Oxidation Stability of Methyl Esters Studied by Differential Thermal Analysis and Rancimat

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ABSTRACT: The oxidation stability of methyl esters derived from fresh rapeseed oil and waste frying oil, used as alternative biodiesel fuels, both distilled and undistilled, unstabilized and stabilized by pyrogallol and BHT, was studied by differential thermal analysis (DTA) under nonisothermal conditions at various heating rates and by the Rancimat test under isothermal conditions at 110°C. The results obtained by both techniques are compared. Both techniques show that oxidation stability increases considerably with the addition of antioxidants and that pyrogallol is very efficient. Distillation of the methyl esters prepared from rapeseed oil decreases their oxidation stability, obviously owing to the removal of natural antioxidants. The stability of methyl esters prepared from the waste frying oil is determined mainly by the history of the oil. From the DTA measurements, the kinetic parameters of an Arrhenius-like equation describing the temperature dependence of the oxidation induction period were obtained. The parameters enable one to assess the protective factor of antioxidants for temperatures outside the measuring region, estimate the residual stability, and model the process of biodiesel oxidation under nonisothermal conditions.

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KEY WORDS: Antioxidants, biodiesel fuels, differential thermal analysis, kinetics, methyl esters, oxidation induction period, Rancimat test.

Methyl esters of higher FA, prepared from vegetable oils and animal fats by alkali-catalyzed transesterification with methanol, are presently considered as alternative biofuels for diesel engines. The properties of methyl esters are close to those of the fossil diesel fuel and can be mixed with it at any ratio. Methyl esters can be produced from domestic and renewable sources, are fully biodegradable, and contain no sulfur; their exhaust gases contain much less soot and polycyclic aromatic hydrocarbons compared with the fossil diesel. A wider commercial use of this commodity is hindered mainly by the high price of input oil/fat. The use of waste cooking oil instead of virgin oil to produce biofuels is a way to reduce the raw material costs because it is estimated to be about half the price of virgin oil (1). In addition, using the waste cooking oil could also help to solve the problem of waste oil disposal. Several recent papers (1–3) dealt with differences in methyl esters prepared from waste and fresh oils/fats.

The quality of methyl esters used as diesel fuel is designated by several standards; in the European Union, the standard is EN 14214 (4). The oxidation stability is among the monitored parameters. To estimate the stability, the sample is usually subjected to an accelerated oxidation test under standardized conditions, where heating is the most common means of accelerating the oxidation.

Oxidation in the condensed phase exhibits an induction period (IP), which precedes the main oxidation process. The existence of the reactions occurring during the IP is not detected by the experimental technique used so that seemingly no reaction takes place. In fact, IP is a preparatory stage in which the entities needed for the full development of autooxidation are formed. The length of the IP is considered a relative measure of the stability of materials. It is reported as the time of a sudden increase in the rate of oxidation (5–7). Within the European specifications, the IP for methyl esters, measured by using the Rancimat instrument, should be longer than 6 h at 110°C under air. The Rancimat test, EN 14112 (8), is a prescribed method for evaluating the oxidation stability of methyl esters as alternative diesel fuels. For isothermal measurements by thermoanalytical techniques, such as differential thermal analysis (DTA) or DSC, the IP measured at a constant temperature is often called the oxidation induction time (OIT).

Oxidation is an exothermic process, and the reaction heat evolved makes it possible to use DSC or DTA for its study. Surprisingly, we have encountered only a few papers dealing with DSC or DTA study of the oxidation of oils or fats (9–14). To our knowledge, no paper has been published on the thermoanalytical study of biodiesel fuels. Thermoanalytical methods are generally very efficient in the study of oxidation stability (15). That these methods are not used more widely for oils and fats probably is due to the fact that in isothermal tests, mainly at lower temperatures, the exothermic peak of oxidation is flat and its onset, corresponding to the end of the IP, cannot be determined unambiguously. When studying oxidation at various heating rates, we realized that, contrary to the isothermal measurements, the oxidation peak is distinct in these nonisothermal measurements and the onset temperature can be read accurately and unambiguously. Hence, a new method has been proposed for obtaining the kinetic parameters of the IP from the oxidation onset temperatures (OOT) of nonisothermal runs with a linear increase of temperature (16–18).

