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ORIGINAL PAPER

The Influence of Tocopherols on the Oxidation Stability of Methyl Esters

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Abstract Tocopherols were found to be the principal natural antioxidants in biodiesel grade fatty acid methyl esters. The stabilising effect of α-, γ- and δ- tocopherols from 250 to 2,000 mg/kg was evaluated by thermal and accelerated storage induction times based on rapid viscosity increase, in sunflower (SME), recycled vegetable oil (RVOME), rapeseed (RME) and tallow (TME) methyl esters. Both induction times showed that stabilising effect is of the order of δ- > γ- > α-tocopherol, and that the stabilising effect increased with concentration. The correlation between the two induction times however was poor, which is probably due to the fact that the time they correspond to two different stages of oxidation. Tocopherols were found to stabilise methyl esters by reducing the rate of peroxide formation while present. The deactivation rates of tocopherols increased with unsaturation of the particular methyl ester and in the present work they were of the order of SME > RME > RVOME > TME. While α-tocopherol was found to be a relatively weak antioxidants, both γ- and δ- tocopherols increased induction times significantly and should be added to methyl esters without natural antioxidants.

Keywords Natural antioxidants · Tocopherols · Biodiesel · Fatty acid methyl esters · Thermal and accelerated oxidation induction periods · Oxidation stability

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Introduction

Biodiesel grade methyl esters have been used in diesel engines for over a decade, and current European production is around 3 million tons per annum. While the physical properties of biodiesel are very similar to those of mineral diesel, differences in chemical properties make biodiesel more susceptible to atmospheric oxidation. Previous studies carried out on the stability of rapeseed oil ethyl and methyl esters stored in open containers found that there was a gradual deterioration of the methyl ester and suggested the addition of antioxidants [1]. Several authors have reported the addition of synthetic antioxidants to methyl esters [2–4], and some commercial synthetic antioxidants were found to be effective [5]. On the other hand, work to date on the stabilising effect of natural antioxidants is far more limited, although the antioxidant effect of tocopherols has been studied extensively in edible oils [6–8]. It has been shown however, that tocopherols present in rapeseed oil remain in the methyl ester after esterification [9], and removal of tocopherols reduces the stability of the methyl ester [2]. Other authors demonstrated that α-tocopherol reduces the rate of viscosity, peroxide and fatty acid increase [4] in soya methyl esters, and the stabilising effect of α-tocopherol in the same methyl ester was also shown by pressurised differential calorimetry [3]. It was also reported that tocopherol mixtures rich in γ-tocopherol nearly doubled the thermal induction time of used frying oil methyl ester [5]. Tocopherols have some advantages over synthetic antioxidants, insofar as they dissolve easily in methyl esters, and their presence does not devalue the ''natural'' character of biodiesel. The objective of the present work is to carry out a study on the effect of available tocopherols on the oxidative stability of biodiesel grade methyl esters.

Materials and Methods

Materials

Tocopherols, α-, γ- and δ- and pure methyl esters palmitic, stearic, oleic, linoleic and linolenic acid and activated carbon (DARCO G60~100 mesh), were obtained from Sigma-Aldrich (Ireland) Ltd., and mixed tocopherols from Vita-Blend BV, Volwega, The Netherlands. Commercial sunflower, rapeseed, and recycled vegetable oils, tallow and raw palm oil were obtained from wholesalers, and raw sunflower oil was pressed at Oak Park from dehulled seeds. The oils were esterified according to the method used at Oak Park for the preparation of biodiesel grade methyl esters [10]. Methyl esters were destabilised by stirring at 100–110 °C, until peroxide levels increased to 30–35 mg/kg, about 1–5 h depending on the methyl ester. Tocopherol free methyl esters were prepared by passing PME or RME (15 mL) through a column (10 × 50 mm) of dry activated carbon [11] overnight. Synthetic palm oil and rapeseed oil methyl esters were made up by blending palmitic, stearic, oleic, linoleic, and linolenic acids in the same proportions as found in the natural methyl esters.

