STORAGE STABILITIES OF FUEL GRADE CAMELINA, SUNFLOWER AND RAPESEED METHYL ESTERS

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SUMMARY

The storage stabilities of fuel grade camelina, sunflower and rapeseed methyl esters were evaluated in airtight and open containers. Commercial amounts (200 litres) of the methyl esters were stored in airtight drums and sampled regularly, and the effects of air exposure were evaluated from sixteen days laboratory-scale accelerated storage tests at 65°C. None of the methyl esters in airtight drums deteriorated during eighteen months of storage; composition, viscosities and free fatty acid levels remained unchanged. The accelerated storage test in open containers, however, indicated that exposure to air can cause rapid oxidation of each of the three methyl esters. However, oxidation can be delayed by the presence of tocopherols (natural antioxidants) in the methyl ester, and it can be further delayed by the presence of an unidentified carotenoid. The exceptional stability of rapeseed methyl ester seems to be due to a combination of relatively high levels of M-tocopherol and the unidentified carotenoid. The rates of oxidation (i.e. rate of increase of viscosity etc.) of sunflower and camelina methyl esters were about the same, but rapeseed methyl ester oxidised slower. The observed relative rates of oxidation could be predicted from the levels of reacting double bonds calculated from the oxidation data, but not from iodine numbers.

INTRODUCTION

Biodiesel, a mixture of fatty and methyl esters obtained from vegetable oils and animal fats, is a biodegradable alternative to mineral diesel. One of the drawbacks of biodiesel over mineral diesel is that it can be more susceptible to oxidation at ambient temperature, and it is expected to be less stable in storage. The lower oxidative stability of biodiesel is probably caused by the higher level of unsaturation and possibly by the larger amounts of dissolved oxygen. Previous studies on the storage stability of biodiesel were limited to soya and rapeseed methyl esters and they involved relatively small amounts (5 litres) of the two biofuels (Thompson *et al.*, 1998). These studies concluded that there was a deterioration of the methyl ester with time, and recommended underground storage with the addition of 0.5% BHT as antioxidant. There is no reported work, however, on the storage stabilities of commercial quantities of methyl esters or of methyl esters of vegetable oils which are relatively cheap to produce in Europe,

such as camelina and sunflower. These methyl esters are considerably more unsaturated than rapeseed methyl ester (i.e. higher iodine value), hence they are expected to be less stable in storage. The objective of the present work is to evaluate the storage stabilities of commercial amounts of rapeseed, camelina and sunflower methyl esters (RME, CME and SME) in airtight and open containers, and determine if stability is affected by the composition of the methyl ester.

MATERIALS AND METHODS

CME for the long-term storage test was prepared from unrefined camelina oil obtained from seeds grown and pressed at Oak Park, and SME and RME for the same test were prepared from refined commercial oils. Esterification was carried using the method described by Fröhlich and Rice (1995), which is suitable for the production of pilot scale quantities of biodiesel grade methyl ester with simple equipment. Methyl ester quality was determined according to the methods specified in the EU draft specifications for biodiesel (CEC, 1993). The methyl esters were stored for eighteen months in 210 litre airtight steel drums out of doors, and the containers were opened once a month for 1 hour to take samples and to simulate periodic venting. Samples were stored at -20^{o}C until analysed. In order to test the effect of headspace, two lots of camelina methyl ester were stored with headspaces of 3.5 and 26% of total container volume.

Accelerated storage in open containers was carried out according to the Schaal test (Jacobs, 1958), eight 50 g samples each of camelina, sunflower and rapeseed methyl esters were stored at 65^{o}C for sixteen days in 250 ml beakers of identical geometry covered with watch glasses. In order to evaluate the effect of processing on oxidation rates, accelerated storage tests were carried out with methyl esters prepared both at Oak Park and by BLT in Wieselburg, Austria. In the Wieselburg process, the methyl ester is dried under vacuum at 60^{o}C, whereas in the Oak Park process drying took place at 115^{o}C. Low temperature drying is less likely to destroy natural antioxidants.

