Available online at www.sciencedirect.com
SCIENCE DIRECT
Fuel 85 (2006) 867–870
FUEL
www.fuelfirst.com

Short Communication

The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel

Yung Chee Liang [a,b], Choo Yuen May [a,*], Cheng Sit Foon [a,b], Ma Ah Ngan [a], Chuah Cheng Hock [b], Yusof Basiron [a]

[a] *Engineering and Processing Research Division, Malaysian Palm Oil Board (MPOB), P.O. BOX 10620, 50720 Kuala Lumpur, Malaysia*
[b] *Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Received 17 May 2005; received in revised form 4 September 2005; accepted 4 September 2005
Available online 27 September 2005

Abstract

Crude and distilled palm oil methyl esters conveniently known as palm diesel have been successfully evaluated as diesel substitute. Crude palm oil methyl esters are produced from transesterification of crude palm oil with minor components such as carotenes and vitamin E still intact and they are reddish in colour. The distilled palm oil methyl esters are obtained after the recovery of minor components (e.g. Carotenes and vitamin E) From the crude palm oil methyl esters. These valuable minor components are preferably to be recovered as they can be sold as value-added products before they are burnt together with the methyl esters as fuel. Although both possesses fuel characteristics which are comparable to those of petroleum diesel, crude palm oil methyl esters are found to exhibit better oxidative stability (rancimat induction period >25 h) than distilled palm oil methyl esters (about 3.5 h). It is attributed to the presence of vitamin E (about 600 ppm), a natural antioxidant in the former. While the distilled palm oil methyl esters contain practically no vitamin E (<50 ppm) and as a result, they exhibit poor oxidative stability. Thus, the crude palm oil methyl esters meet the european standard for biodiesel (EN 14214) which has set a minimum rancimat induction period of 6 h. In the present study, research was conducted to enhance the oxidative stability of distilled palm oil methyl esters in order to meet the aforementioned standard. Natural and synthetic antioxidants were used in the present study to investigate their effect on the oxidative stability of distilled palm oil methyl esters. It was found that both types of antioxidant showed beneficial effects in inhibiting the oxidation of distilled palm oil methyl esters. Comparatively, the synthetic antioxidants were found to be more effective than the natural antioxidants as lower dosage (17 times less) was needed to achieve the minimum rancimat induction period of 6 h.

Keywords: Oxidative stability; Antioxidants; Palm oil methyl esters

1. Introduction

Biodiesel is defined as mono alkyl esters derived from vegetable oils or animal fats. It is an alternative fuel for diesel engines. Biodiesel exhibits comparable fuel properties compared with conventional petroleum diesel [1–3]. Biodiesel provides enhanced lubricity properties and produces low exhaust emissions, such as particulate matter, polycyclic aromatic hydrocarbons, carbon dioxide, sulphur dioxide and smoke [4,5].

However, biodiesel is susceptible to oxidation. The oxidative stability test on methyl and ethyl esters of sunflower oil showed that methyl esters showed slightly better stability than ethyl esters [6]. Storage behaviour for these esters was also evaluated at different storage conditions for a period of 90 days. Deterioration study of various biodiesel e.g. rapeseed oil methyl esters, used frying oil methyl esters, tallow methyl esters, sunflower oil methyl esters under different storage conditions were also investigated [7–10]. It was found that the kinematic viscosity, peroxidae value and acid value increased over storage. Recommendations from these studies are that fatty acid esters fuels should be stored in airtight, rust free mild steel container and the storage temperature should be less than 30 °C.

The recent published European standard for biodiesel (EN 14214) has set a lower limit of 6 h as the minimum Rancimat induction period [11]. A standard method of determination of oxidation stability of fatty acid methyl esters using accelerated oxidation test has been established (EN 14112). The usage of natural and synthetic antioxidants to retard the oxidative degradation or increase the Rancimat

* Corresponding author. Tel.: +60 3 89259592; fax: +60 3 89262971.
E-mail address: choo@mpob.gov.my (C.Y. May).

0016-2361/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2005.09.003

induction period of both distilled and/or undistilled biodiesel were studied [12–15]. It was reported that different types of antioxidant have different enhancement effects on different types of biodiesel.

In this paper, the oxidative stability of crude palm oil methyl esters (CPOME) and distilled palm oil methyl esters (DPOME) were investigated using Rancimat test (EN 14112) as recommended in the EN 14214. Study on the effect of antioxidants on DPOME was also conducted.

2. Experimental

2.1. Materials

Crude palm oil methyl esters (CPOME) were produced from transesterification of crude palm oil with minor components such as carotenes and vitamin E still intact and it is reddish in colour [16]. The distilled palm oil methyl esters (DPOME) were obtained after the recovery of minor components (e.g. carotenes and vitamin E) from the CPOME. Butylated hydroxyltoluene (BHT) (Barcelona, Spain) and tert-butyl hydroquinone (TBHQ) (Singapore) were complimentary from Degussa Fine Chemicals and SUKA Chemicals Sdn. Bhd., respectively. The α-tocopherol (α-T) (Missouri, USA) was purchased from Sigma–Aldrich (M) Sdn. Bhd.

2.2. Determination of fatty acid composition (FAC) of biodiesel samples by gas chromatography

The fatty acid composition (FAC) of palm oil methyl esters were analysed using MPOB test method [17]. The methyl esters samples were prepared by diluting 0.02 g methyl esters with 1.5 ml hexane in a small vial. 2 μl of the diluted sample was injected into a Perkin–Elmer GC equipped with a flame ionisation detector (FID) for FAC analysis. Identification of each peak was done by comparison with external standard reference mixture of fatty acid methyl esters. The concentrations of the identified peaks were added as an absolute value. The percentages of each peaks/methyl esters were calculated based on this absolute value.