Determination of Oxidation Stability

A modified Schaal oven test [12] was carried out by storing 25 g methyl ester samples in 250 mL beakers of identical geometry covered with watch glasses at 65 °C, until the viscosity increase exceeded 0.5 cSt (8–20 days). A 25 g sample was taken from the oven each day and stored at –20 °C until further use. Peroxide levels and viscosities of the collected samples were determined by standard methods [13, 14] and tocopherols were determined by HPLC at 295 nm, with amino-reverse phase column (250 × 4.6 mm Jones Chromatography, Glamorgan, UK), using 80:20 heptane-ethyl acetate mobile phase at 0.5 mL/min [9]. Tocopherol deactivation times (time to reach zero tocopherol level) were determined from the linear regression line, or from the linear equation when only two points of tocopherol concentration against time were available. Tocopherol deactivation was linear (R^2 = 0.91–0.97) in RME, RVOME and TME, but in SME it was linear (R^2 = 0.95–0.98) only after the first day of oxidation. Average tocopherol deactivation rates were calculated by dividing initial tocopherol concentrations by the corresponding tocopherol deactivation times. Peroxide rates were calculated from the regression line of the linear portion of the peroxide level increase versus time. Peroxide increase was linear (R^2 = 0.93–0.99) while tocopherols were present. Accelerated storage induction time was defined as the time in days required to reach a viscosity increase of 0.5 cSt, and it was calculated from the straight line between the viscosity increase above and below 0.5 cSt. The difference between repeated accelerated storage times was 0.3 days. Thermal induction times were determined by a Rancimat Model 743 Instrument (Metrohm). Air flow was set at 10 L/h and the temperature of the heating block was 110 °C [5]. The temperature correction factor ΔT was set at 1.5 °C as recommended by the manufacturer. Determinations were carried out in duplicate, and the maximum difference between the two values was 0.1 h.

Results and Discussion

Tocopherols and Stability

There is some data to indicate that tocopherols have a stabilising effect on methyl esters derived from vegetable oils [3, 4], but it has not been demonstrated so far that tocopherols are the main natural antioxidants in these methyl esters. Hence before evaluating the effect of different tocopherols on methyl esters, it was necessary to show that the oxidative stability of vegetable oil methyl esters is due mainly to the presence of these antioxidants. The stabilising effect of tocopherols was determined by comparing the thermal induction times of rapeseed and palm oil methyl esters made from fresh raw oils, before and after the removal of tocopherols. Complete removal of tocopherols from RME and PME with activated charcoal reduced thermal induction times from 7.8 to 1.0 h and 15.4 to 5.7 h, respectively (Table 1). Subsequent addition of α- and γ- tocopherols at about the same concentration as in the original RME, restored both thermal induction times to near the original value (Table 1), thus indicating that tocopherols are the main natural antioxidants in both RME and PME.

In order to confirm that tocopherols are the main natural antioxidants in methyl esters derived from vegetable oils, and to rule out synergism between tocopherols and some unknown antioxidants not removed by charcoal, thermal induction times of synthetic RME and PME with and without added tocopherols were compared. Synthetic methyl esters were made up with commercially available fatty acid methyl esters, and α- and γ- tocopherols were added at about the same concentration as was found in PME and RME before the removal of tocopherols. Added tocopherols increased the thermal induction time of synthetic RME from 0.1 to 7 h and of synthetic PME from 2.4 to 32.4 h (Table 1), which rules out significant synergistic effects of unidentified antioxidants. These results confirm that tocopherols are the main antioxidants in vegetable oil methyl esters, but they also show that composition has a very strong effect on stability. Synthetic PME with about 47%

Table 1 Thermal induction times (h) of normal, tocopherol—free and synthetic methyl esters

Methyl ester	Induction time	αT[a]	γT[a]	C 16:0	C 18:0	C 18:2	C 18:3
PME	15.4	267	150	43.3	40.5	9.6	0.3
T free PME	5.7	ND	ND	43.3	40.5	9.6	0.3
T free PME + T	17.7	178	486	43.3	40.5	9.6	0.3
Synthetic PME	2.4	ND	ND	42.9	42.2	9.7	0.6
Synthetic PME + T	32.9	130	331	42.9	42.2	9.7	0.6
RME	7.8	210	291	4.0	60.5	20.3	9.4
T free RME	1.0	ND	ND	4.0	60.5	20.3	9.4
T free RME + T	7.0	151	351	4.0	60.5	20.3	9.4
Synthetic RME	0.1	ND	ND	5.8	60.2	20.9	10.5
Synthetic RME + T	7.0	120	318	5.8	60.2	20.9	10.5

T tocopherol, *ND* not detected

[a] Tocopherol content (mg/g)

Table 2 Thermal induction times of methyl esters with different tocopherols

Antioxidant (mg/kg)	SME			TME			RME	RVOME
	αT (h)	δT (h)	γT (h)	αT (h)	δT (h)	γT (h)	δT (h)	δT (h)
250	0.30	0.14	0.80	1.09	9.99	7.38	–	–
500	1.04	0.84	1.11	1.92	21.93	15.31	–	–
1,000	1.08	1.11	1.45	4.07	28.54	20.11	3.27	4.14
2,000	1.48	2.80	–	–	–	–	–	–
0		0.20			0.20		0.50	0.60

saturated methyl esters is has far longer thermal induction time with or without antioxidants than synthetic RME with 6% unsaturated methyl esters.