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The aim of this paper is to study the thermooxidative behavior of two kinds of methyl esters, both distilled and undistilled, stabilized and unstabilized, by using DTA. For the stabilization, two antioxidants are used: (i) pyrogallol (PY), which is a commonly used and inexpensive product, and (ii) *t*-butylhydroxytoluene (BHT), which is often used in the chemistry of oils/fats. The results obtained by DTA are compared with the oxidation stability tests measured by Rancimat 679 under isothermal conditions.

EXPERIMENTAL PROCEDURES

Materials. Four basic samples of methyl esters were studied: (i) Methyl esters based on crude cold-pressed rapeseed oil prepared by alkali-catalyzed transesterification with methanol (19) after a final treatment comprising the removal of unreacted methanol, washing with water, and drying. These esters were denominated as MERO undistilled. The acid number of the input oil was 2.6 mg KOH/g; water content, 0.06 wt%; conversion of the acylglycerols to methyl esters, 98.5 %. (ii) The same methyl esters as in point (i) distilled in a molecular evaporator with a wiped film (20), termed MERO distilled. Distillation parameters were: temperature 140°C, pressure 5 Pa, distillate acid number 0.07 mg KOH/g, yield 97%. (iii) Methyl esters based on waste frying oil/fat, prepared by alkali-catalyzed transesterification with methanol after the final treatment as in point (i), denominated as MEFRIT undistilled. The acid number of the input oil was 1.6 mg KOH/g, conversion was 99.0%. (iv) Methyl esters as in point (iii) distilled in a molecular evaporator with wiped film, marked as MEFRIT distilled. Distillation parameters were: temperature 140°C, pressure 5 Pa, yield 96%. The FA profiles of the methyl esters are listed in Table 1. Distilled and undistilled MERO and MEFRIT samples were stabilized by adding PY and BHT.

Methods. Two techniques were used to evaluate the oxidation stability of the samples: (i) Simultaneous DTA/thermogravimeter Shimadzu DTG-60. The temperature scale was calibrated using In and Zn standards. Samples of 2–3 mg were placed in open standard aluminum pans. The purge gas, also forming the oxidation atmosphere, was oxygen at a flow rate of 50 mL/min. The measurements were carried out in the temperature range 50–300°C with heating rates of 1.5, 3, 5, 7, 10, and 15 K/min. (ii) RANCIMAT 679 Metrohm (Herisau, Switzerland). The kinetics of oxidation was followed by the increase in conductivity at a constant volume under isothermal conditions at 110°C. The oxidation medium was air, and the flow rate was 20 L/h. The sample size was 3 g. Six parallel measurements were carried out for each sample.

A Hewlett-Packard 5890 series II gas–liquid chromatograph, equipped with FID and a glass column 1.4 m × 3 mm i.d. packed with 10% diethylene glycol adipate on 0.125–0.16 mm Chromatone NAW DMCS (Lachema, Brno, Czech Republic), was used for the determination of the FA profiles. Nitrogen was used as a carrier gas at a flow rate of 30 mL min^{-1}. The oven temperature was kept constant at 200°C; the injector and detector temperatures were 230 and 250°C, respectively.

Treatment of DTA experimental data. The dependence of the OIT, t_i, on temperature can be expressed by an Arrhenius-like relationship (16,17):

$$t_i = A \exp (B/T) \qquad [1]$$

where A and B are constants and T is the absolute temperature. According to the method recently developed in our laboratory (16,17), the parameters A and B in Equation 1 can be obtained from Equation 2 for a set of runs with a linear increase of temperature:

$$\beta = \int_0^{T_i} \frac{\mathrm{d}T}{A \exp (B/T)} \qquad [2]$$

where T_i is the temperature corresponding to the end of the IP, i.e., the OOT. From the nonisothermal measurements, the kinetic parameters A and B in Equation 2 were obtained by minimizing the sum of squares between the experimental and theoretical values of onset temperatures for various heating rates by the simplex method (21). The integration indicated in Equation 2 was carried out by the Simpson method. The SD of A and B are calculated by assuming a quadratic surface near the minimum (21).

OIT and OOT are interrelated: The links between them are the parameters A and B. The denominator in the integral term at the right side of Equation 2 is equal to OIT expressed by Equation 1. Hence, when obtaining the parameters A and B from the dependence of OOT on heating rate using Equation 2, the value of OIT for a chosen temperature can be calculated.