Peroxide and free fatty acid levels and viscosities were determined by standard methods (AOAC, 1984). Oxidised methyl ester levels were quantified by gas chromatography using methyl heptadecanoate as internal standard. Natural antioxidants (Simkowsky, 1997) and polymers (AOCS, 1989) were determined by high pressure liquid chromatography with reverse phase and gel permeation

columns, respectively. Carotenoid levels were determined with spectrophotometer at 450 nm.

RESULTS

Analytical methods

The parameters used here to evaluate storage stability of methyl esters determine both the physical and chemical changes caused by oxidation and which have an effect on the fuel specific properties of the methyl esters. Peroxides are primary oxidation products, and high levels are an indication of more permanent chemical changes. Changes in composition and increase in polymer and free fatty acid levels indicate the type of chemical changes caused by oxidation, and viscosity shows how these changes affect the physical properties of methyl esters. Aldehydes, usually determined in edible oil, were found to occur in very low levels which are unlikely to affect the physical properties of fuel grade methyl esters.

Long-term storage

Peroxide levels

Initial peroxide levels of the two CMEs were low and the two values were very close, but those of RME and SME were considerably higher (Table 1). The difference between the initial values must be partly due to the different amounts of oxygen absorbed during esterification and partly to differences in composition. Considerably higher initial peroxide level, however, is also obtained in SME prepared in the laboratory where oxygen absorption is relatively uniform, but those of RME and the CMEs are nearly the same. Hence, SME seems to be more susceptible to initial peroxide formation than either RME or CME. After the initial increase, peroxide levels of the four methyl esters fluctuate, but there is no trend to indicate a gradual increase or decrease during the eighteen months of the test (Table 2).

Table 1: Initial peroxide values of stored methyl esters (mmole/kg)

Month no.	1	2	3	4	5
Camelina 1	1.7	2.5	2.9	3.3	3.6
Camelina 2	2.5	4.4	4.2	4.3	8.5
Sunflower	12.7	20.8	13.3	15.2	20.8
Rapeseed	7.8	7.6	8.9	8.1	9.1

Table 2: Peroxide levels of stored methyl esters (mmole/kg)

Date	CME 1	CME 2	SME	RME
7/97	1.7	2.5	12.7	-
12/97	3.6	8.5	20.8	7.8
6/98	2.5	7.1	27.4	8.6
12/98	1.5	8.5	33.1	10.6

The found peroxide levels are small, in real terms, even 30 mmole/kg obtained in SME is only about 0.37% of peroxides by weight, if there is only one peroxide group per methyl ester. Probably there is more than one peroxide group per molecule, hence the real peroxide level could be lower than calculated.

Composition

The levels of individual methyl esters most likely to oxidise, namely linoleate and linolenate in CME and RME, and oleate and linoleate in SME, varied within narrow ranges (Table 3), and the observed variation as expressed by standard deviations was about the same as the variations obtained from ten repeat determinations of CME fatty acid profiles. Variation in the levels of the other individual methyl esters was equally small. In each case, variation within the obtained range is random and no trend can be observed. Allowing for experimental error, the composition of the four methyl esters, at the end of the eighteen months storage period, was identical to that obtained before storage.

Table 3: Oxidisable methyl ester levels (%)

Date	CME 1		CME 2		SME		RME	
	C18:2	C18:3	C18:2	C18:3	C18:1	C18:2	C18:2	C18:3
7/97	15.6	38.5	15.5	37.2	22.1	65.4	-	-
12/97	15.5	38.2	15.5	37.2	21.9	65.9	21.3	10.5
6/98	15.3	38.6	15.3	37.6	21.6	65.9	21.2	10.5
12/98	15.7	39.2	15.4	37.0	22.2	65.9	21.2	10.2