Evaluation of Tocopherols, Thermal Induction Times

The stabilising effect of tocopherols most likely to occur in vegetable oil methyl esters, α-, δ-, and γ- tocopherols, were evaluated by adding amounts ranging from natural concentrations (250–500 mg/kg) to 2,000 mg/kg to sunflower oil methyl ester (SME) and tallow methyl ester (TME). The particular methyl esters were used, because SME was found to be the least stable commercial biodiesel [5], and TME has no natural antioxidants. The tocopherol with good stabilising effect, was added to other commercial biodiesel, namely RME and RVOME (recycled vegetable oil methyl ester). In order to eliminate stabilising effects other than other than those of the added tocopherols the methyl esters were destabilised by increasing the peroxide level to 30 mg/kg before the addition of the antioxidants. The destabilised methyl esters contained no natural tocopherols and their viscosity increased significantly (0.4–0.6 cSt) after 1 day at 65 °C. The stabilising effect was determined by both thermal and accelerated storage induction times.

According to the thermal induction times obtained, α- was the least and γ- was the most effective of the three tocopherols in SME up to 1,000 mg/kg (Table 2). However differences between induction times were very small, and none of the three tocopherols showed a particularly strong stabilising effect in SME. The stabilising effects were much stronger in TME than in SME, and the effect of concentration was much more obvious. Again α-tocopherol was the least effective of the three tocopherols in TME, but unlike in SME, δ-tocopherol was the most effective of the three antioxidants. The difference between the thermal induction times of α- and either δ- or γ- tocopherols in TME was much larger than the differences between the latter two. The stabilising effect of the three tocopherols increased with concentration, and the effect of concentration is much more obvious in TME than in SME. δ-Tocopherol also stabilised RME and RVOME, more effectively than SME, and the corresponding thermal induction times were much longer in each case than those of the tocopherol free methyl esters (Table 2).

Evaluation of Tocopherols, Accelerated Storage Induction Times

Considering that the differences between thermal induction times of SME were very small below 2,000 mg/kg of added tocopherol (Table 2), the three antioxidants were also evaluated by using induction times based on the Schaal oven accelerated storage test. In order to determine the most suitable oxidation parameter for the definition of accelerated storage induction time, methyl esters with added antioxidants were exposed to air at 65 °C, and peroxide levels, tocopherol levels and viscosities were

monitored. The data obtained indicated that tocopherol levels decreased continuously and peroxide levels increased until they reached a plateau between 150 and 250 mmol/kg. Viscosities increased very slowly, initially up to about 0.5 cSt, and more rapidly thereafter [15]. Viscosities of RME and SME, which were not destabilised, remained constant initially, and then they increased very rapidly.

Change in the rate of peroxide formation has been used for the determination of accelerated storage induction time in lard and tallow stabilised with synthetic antioxidants [16]. However changes in peroxide rates could not be determined accurately from the data obtained in the present work. On the other hand, it was possible to determine tocopherol deactivation times accurately from the linear regression of tocopherol deactivation, and it was shown before that no secondary oxidation of lipids such as dimerization occurs while antioxidants are present [17]. Furthermore, when 90–100% of the tocopherols were deactivated, viscosity increased by about 0.5 cSt (Table 3) and more rapidly thereafter. Hence the time to reach a viscosity increase of 0.5 cSt could also be used as accelerated storage induction time. Considering that tocopherols were evaluated partly by comparing tocopherol-free methyl esters to methyl esters with added tocopherols, viscosity-based accelerated storage induction times were used in the present work. There is a good correlation ($R^2 = 0.98$) between tocopherol deactivation and accelerated storage induction times.