RESULTS AND DISCUSSION

An example of the simultaneous DTA/thermogravimetric analysis record with linear heating of the sample is shown in

TABLE 1
FA Profiles of the Methyl Esters[a] Under Study (GLC area %)

FA	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
MERO undist.	4.8	0	1.4	66.8	19.7	7.2
MERO dist.	5.4	0	1.1	66.9	19.3	7.2
MEFRIT undist.	8.4	0.2	2.4	69.6	15.5	2.9
MEFRIT dist.	9.0	0.2	2.6	71.4	11.3	1.7

[a] MERO, methyl esters based on crude cold-pressed rapeseed oil prepared by alkali-catalyzed transesterification with methanol; MEFRIT, methyl esters based on waste frying oil/fat prepared by alkali-catalyzed transesterification with methanol; undist., undistilled; dist., distilled.

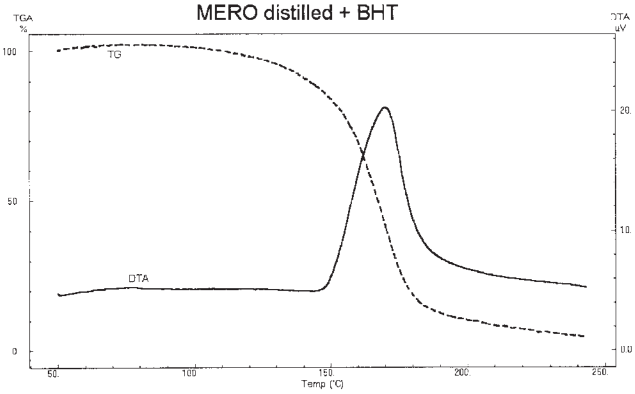

FIG. 1. Simultaneous DTA/TG record of the oxidation of the sample MERO distilled, stabilized with BHT, heating rate 1.5 K/min, oxygen atmosphere. DTA, differential thermal analysis; TG, thermogravimetry; MERO, methyl esters based on crude cold-pressed rapeseed oil prepared by alkali-catalyzed transesterification with methanol.

Figure 1. In the range of 50–250°C, the oxidation of methyl esters occurs in one stage. At the OOT, up to 10% of the sample evaporates. This was why we chose oxygen as an oxidation medium instead of air for the DTA studies. In the air atmosphere, the OOT are shifted toward higher values and, consequently, a greater part of the sample evaporates before the onset of oxidation is reached.

First of all, we tested the dependence of the DTA OOT on the concentration of antioxidants. The dependence for MEFRIT distilled is shown in Figure 2; the dependences for the other methyl esters are similar (data not shown). In the concentration range 0.01–0.1 wt%, OOT increases monotonically so that there exists no optimum antioxidant concentration leading to the maximum stability. The stability of the samples increases monotononically with increasing antioxidant content. In the entire concentration range, the curve for PY is well above the one for BHT, which indicates that PY is a much more efficient antioxidant. For further study we chose the concentrations 0.05 wt% for BHT and 0.04 wt% for PY. These concentrations mostly suffice to meet the requirement of the standard EN 14214 (4) for the oxidation stability of biodiesel. Moreover, these weight concentrations represent approximately the same molar concentrations, i.e., about 3.2×10^{-3} mol dm^{-3} ($M_{\mathrm{BHT}} = 150.2$ g/mol, $M_{\mathrm{PY}} = 126.1$ g/mol).

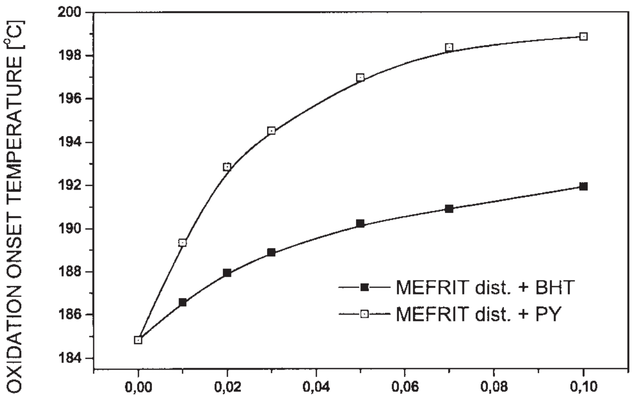

FIG. 2. Dependence of the onset oxidation temperature on the antioxidant concentration for the sample MEFRIT distilled, heating rate 10 K/min. MEFRIT, methyl esters based on waste frying oil/fat prepared by alkali-catalyzed transesterification with methanol; PY, pyrogallol; dist., distillled.

