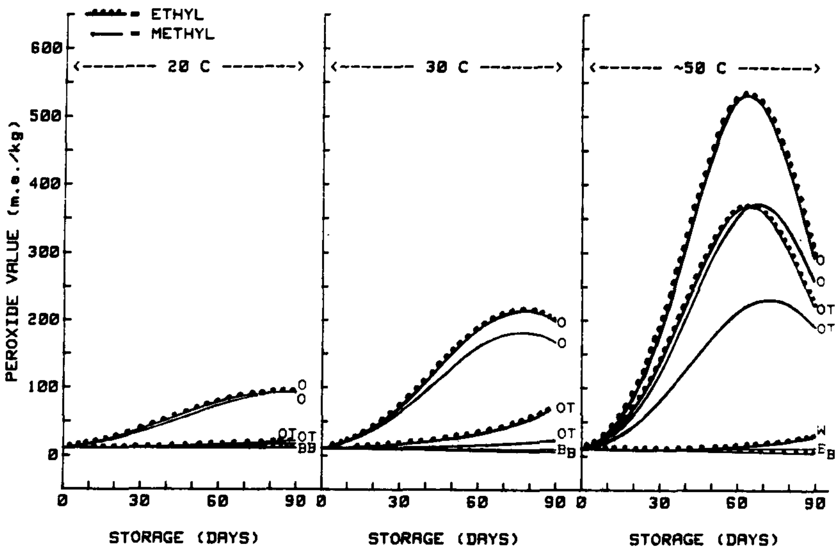

FIG. 2. The effect of storage on the peroxide values of fatty acid esters.

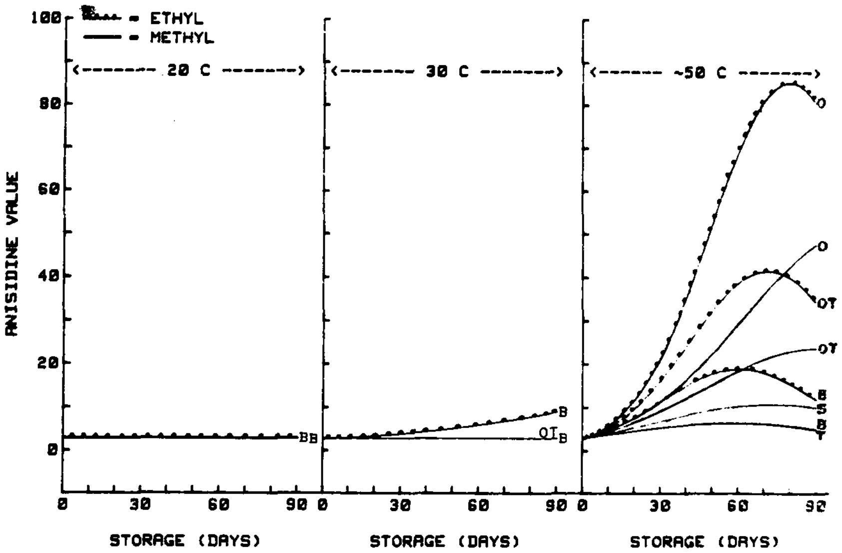

FIG. 3. The effect of storage on the anisidine values of fatty acid esters.

given in Figure 1. The two curves B and B' for methyl and ethyl esters at temperature level 20 C indicate a very slight change with time. The single B curve means that there is no significant difference between the different treatments described in Table I.

At 30 C a moderate increase for all treatments is shown. However, in the case of esters exposed to air (curves O and O'), a more pronounced increase is indicated.

The highest temperature level (~50 C) resulted in moderate increases for all sample treatments (B and B' curves) with the exception of samples exposed to air (curves O and O') and ethyl esters exposed to light (W' curve), which increased sharply.

Effect of Storage on Peroxide Values

Exposure to air (O-curves) resulted in moderate increases in peroxide values at 20 C, sharp increases at 30 C and very sharp increases at ~50 C (Fig. 2).

By addition of TBHQ (OT-curves) at a 0.04% concentration peroxide formation at 20 C could be controlled. However, at 30 C and especially at ~50 C TBHQ was ineffective.

Exposure to light (W' curve) at ~50 C affected only the ethyl esters.