Viscosity

The viscosities of the four methyl esters did not change significantly during storage, and considering that the composition remained constant during storage, no change is expected (Table 4). Although viscosities varied within ranges of 0.16 to 0.25 cps, the variation was random and there was no trend in either direction. The range of variation, however, is relatively large, considering that viscosity determinations can be repeated within 0.05 cps. The observed range is probably due to the $\pm 0.6^{o}C$ variation in temperature during viscosity determinations, which is considerably higher than the $\pm 0.1^{o}C$ specified. The obtained viscosity for RME and SME is well within the range of reported values (Rathbauer and Bachler, 1995), and the present viscosities for CME were obtained before in this laboratory. Differences between the viscosities of SME, CME and RME are due to differences in composition and not to different levels of initial oxidation.

Table 4: Viscosities of methyl esters (cps)

Date	CME 1	CME2	SME	RME
7/97	6.55	6.55	6.64	-
12/97	6.60	6.80	6.76	7.25
6/98	6.58	6.74	6.77	7.25
12/98	6.61	6.70	6.69	7.26

Free fatty acid levels

It was reported that FFA (free fatty acid) levels increase during oxidation possibly because traces of moisture hydrolyse the methyl ester (Thompson *et al.*, 1998). The obtained FFA levels of the four methyl esters were low, and the initial differences between the obtained levels are due to different levels of hydrolysis during the final stages of the process (Table 5). The variation of the FFA levels in

RME and SME, as expressed by standard deviations, was the same as that of ten repeat determinations, but in the two CMEs it was considerably higher. The unexpectedly high variation in these methyl esters was caused by several high FFA levels obtained at different times, which we cannot explain. However, no definite trend was observed in FFA levels in any of the four methyl esters, hence it can be safely assumed that they remain stable under the storage conditions used here.

Table 5: Free fatty acid levels of methyl esters (mmoles/kg)

Date	CME 1	CME 2	SME	RME
7/97	5.6	7.2	4.4	-
12/97	4.8	5.6	4.8	2.2
6/98	4.2	8.6	4.6	2.6
12/98	6.6	6.0	5.2	2.0

Accelerated storage

Wieselburg methyl esters

The peroxide level of each methyl ester rises to a maximum value at different rates during the accelerated storage test (Fig. 1) and it becomes more stable afterwards. SME shows the most rapid rise of peroxide level, it reaches a maximum value of 178 mg/kg within eight days, but CME and RME reach their maximum peroxide levels only after fourteen days. The three methyl esters show a period of slow increase (induction period) before the rapid rise of peroxide levels, which is two, four and about eight days in SME, CME and RME, respectively.

Individual methyl ester to internal standard (heptadecanoic acid methyl ester) peak area ratios, at the beginning and at the end of accelerated storage, indicated that only linoleate and linolenate in CME and RME, and only oleate and linoleate in SME were oxidised during the test. Therefore, changes in oleate, linoleate and linolenate contents determined by gas chromatography, could be used to determine the levels of oxidised methyl esters. Similarly to peroxide levels, oxidised methyl ester levels of the three methyl esters also show an induction period at the start of the accelerated storage (Fig. 2). During the observed induction period there is no increase in oxidised methyl ester levels, and the period corresponds to two, four and eight days in SME, CME and RME, respectively. After the induction period, oxidised methyl ester levels increase continuously, the fastest increase is shown by SME followed by CME and RME.