TABLE 2
Kinetic Parameters A and B and Their SD[a]

Sample	$10^9 \times A$ (min)	B (K)
MERO dist.	160 ± 16	7690 ± 40
MERO dist. + BHT	45.9 ± 7.2	8160 ± 60
MERO dist. + PY	0.804 ± 0.076	10200 ± 40
MERO undist.	197 ± 26	7590 ± 50
MERO undist. + BHT	8.26 ± 0.06	9060 ± 30
MERO undist. + PY	0.172 ± 0.021	10930 ± 50
MEFRIT dist.	9580 ± 1600	5830 ± 60
MEFRIT dist. + BHT	2400 ± 290	6530 ± 50
MEFRIT dist. + PY	100 ± 10	8040 ± 40
MEFRIT undist.	598 ± 99	6040 ± 60
MEFRIT undist. + BHT	519 ± 72	7150 ± 50
MEFRIT undist. + PY	20.5 ± 1.9	8800 ± 40

[a] PY, pyrogallol; for other abbreviations see Table 1.

Further DTA oxidative tests were carried out for the chosen antioxidant concentrations for various heating rates. From the dependences of OOT on heating rate, the parameters describing the length of the IP on temperature were obtained using Equation 2. The values of the parameters A and B for all samples are listed in Table 2. The experimental and fitted values of the OOT are shown in Figure 3 for MERO undistilled. The agreement between the experimental and fitted points is very good; a similar good agreement was reached for the other samples studied. From the values of A and B, the OIT for a chosen temperature can be calculated using Equation 1. As an example, the dependence of OIT on temperature for MEFRIT undistilled is shown in Figure 4.

From Figure 4 it can be clearly seen that the curve of OIT for MEFRIT undistilled stabilized by PY is higher than the curve for MEFTRIT stabilized by BHT. This points out again that PY is a much more efficient antioxidant than BHT. However, as discussed by Šimon *et al.* (22), the temperature range of accelerated stability tests differs from the temperature range where the stability of the sample should be predicted. The change in temperature can lead to a change in the reaction mechanism so that the extrapolation of absolute values of OIT can lead to nonrealistic estimations. A better estimation can be obtained using the ratio of the OIT of stabilized and unstabilized samples (16,23), since it can be expected that the same structural units are responsible for the oxidation both in stabilized and unstabilized samples (22,23). This ratio is called the protective factor (PF):

$$PF = \frac{t_i\ (\text{stabilized sample})}{t_i\ (\text{unstabilized sample})} \qquad [3]$$

If the value of PF is greater than one, the additive has a stabilizing effect on the sample. The greater is the value of PF, the

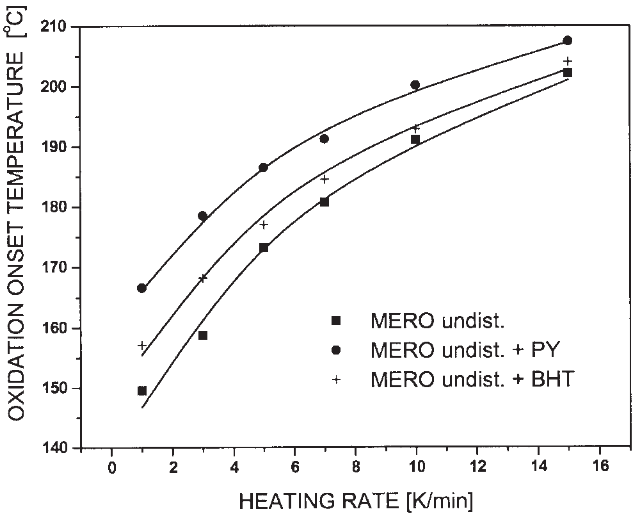

FIG. 3. Experimental and fitted values of the onset oxidation temperatures for various heating rates for MERO undistilled. Undist., undistilled; for other abbreviations see Figures 1 and 2.

higher is the antioxidant effectiveness of the additive. It follows from Equation 1 that the OIT depends on temperature; hence, the protective factor depends on temperature as well. The dependences of the protective factor on temperature are shown in Figures 5 and 6. As one can see, the antioxidant activity of both antioxidants decreases with increasing temperature. For both antioxidants, the PF are higher for undistilled esters than for the distilled ones. PY exhibits a considerably higher antioxidant activity compared with BHT. The values of protective factors depend also on the methyl ester matrix. For MEFRIT undistilled, the protective factor of PY extrapolated to 25°C reaches a value of about 400, whereas the PF for MERO undistilled is about 80 for the same temperature.