Accelerated storage induction times were consistent with the thermal induction times obtained. Again α- was less effective than δ-tocopherol, and induction time increased with concentration of the antioxidant (Table 4). However accelerated storage induction times also indicated that the two antioxidants are effective in SME at 250–500 mg/kg. In addition, they showed that there is concentration for each tocopherol, 1,000 mg/kg for α- and 500 mg/kg for δ-tocopherol, above which increase in concentration produces only a small gain in stability. Furthermore the differences between the accelerated storage induction times of SME, RME, RVOME were also considerably smaller than the differences between thermal induction times. Viscosity increase obtained with γ-tocopherol in destabilised SME did not show a consistent trend, and it was not possible to determine accelerated storage induction times.

Stabilisation of Biodiesel Grade Methyl Esters with Tocopherols

Considering that only destabilised methyl esters and purified tocopherols were used for the evaluation of tocopherols, the

Table 4 Accelerated storage induction times (days) of methyl esters with different tocopherols

mg/kg	SME		RME	RVOME	TME
	αT	δT	δT	δT	δT
250	1.5 (1.5)[a]	3.3 (4.7)	–	–	–
500	2.1 (2.2)	7.2 (7.1)	–	–	–
1,000	6.5 (7.0)	8.0 (8.7)	8.5 (9.3)	9.5 (12.5)	30+
2,000	7.0 (8.0)	9.0 (9.3)	–	–	–
0	1.0	1.0	1.3	1.2	1.0

[a] Tocopherol deactivation time is given in parentheses

Table 3 Viscosity increase and tocopherol levels of SME with added tocopherols

Days[a]	α-Tocopherol (1,000 mg/kg)			α-Tocopherol (2,000 mg/kg)			α-Tocopherol (250 mg/kg)			α-Tocopherol (500 mg/kg)		
	$\Delta V1$[b]	$\Delta V2$[c]	α–T[d]	$\Delta V1$	$\Delta V2$	α-T[d]	$\Delta V1$	$\Delta V2$	δ-T[d]	$\Delta V1$	$\Delta V2$	δ-T[d]
1	0.00	0.00	485	0.05	0.05	1,074	0. 12	0.12	66	0.06	0.06	384
2	0.06	0.06	383	0.12	0.07	869	0.28	0.16	47	0.10	0.10	229
3	0.12	0.06	346	0.22	0.10	728	0.34	0.06	39	0.11	0.01	217
4	0.22	0.10	287	0.32	0.10	418	**0.89**	0.55	11	0.21	0.10	93
5	0.24	0.02	160	0.40	0.08	418	0.96	0.07	ND	0.22	0.00	89
6	0.26	0.02	78	0.46	0.06	300	1.72	0.76	ND	0.36	0.12	52
7	**0.77**	0.51	ND	0.49	0.03	281	2.39	0.67	ND	0.43	0.07	43
8	1.75	0.98	ND	**0.80**	0.31	15	3.71	1.32	ND	**0.77**	0.34	17

ND not detected

[a] No. of days at 60 °C

[b] Cumulative viscosity increase (cSt), i.e. viscosity at day *n* – initial viscosity, $\Delta V1 > 0.5$ in bold

[c] Daily viscosity increase (cSt), i.e. viscosity at day *n* – viscosity at day n – 1

[d] Tocopherol level (mg/kg)

Table 5 Induction times of methyl esters with added Vita Blend tocopherol mixtures

Methyl ester	Amounts of γ-tocopherol (mg/kg)	Thermal induction time (h)	Acc. storage induction time (days)
SME	None	0.50	2.5
SME	500	0.18	5.0 (5.0)[a]
SME	1,000	2.31	7.5 (7.0)
RVOME	None	5.40	8.0
RVOME	500	13.0	15.0 (17.0)
TME	None	11.9	2
TME	500	25.5	20+

[a] Tocopherol deactivation time is given in parentheses

stabilisation of biodiesel grade methyl esters with a commercial tocopherol mixture was also examined. The methyl esters evaluated were RVOME, TME and SME, because the former two have no natural tocopherols, and SME is probably the least stable of the methyl esters used as biodiesel [5]. The commercial tocopherol mixture (Vita Blend) used here contained 43% γ- and 7% δ-tocopherol in rapeseed oil. Methyl esters were prepared from raw materials normally used for the manufacturing of biodiesel grade methyl esters, namely raw sunflower oil, commercial tallow and commercial recycled vegetable oil, and they were not destabilised.