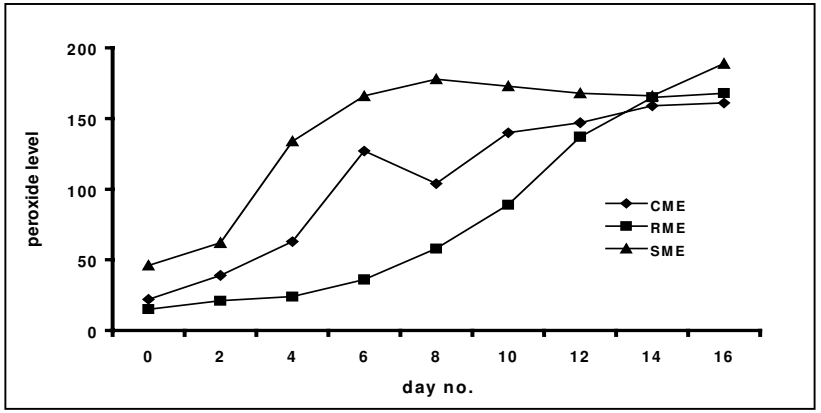

Fig. 1: Peroxide levels, accelerated storage, WMEs

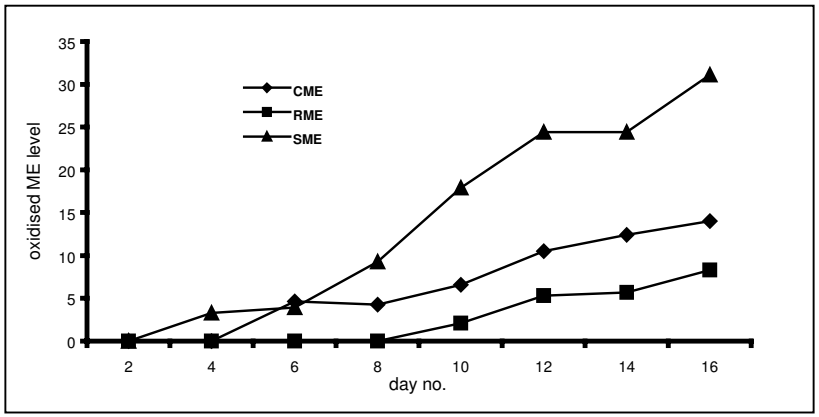

Fig. 2: Oxidised ME levels, accelerated storage, WMEs

Viscosities of the three methyl esters during accelerated storage start to increase at about the same time as oxidised methyl esters and continue to increase during the sixteen-day period (Fig. 3). Viscosities at the end of the accelerated storage also reflect the final oxidised methyl ester levels. SME (31% oxidised) has a final viscosity of 14.6 cps, whereas RME and CME, with much lower oxidised methyl

ester levels (8 and 14% oxidised) have final viscosities of 9.7 and 11.4 cps, respectively.

The dependence of viscosities on oxidised methyl ester levels indicates that oxidation converts methyl esters into more viscous products and analysis of oxidised samples confirms this observation. Levels of products with molecular weights higher than those of methyl esters, determined by gel permeation chromatography, are nearly the same as the levels of oxidised methyl esters after sixteen days of accelerated storage.

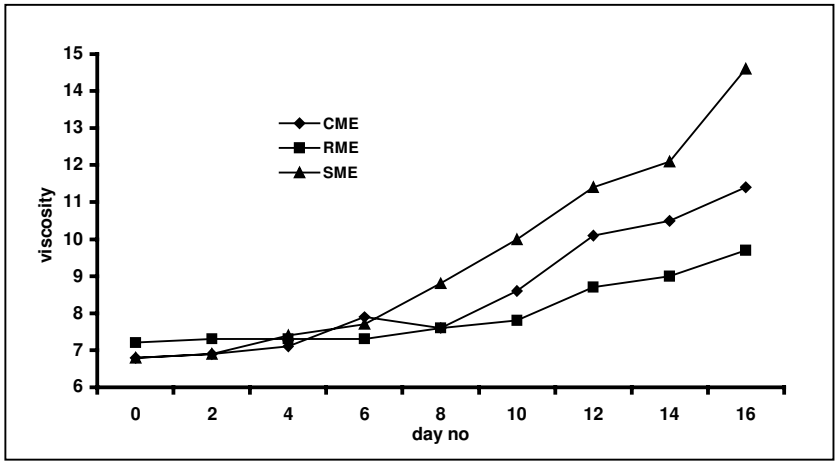

Fig. 3: Viscosities, accelerated storage, WMEs

Oak Park methyl esters

The peroxide levels of the three Oak Park methyl esters nearly treble in the first two days of accelerated storage, continue rising almost linearly until a maximum value is reached and fluctuate within a narrow range thereafter. The maximum peroxide levels of the three methyl esters are similar (170-180 mmoles/kg), peroxide levels of CME and SME increase at about the same rate, but considerably slower in RME (Fig. 4).