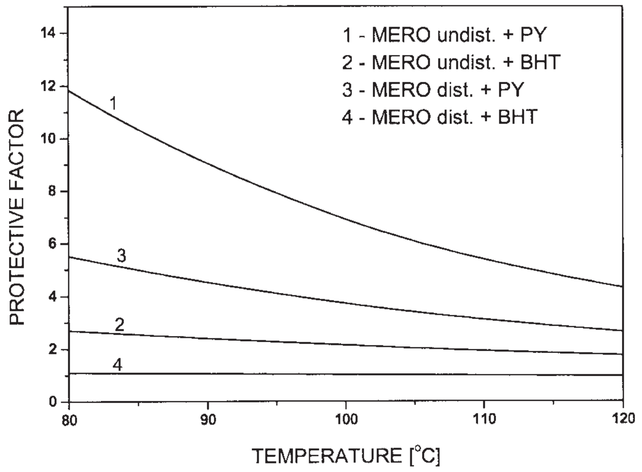

FIG. 5. Dependence of the protective factors on temperature for MERO distilled and undistilled, stabilized with BHT and PY, calculated by using Equations 1 and 3. For abbreviations see Figures 1–3.

The IP of oxidation measured by the Rancimat test at 110°C are summarized in Table 3. For comparison, Table 3 also includes the OIT calculated by Equation 1 for the same temperature, using data from Table 2 obtained from the DTA measurements. It can be seen that the DTA IP are shorter than the Rancimat ones. This can be accounted for by the fact that the oxygen used in DTA measurements is a stronger oxidative medium than the air used in the Rancimat test. However, a straightforward correlation between the IP determined by both techniques is not observed. It is known that OIT data appear to diverge when run under an air atmosphere compared with an oxygen environment (24). A further reason for the differences can be attributed to a different sample surface/volume ratio for both techniques, as discussed by Šimon *et al.* (16). For the DTA instrument, the ratio is approximately two orders of magnitude

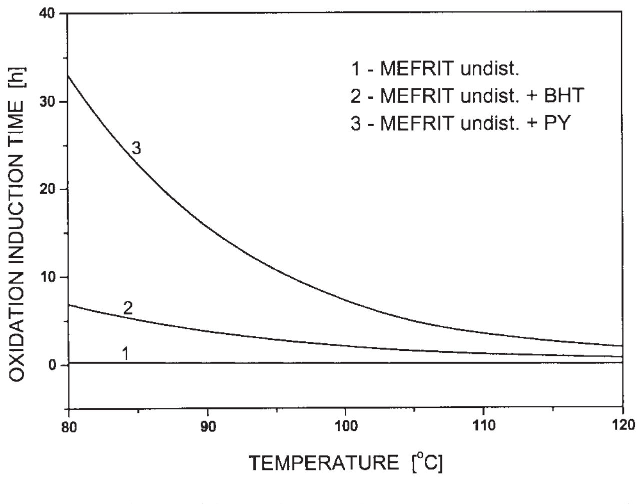

FIG. 4. Dependence of the oxidation induction time on temperature for MEFRIT undistilled, calculated by Equation 1. For abbreviations see Figures 2 and 3.

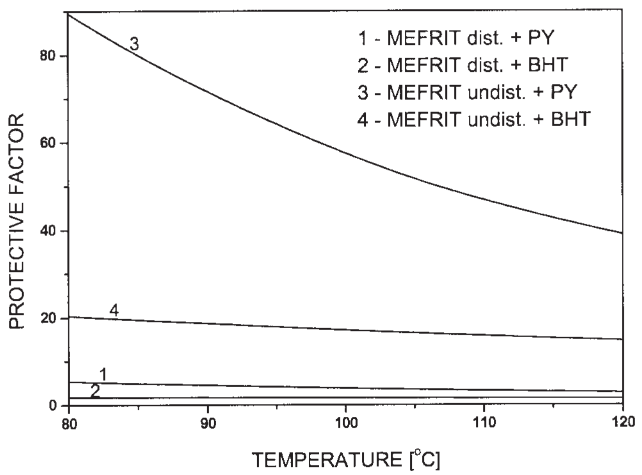

FIG. 6. Dependence of the protective factors on temperature for MEFRIT distilled and undistilled, stabilized with BHT and PY, calculated by using Equations 1 and 3. For abbreviations see Figures 2 and 3.