Effect of Storage on Anisidine Values

Exposure to air (O-curves) at 20 C and 30 C had very little effect on the anisidine value of all sample treatments. At the higher temperature (~50 C), the values increased sharply (Fig. 3).

Addition of TBHQ (OT-curves) controlled the anisidine values of samples stored at ~50 C.

Steel had a very slight influence on the anisidine values of all samples; only methyl esters, at ~50 C, were affected significantly.

Effect of Storage on Ultraviolet (UV) Absorption

Exposure to air (O-curves) was responsible for increases in the UV absorption. A moderate increase at 20 C, a sharp increase at 30 C and a very sharp increase at ~50 C were recorded (Fig. 4).

TBHQ was effective in preventing the formation of UV-absorbing conjugated dienes under the 20 C condition, only partially effective at the 30 C and ineffective at the higher temperature.

Exposure to light (W'-curve) under the ~50 C condition caused higher UV absorption of the ethyl esters (Fig. 4).

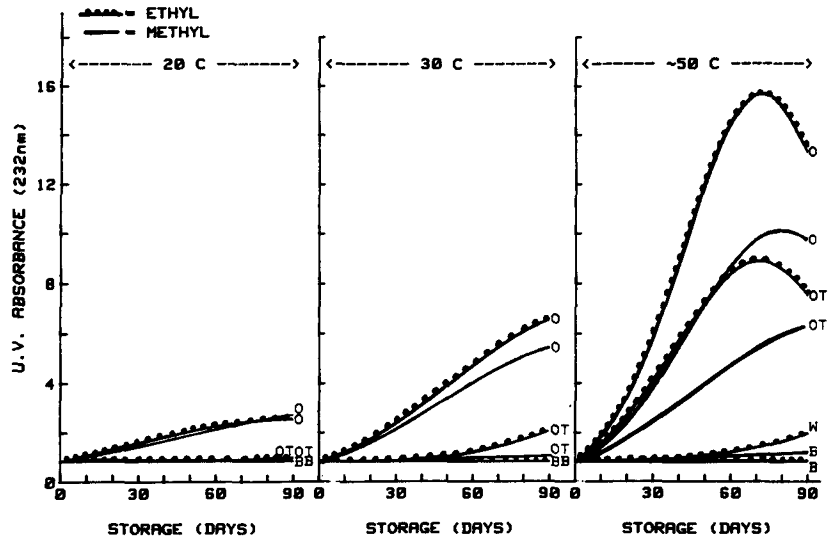

FIG. 4. The effect of storage on the UV-absorption (232 nm) of fatty acid esters.

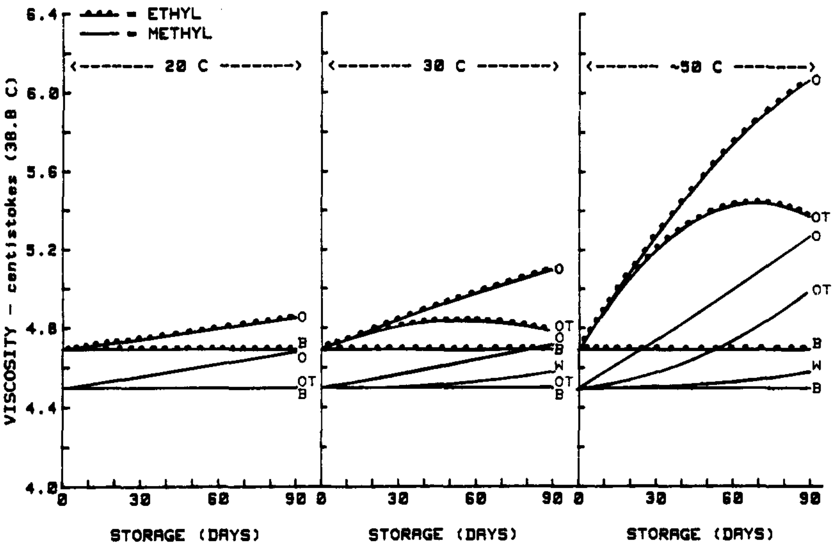

FIG. 5. The influence of storage on the viscosity of fatty acid esters.