Similarly to peroxide levels, oxidised methyl ester content of the three methyl esters also starts to increase from day 0 and continue to increase during accelerated storage (Fig. 5). Oxidation is fastest in SME, followed by CME and RME, and the

final oxidised methyl ester contents, 28.1, 21.8 and 10.2%, respectively, reflect these differences.

Viscosities of the three methyl esters also increase continuously during the period of accelerated storage. The rate of increase reflects increases in oxidised methyl ester levels, and at the end of the accelerated storage, SME (28.1% oxidised) has a final viscosity of 12 cps, whereas the viscosity of RME (10.5% oxidised) at the same time is only 10.2 cps. CME, however, has a 2.6 cps higher final viscosity than SME in spite of its lower oxidised product content (21.3%). We have no explanation for the seemingly anomalous results (Fig. 6).

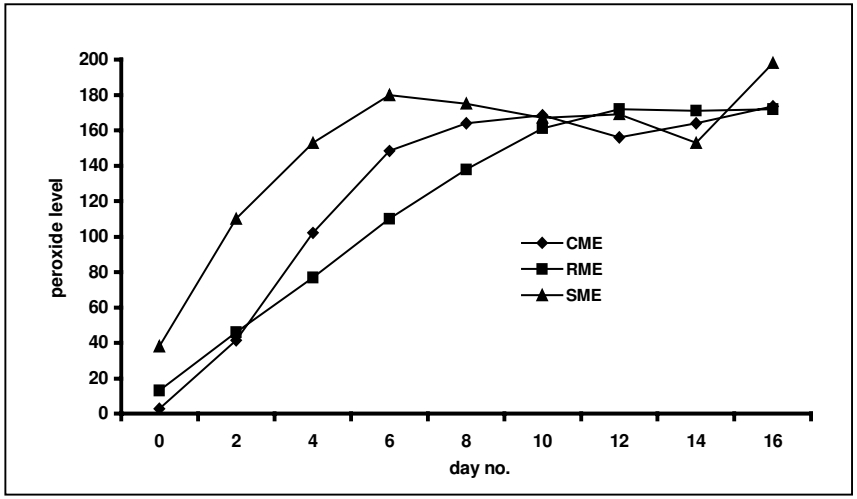

Fig. 4: Peroxide levels, accelerated storage, OPMEs

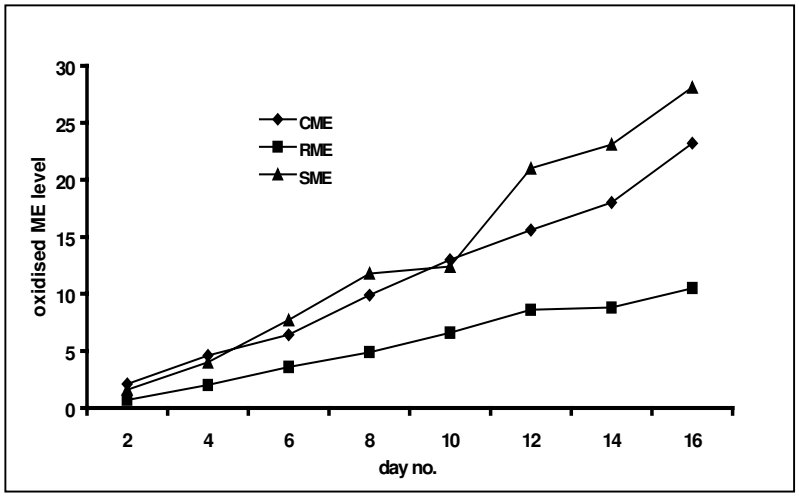

Fig. 5: Oxidised ME levels, accelerated storage, OPMEs

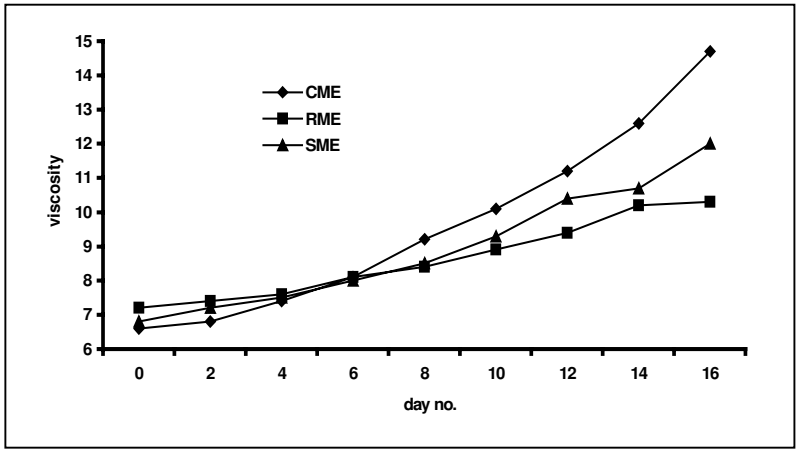

Fig. 6: Viscosities, accelerated storage, OPMEs

DISCUSSION

Long term storage and quality

According to the results obtained here, eighteen months of storage in airtight drums with periodic venting does not affect the quality of RME or of methyl esters with higher levels of unsaturation such as CME and SME. The composition of the three methyl esters remained unchanged after eighteen months of storage, and even levels of linoleate and linolenate, which are most susceptible to oxidation, remained stable (Tables 1-5). As there is no change in composition, viscosity does not increase and another indicator of oxidation, FFA levels, also remain unchanged. Only peroxide levels increase initially, but as it occurs only in the first months of storage, it is probably caused by oxygen absorbed during the process. Absorbance of oxygen from the headspace would cause a continuous increase in peroxide levels which was not observed.