TABLE 3
Lengths of Induction Periods Determined by Rancimat (measured) and DTA[a] (calculated using Eq. 1) for the Temperature 110°C

Sample	Induction period (h) Rancimat	Induction period (h) DTA
MERO dist.	4.78 ± 0.05	1.39 ± 0.28
MERO dist. + BHT	8.65 ± 0.05	1.37 ± 0.44
MERO dist. + PY	25.3 ± 0.2	4.29 ± 0.84
MERO undist.	6.94 ± 0.15	1.32 ± 0.35
MERO undist. + BHT	9.58 ± 0.19	2.53 ± 0.22
MERO undist. + PY	24.1 ± 0.1	7.0 ± 1.8
MEFRIT dist.	1.46 ± 0.05	0.66 ± 0.21
MEFRIT dist. + BHT	5.35 ± 0.13	1.00 ± 0.25
MEFRIT dist. + PY	23.4 ± 0.1	2.12 ± 0.42
MEFRIT undist.	2.90 ± 0.04	0.070 ± 0.023
MEFRIT undist. + BHT	7.3 ± 0.1	1.10 ± 0.30
MEFRIT undist. + PY	25.2 ± 0.4	3.23 ± 0.62

[a]DTA, differential thermal analysis; for other abbreviations see Tables 1 and 2.

higher than for the Rancimat. Consequently, oxidation of the sample in a Rancimat instrument is mostly controlled by diffusion since the rate of oxygen uptake is greater than its supply to the sample by diffusion. This may be an additional reason for the indistinct correlation in the values of IP determined by DTA and by Rancimat.

Generally, the IP of unstabilized methyl esters do not comply with the requirements of the standard EN 14214 (4). The addition of BHT or PY increases the stability of methyl esters to the level of compliance with the standard. The results of the Rancimat test summarized in Table 3 indicate that BHT prevents oxidation of both methyl esters, and the stabilizing effect is stronger for MEFRIT. The Rancimat IP also document extremely high antioxidant efficiency of PY, which is in agreement with data reported previously (18,25). BHT can be considered an antioxidant of a lower efficiency. Regarding PY, the Rancimat IP are approximately four times longer than those required by the standard. If one needs merely to meet the standard requirements, a smaller concentration of PY may be used for stabilization than chosen for the study in this paper. The concentration of the antioxidants in methyl esters is so low that they cannot affect the physical properties of methyl esters and their use as a biodiesel fuel.

Both Rancimat and DTA IP indicate lower stability of MEFRIT samples compared with the corresponding MERO samples. This finding is quite unexpected since MEFRIT contains less polyenic acyls prone to oxidation than MERO (see Table 1). The lower oxidation stability of MEFRIT samples is most likely connected with the presence of prooxidative agents that were formed in the waste oil during frying and that remain in MEFRIT after transesterification. The oxidation stability of methyl esters prepared from waste edible oils/fats depends also on the food processed. For example, high oxidation stability of frying oils after the processing of potato products is well known (26). In our previous measurements with another MEFRIT sample, the higher oxidation stability for MEFRIT distilled was observed (18) in comparison with MEFRIT undistilled. The stability of methyl esters prepared from waste frying oils is hence determined by the history of the oils.

The data in Table 3 outline the influence of distillation on the stability of methyl esters. For MERO, both the Rancimat and DTA IP indicate that distillation decreases the oxidation stability. This fact has been accounted for by the removal of natural antioxidants (27). For MEFRIT, the Rancimat IP also indicate decreasing oxidation stability with distillation whereas the DTA IP exhibit no unambiguous trend.

In comparing the two techniques used in this paper for the study of the thermooxidation stability of methyl esters, one finds that the main advantage of the Rancimat test is that it is a very simple method providing just one number characterizing the stability. This simplicity is obviously the reason this is the procedure recommended in the standard. However, as discussed above and in Šimon *et al.* (16), the rate of oxygen diffusion rather than the rate of oxidation itself may be measured for labile samples. On the contrary, DTA (or DSC, as used in Ref. 16) provides a kinetic description of the IP. It enables one to estimate the protective factors of the stabilizers for lower temperatures by extrapolation outside the temperature region of measurements. Knowing the kinetic parameters A and B, one can carry out modeling of the oxidation processes occurring in methyl esters during their production, transport, and storage and calculate the length of IP for any temperature regime (16,17).

For the treatment of nonisothermal DSC data, the program TIND has been written in FORTRAN-77. The DOS version of the program is available on request.

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