Effect of Storage on Viscosity

The curves in Figure 5 show that viscosity measurements reflect the oxidation condition of the esters. Viscosity increased at all three temperature levels. Ethyl esters were more affected by air oxidation than methyl esters, and viscosity changes were therefore in line with the previously discussed chemical changes.

TBHQ prevented viscosity changes under the 20 C and 30 C conditions (OT and B-curves), but it failed under the ~50 C condition.

The viscosity of methyl esters was slightly affected by exposure to light (W-curve).

Effect of Storage on Induction Periods

Induction periods of esters that were sampled after different storage intervals were determined with the Rancimat instrument. Only methyl esters were analyzed and only three experimental treatments were included, viz. exposure to air, addition of TBHQ and contact with steel.

Exposure to air (O-curves) reduced the induction periods of esters at all three temperature levels (Fig. 6). Storage of esters at higher temperatures resulted in drastic decreases in induction periods. In the case of esters stored in closed containers, with and without steel strips (S-curves and B-curves respectively), no significant decrease in the induction periods occurred.

The effect of TBHQ (T-curve) on esters in closed containers was similar to that previously reported (7). The induction period of the treated esters was approximately four times longer than that of untreated esters. Addition of TBHQ to esters kept in open containers delayed their decomposition significantly. As previously shown (7), higher levels of TBHQ (0.1 to 0.3% added) should increase the induction periods even more and delay the oxidation process.

The influence of air was the outstanding treatment effect evident in Figures 1 to 6. Contact with air caused higher viscosity values at all three temperature levels. Exclusion of air or oxygen during storage should limit oxidation and related physical changes.

This study also confirms our previous findings (7) regarding the differences in stability of methyl and ethyl esters. Our results are verified by other reports (5) that confirm thermal stability differences between the two ester types. It is possible that the small differences in acid values and tocopherol contents of the original esters (Table II) could contribute to some extent to the stability differences.

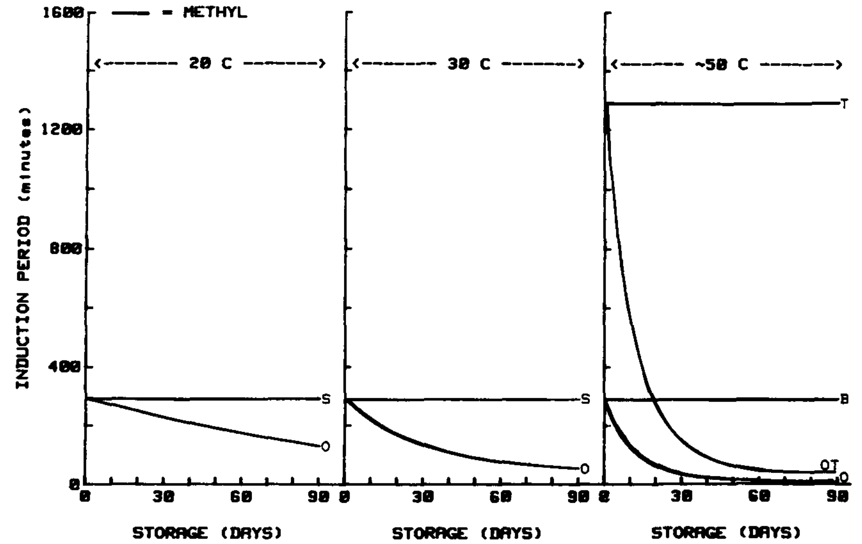

FIG. 6. The influence of storage on the induction periods (Rancimat instrument) of fatty acid methyl esters.

TABLE II

Chemical and Physical Characteristics of the Original Sunflowerseed Fatty Acid Esters

	Methyl esters	Ethyl esters
Ester content (%)	95.5	92.0
Moisture (%)	0.078	0.065
Residual alcohol (%)	<0.1	<0.5
Minerals (ppm)		
Na	2.5	2.0
P	0.4	1.0
Cu	0.1	0.1
Fe	0.5	0.2
Zn	0.1	0.1
Total ash (%)	<0.001	<0.001
Acid value (mg KOH/g)	0.11	0.22
Peroxide value (me/kg)	12.0	11.0
UV absorption (232 nm)	0.73	0.71
Anisidine value	3.77	3.49
Viscosity (cSt)	4.44	4.77
Tocopherols (mg/100g)	61.5	55.6
Induction periods (minutes)	394	203

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