Accelerated storage and oxidation

The accelerated storage test indicates whether exposure to air at ambient temperature will have a measurable effect on methyl esters, and the test can also be used to determine relative stabilities and oxidation rates of the same. At 65^{o}C, the temperature of the test, there is no thermal oxidation, and the same chemical changes occur as at room temperature, but faster. Hence by using the test, it is possible to obtain data on oxidation caused by exposure to air in sixteen days that would probably require several months at ambient temperature. The test is used regularly for evaluating flavour and odour development in edible oils.

The results from accelerated storage (Figs. 1-6) show that all three methyl esters in the two sets of samples are oxidised when exposed to air at 65^{o}C, and the effect of oxidation on composition and viscosity is considerable. Oxidation of the Oak Park methyl esters starts within two days; the Wieselburg samples are somewhat more stable, but after sixteen days 10% to 30% of all methyl esters is oxidised. Increasing oxidised methyl ester levels increase viscosities, and on account of high viscosities none of the methyl esters can be used as diesel fuel after fourteen days of exposure to air at 65^{o}C. If methyl esters oxidise at 65^{o}C, oxidation will also occur at room temperature, but slower. Therefore, in order to prevent

deterioration in storage, fuel grade methyl esters should be stored in airtight containers, or protected from oxidation by the addition of suitable antioxidants.