The tocopherol mixture had a very pronounced stabilising effect on the three methyl esters. Addition of a tocopherol mixture equivalent to 500 mg/kg γ-tocopherol more than doubled the thermal induction times of both TME, RVOME (Table 5). The same amount of γ-tocopherol had little effect on SME, but 1,000 mg/kg increased the thermal induction time from 0.1 to 2.3 h (Table 5). The doubling of induction times with the addition of 1,000 mg/kg γ- tocopherol to RVOME in a commercial mixture has been reported [5]. Thermal induction times of TME were longer with 500 mg/kg γ-tocopherol added as commercial mixture than with 1,000 mg/kg of pure γ-tocopherol (25.5 vs. 20.1 h), probably because the methyl esters were not destabilised before the addition of the tocopherol mixture.

Stabilisation of the methyl esters with the commercial tocopherol mixture was also indicated by the accelerated storage induction times. Addition of 500 mg/kg γ-tocopherol to RVOME doubled its accelerated storage induction time, and increased that of TME by a factor of ten (Table 5). Unlike thermal induction time however, accelerated storage induction time also indicated that SME was stabilised by 500 mg/kg γ-tocopherol (Table 5). Addition of 500 mg/kg γ-tocopherol to SME doubled its accelerated storage induction time, and 1,000 kg/mg increased it by a further 50%.

Determination of Methyl Ester Stability

While the order of stabilisation of methyl esters with added tocopherols was the same with both thermal and accelerated storage induction times, there is no linear correlation between the two sets of values. In order to have good linear correlation, the ratios between the two induction times should be about the same for each methyl ester. However ratios between the two induction times ranged from 0.13 for SME to 1.3 for TME, hence the poor correlation. The ratios vary probably because the two induction times determine two different stages of oxidation, thermal induction time the formation of volatile aldehydes, and accelerated storage induction time the beginning of rapid dimerization (i.e. rapid viscosity increase), which occurs later [18]. The relative times of these two stages of oxidation are not necessarily the same for each methyl esters.

Accelerated storage induction time is probably a more realistic parameter of methyl ester storage stability than thermal induction time, as it corresponds to the time elapsed before the beginning of rapid dimerization or irreversible oxidation, under conditions similar to normal storage. However determination of accelerated storage induction time, involving 8–10 days storage of the particular sample followed by tocopherol or viscosity determinations, is not a suitable method in its present form for routine determinations of stability. On the other hand thermal induction times can be determined rapidly with good precision by the Rancimat apparatus used here, or other similar instruments, hence at present it is a more convenient stability parameter for biodiesel than accelerated storage induction time.

Effect of Tocopherols on Methyl Esters

Data obtained in the present work show that naturally occurring tocopherols stabilise methyl esters by reducing the rates of peroxide formation (Table 6). Peroxide rates of methyl esters stabilised with tocopherols are consistent with both induction times, peroxide rates decrease as induction times increase, and α- is less effective in reducing peroxide rates than δ-tocopherol, and rate reduction is less effective above optimum tocopherol concentrations. There is also some correlation ($R^2 = 0.7$) between peroxide rates and accelerated storage induction times. Generally a peroxide level of about 50–120 mg/kg (depending on methyl ester and tocopherol) needs to be reached before secondary oxidation, i.e. rapid increase of viscosity, begins. Therefore by reducing peroxide rates, tocopherols delay secondary oxidation of methyl esters.

Differences in antioxidant activity and optimum tocopherol concentrations can be explained in terms of side reactions which occur alongside antioxidation, and the

Table 6 Rates of peroxide formation and tocopherol deactivation of methyl esters with added tocopherols

mg/kg	SME (mmol/kg/day)			RME (mmol/kg/day)	RVOME (mmol/kg/day)	TME (mmol/kg/day)
	αT	δT	γT[a]	δT	δT	δT
0	120	120	120	48	45	19.5
250	44.0 (167)[b]	18.2 (55)	–	–	–	–
500	28.0 (227)	9.8 (70)	9.6 (100)	–	–	–
1,000	14.2 (143)	8.3 (115)	4.4 (142)	2.7 (107)	2.2 (80)	0 (46)
2,000	12.5 (250)	6.2 (215)	–	–	–	–