While both sets of methyl esters oxidise during accelerated storage, there are significant differences between the oxidation patterns of the Wieselburg and Oak Park methyl esters. The Oak Park methyl esters start to oxidise immediately, as indicated by the increasing viscosity, oxidised methyl ester and peroxide levels, whereas the Wieselburg methyl esters have a period of induction during which methyl esters resist oxidation and viscosities and oxidised methyl ester levels remain constant. The period of induction is two days for both CME and SME and six days for RME at 65°C. After the end of the induction period the three methyl esters begin to oxidise at the same rate as those without induction period. The rapid oxidation of the Oak Park methyl esters is in line with previous findings, which indicated that at 40°C linolenic and linoleic acid methyl esters start to oxidise within 2 and 20 hr, respectively (Privett and Blank, 1962).

The effect of natural antioxidants

Considering that the observed induction periods could be due to natural antioxidants, the two sets of methyl esters were analysed for tocopherols. No tocopherols were detected in the Oak Park methyl esters, but the levels found in the Wieselburg methyl esters were substantial. Seemingly, the method of drying used at Oak Park (and in several commercial biodiesel plants) leads to the decomposition of antioxidants. Mainly α and M tocopherols were found and their levels in RME, SME and CME were 158, 347 and 55, and 263, 10 and 273 mg/kg, respectively. Smaller amounts of β and δ tocopherols were also present, but they could not be confirmed. The found tocopherol levels are within the range reported for the corresponding raw vegetable oils (Budin *et al.*, 1985; Simkowsky, 1997).

The absorbance spectrum of the three methyl esters was checked, because it was noted that their colour changed suddenly from intense yellow to nearly colourless at the end of the induction period. Each methyl ester had a maximum absorbance at 450 nm, thus indicating that the yellow colour is probably due to a carotenoid. It is none of the listed carotenes (α,β,M,δ) however, because each of those has two maximum absorbances between 400 and 500 nm. The highest carotenoid level was found in the Wieselburg RME, the levels detected in CME and SME were much lower. The methyl esters produced at Oak Park had no absorbance in the

visible spectrum, consequently high drying temperatures could also be detrimental to carotenoids.

Tocopherol levels decline gradually during accelerated storage (Table 6), but measurable oxidation does not occur until certain levels are reached. M Tocopherol in both RME and CME must be reduced to 100 mg/kg and α in SME to 0 level before there is evidence for oxidation of the methyl esters. Considering that when tocopherols are absent there is no initial resistance to oxidation, and when present they must be reduced to a definite level before oxidation begins, the observed induction periods must be partly due to the presence of tocopherols.

The length of the induction period depends on how long tocopherols persist in the methyl ester (Table 6), which in turn depends on the stability of the particular tocopherol and on carotenoid levels. α Tocopherol is less stable than M tocopherol; the former is eliminated from RME within four days, whereas the latter persists for ten days. Carotenoid levels have an even more marked effect on the induction period than tocopherol levels. When natural levels of tocopherol (200-300 mg/kg) are combined with relatively low levels of carotenoid as in CME and SME, the induction period is only two days. However, when a slightly higher tocopherol level is combined with a much higher amount of carotenoid in RME, the rate of tocopherol degradation is much slower and the induction period is extended to six days. Furthermore, there is more resistance to oxidation during the extended induction period of RME than during the shorter period of CME and SME, because apart from oxidised methyl ester levels, peroxide levels are also more stable. Consequently, tocopherol in combination with certain levels of carotenoid seems to have a far stronger effect on the induction period than tocopherol alone.

It is not possible to establish the nature of tocopherol-carotene interaction from data available in the present work. β Carotene alone does not retard oxidation of the methyl ester, thus the effect of the carotenoid on tocopherol is probably not the additive effect of another antioxidant. It is known that carotenes are very effective in quenching the reactive singlet oxygen (Gunstone, 1984) and return it to the unreactive triplet state. However, the reactivity of singlet oxygen is only important in light induced oxidations, and accelerated storage was carried out in

Table 6: Effect of antioxidants on the oxidation of methyl esters at 65°C

Sample	Day no.	α T (mg/kg)	M T (mg/kg)	Total T	Carotenoids* (mg/kg)	Viscosity (cps)	Peroxide level (mmole/kg)
RW0	0	158	263	421	67	7.24	15
RW1	2	64	197	261	59	7.26	21
RW2	4	-	178	178	47	7.30	24
RW3	6	-	109	109	34	7.34	36
RW4	8	-	7	7	14	7.57	58
RW5	10	-	7	7	13	7.82	89
RW6	12	-	-	-	4	8.72	137
CW0	0	55	273	328	11	6.80	22
CW1	2	-	108	108	8	6.93	38
CW2	4	-	22	22	6	7.13	63
CW3	6	-	-	-	4	7.95	127
SW0	0	347	10	357	4	6.76	45
SW1	2	-	-	-	3	6.89	62
SW2	4	-	-	-	1	7.37	133

RW = Wieselburg RME etc. T = tocopherol * β-carotene used as reference

the dark. It is possible that carotene has a synergistic effect on tocopherols (Patterson, 1989), but further work will need to be carried out to demonstrate such effect.

Relative rates of oxidation

The rate of oxidation of a methyl ester can be defined as the rate of increase of peroxide levels, oxidised methyl ester levels and viscosity, when a methyl ester is exposed to air. During the induction period there is no oxidation, and the rate of oxidation is determined from the end of this period. Of the three methyl esters examined in the present work, RME has the lowest rate of oxidation in terms of all three oxidation parameters in both sets of samples (Figs. 4-6). SME oxidises somewhat faster than CME when the methyl esters have an induction period and at about the same rate in terms of peroxide and oxidised methyl ester levels and viscosities up to day 6 in samples without induction period. After the sixth day, however, the rate of viscosity increase becomes much faster in CME and at the end of the accelerated storage it is considerably higher. The accelerated storage test of

CME was repeated with a sample prepared in the laboratory which had no induction period, but the sudden increase of viscosity after day 6 could not be repeated. Consequently, it can be concluded that CME and SME oxidise at about the same rate and the oxidation rate of RME is considerably slower.

The order of relative oxidation rates obtained in the present work is at variance with the rates expected from iodine numbers, according to which CME with an iodine number of 155 is expected to oxidise faster than SME with an iodine number of 132 (Shahidi *et al.*, 1994). The possible reason for the unexpected result is that the iodine number is a measure of the total number of double bonds, but not all double bonds are involved in oxidation. Individual methyl esters to internal standard ratios indicate that during accelerated storage only the two methyl esters with the highest number of double bonds were oxidised. Therefore, in a hypothetical mole (i.e. 1 mole of methyl ester with the determined composition) of CME and SME, there are 1.42 and 1.52 moles of reacting double bonds, respectively, whereas in the same amount of RME there are only 0.71 moles. Accordingly, the level of reacting double bonds seems to provide a better explanation for the oxidation rates observed in the present work than the iodine values.

CONCLUSIONS

- Fuel grade rapeseed, camelina and sunflower methyl esters are stable in airtight containers with periodic openings for at least 18 months, even without natural antioxidants.

- All three methyl esters oxidise when exposed to air, and the extent of oxidation within a given period depends on the stability and the oxidation rate of the particular methyl ester.

- Stability, or resistance to oxidation, seems to depend on the level and type of antioxidants present in the methyl ester and the rate of oxidation on the levels of reacting double bonds.

- In the absence of natural antioxidants none of the three methyl esters resists oxidation.

- When natural antioxidants are present, oxidation is delayed longest in rapeseed methyl ester, which has the highest level of antioxidants, followed by camelina and rapeseed methyl esters which have considerably lower levels.

- Of the three methyl esters, rapeseed methyl ester has the lowest rate of oxidation and also the lowest level of reacting double bonds, the oxidation rates and reacting double bond levels of camelina and sunflower methyl esters are about the same.

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