[a] Added in Vita Blend tocopherol mixture

[b] Average tocopherol deactivation rates (mg/kg/day) are given in parentheses

reported rate equation for peroxide formation in lipids with antioxidant [18]. It has been shown that consumption of tocopherol during atmospheric oxidation of sunflower and soybean oil increased with initial tocopherol concentration, and the increased consumption has been attributed to side reactions [19, 20]. Similarly, in the present work rates of tocopherol deactivation in SME indicated that tocopherol consumption in general increased with initial antioxidant concentration (Table 6), which can be also attributed to side reactions. The loss of tocopherol to side reactions can be included in the reported rate equation for peroxide formation [18] in lipids with antioxidant (1), to give the modified rate equation (2). Thus

$$\frac{\mathrm{dROOH}}{\mathrm{d}t} = k\frac{(\mathrm{ROOH})}{(A)} \quad (1)$$

$$\frac{\mathrm{dROOH}}{\mathrm{d}t} = \frac{k_1}{(1-x)(A)} \quad (2)$$

where (A) is the initial tocopherol concentration, x is the fraction of tocopherol lost to side reactions and k_1 is the product of the rate constant k in (1) and the initial peroxide concentration (ROOH) which is constant.

The modified rate equation shows that differences between tocopherols in the inhibition of peroxide formation must be due to side reactions. Both tocopherol consumption after 7 days [19], and tocopherol deactivation rates (Table 6) indicate that α-tocopherol is consumed faster by side reactions than either the γ- or δ- homologue, which is expected on account of its lower redox potential [21]. Faster tocopherol consumption implies that during oxidation of SME a larger fraction of α- than of either γ- or δ-tocopherol must be consumed by side reactions, which according to (2) will result higher rate of peroxide formation at the same initial concentration of antioxidant.

Gradual reduction of peroxide formation rates with increasing initial tocopherol concentrations, and optimum (threshold) tocopherol concentrations, can be also explained by the modified rate equation for peroxide formation (2). Data obtained in the present work show that the rates of peroxide formation are more or less inversely proportional to the initial tocopherol concentration, below 500 and 1,000 mg/kg δ- and α-tocopherol respectively in SME, i.e. peroxide rates are halved with each doubling of initial tocopherol concentration (Table 6). According to rate equation (2) as long as there are no side reactions ($x = 0$) or the fraction of tocopherol consumed by the same remains constant ($x = c$), initial tocopherol concentrations will be inversely proportional to peroxide formation rates. Thus below the initial concentrations of 500 and 1,000 mg/kg δ- and α-tocopherol respectively, usually referred to as optimum antioxidant concentrations, the rates of side reactions must remain constant, or tocopherol must not consumed by side reactions.

Above the optimum tocopherol concentration, peroxide rates were reduced only by 10–20% with each doubling of the initial tocopherol concentration, and they were no longer inversely proportional to the increased concentrations (Table 6). The modified rate equation (2) indicates that the rate of peroxide formation diminishes with increasing initial tocopherol concentration, when the fraction of tocopherol consumed by side reactions is no longer constant, and it increases with concentration. Accordingly, diminishing antioxidant activity above optimum tocopherol concentrations must be due to an increasing loss of tocopherol to side reactions, as the initial concentration of the antioxidant increases. Thus the fraction of tocopherol available as antioxidant will be reduced with increasing initial tocopherol concentration, and the additional antioxidant effect of higher tocopherol concentration will be diminished. Side reactions, whereby the tocopheryl radical participates in chain propagation reactions, which consume additional tocopherol, also referred to as prooxidant effect, were proposed to explain reduction in antioxidant activity at higher tocopherol concentration [8, 20, 22, 23]. The differences between optimum concentrations of α- and δ-tocopherols, observed in the present work cannot be explained adequately without investigation of the side reactions.

Importance of Tocopherols in Biodiesel

Both stability parameters used in the present work, thermal and accelerated storage induction times, indicate that tocopherols stabilise biodiesel grade fatty acid methyl esters.

The stabilising effect was found to depend on the type and concentration of tocopherols, and on the composition of the particular methyl ester (Tables 2, 4). Thus considering that tocopherols are present in vegetable oils used for biodiesel production, it will be necessary to ensure that they are not deactivated during esterification. Also tocopherols can be used to stabilise RVOME and TME, which contain no natural antioxidants. Addition of γ-tocopherol stabilised both RVOME (Table 5) and unstable TME (Table 2) sufficiently to meet the 6 h thermal induction time specified EU biodiesel standard EN 14214. Addition of tocopherols to SME however did not produce the specified thermal induction time (Tables 2, 5), and a synthetic antioxidant [5] needs to be used to obtain the required stability.

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