2.3. Determination of concentration of carotenes and vitamin E

The concentration of carotenes and vitamin E in the CPOME and DPOME was pre-determined before subjecting the respective samples to Rancimat test. Carotenes content in the samples were analysed by ultraviolet–visible (UV–vis) spectrophotometer at 446 nm using MPOB test method [18]. The carotene content of palm oil methyl esters is defined and calculated as β-carotene in parts per milliom (ppm). While the vitamin E content was determined using high performance liquid chromatography (HPLC). The following conditions were used: Lichrosorb analytical silica column (25×0.46 cm ID, stainless steel, 5 μm), solvent system was n-hexane: THF: 2-propanol (1000:50:3 v/v/v) with flow rate at 1.0 ml/min and a Waters 470 Fluorescence detector at 295 nm excitation and 325 nm emission.

2.4. Determination of oxidative stability

Oxidative stability of CPOME and DPOME with and without addition of antioxidant additives were analysed according to Rancimat method using Metrohm 743 Rancimat (Herisau, Switzerland) instrument. Samples of 3 g were analysed under heating block temperature of 110 °C and constant air flow of 10 L/h. The temperature correction factor ΔT was set to 1.5 °C as recommended by Metrohm. All determinations were performed in duplicate and the mean value is reported.

3. Results and discussion

Rancimat test is the specified standard method for oxidative stability testing for biodiesel sample in accordance to EN 14214. In food chemistry, Rancimat test is a test known to determine the oxidative stability by considering the Rancimat induction period (RIP). The RIP values represent the stability of the sample. The greater the RIP value, the sample is less susceptible towards oxidation.

Table 1 shows that the fatty acid compositions for both CPOME and DPOME are similar to each other. These two biodiesel also possess similar fuel properties as shown in Table 2. However, CPOME were found to exhibit much better oxidative stability (RIP >25 h) than DPOME (RIP about 3.5 h). There was no difference noted between the two samples except the former contains 644 ppm of vitamin E (α-tocopherol, 119 ppm; α-tocotrienol, 113 ppm; γ-tocotrienol, 352 ppm; δ-tocotrienol, 70 ppm) and 711 ppm β-carotene while the latter contains practically none (less than 50 ppm). Vitamin E is a known natural antioxidant and β-carotene possesses biological antioxidant activity [19]. They both contribute to the good oxidative stability property of CPOME. As a result, no antioxidant was needed when using CPOME as diesel substitute as the lower limit of oxidative stability as specified in EN 14214 can be met.

DPOME, on the other hand, does not meet the oxidative stability specification of the aforementioned standard. Thus, an antioxidant must be added to enhance their RIP. In the present study, three antioxidants namely α-tocopherol (α-T), butylated hydroxytoluene (BHT) and tert-butyl hydroquinone (TBHQ), were used to study their effect on DPOME (Fig. 1).

Table 1
Fatty acid compositions (FAC) of crude palm oil methyl ester (CPOME) and distilled palm oil methyl ester (DPOME)

Fatty acid composition (%)	Crude palm oil methyl ester (CPOME)	Distilled palm oil methyl ester (DPOME)
C12:0-Methyl laurate	0.26	0.38
C14:0-Methyl myristate	1.09	0.98
C16:0-Methyl palmitate	44.81	43.32
C16:1-Methyl palmitoleate	0.20	0.20
C18:0-Methyl stearate	4.09	3.81
C18:1-Methyl oleate	39.99	40.57
C18:2-Methyl linoleic	8.94	10.25
C18:3-Methyl linolenic	0.27	0.25
C20:0-Methyl arachidate	0.35	0.24

Table 2
Key fuel properties of biodiesel samples

Fuel property	Method	Unit	CPOME	DPOME	EN 14214
Density at 15 °C	ASTM D4052	kg/L	0.8749	0.8783	0.86–0.90
Viscosity at 40 °C	ASTM D445	mm^2/s	4.502	4.415	3.50–5.00
Flash point	ASTM D93	°C	174	182	120 (min.)
Sulfated ash	ASTM D482	% Mass	0.009	0.007	0.02 (max.)
Sulfur	ASTM D4294	mg/kg	<10	<10	10 (max.)
Copper strip corrosion	ASTM D130	Rating	1a	1a	Class 1
Cetane number	ASTM D613	–	62.4	58.3	51.0 (min.)
Cloud point	ASTM D2500	°C	14.5	13.6	–
Pour point	ASTM D97	°C	15	15	–
Carbon residue (on 10% distillation residue)	ASTM D4530	% Mass	0.02	0.02	0.30 (max.)
Acid number	ASTM D664	mg KOH/g	0.08	0.08	0.50 (max.)
Gross heat of combustion	ASTM D240	MJ/kg	40.135	39.825	–
Oxidative Stability at 110 °C	EN 14112	h	25.70	3.52	6.0 (min.)

EN14214-European standard for biodiesel

	R1	R2	R3
Alpha-tocopherol, alpha-tocotrienol	CH_3	CH_3	CH_3
Beta-tocopherol, beta-tocotrienol	CH_3	H	CH_3
Gamma-tocopherol, gamma-tocotrienol	H	CH_3	CH_3
Delta-tocopherol, delta-tocotrienol	H	H	CH_3

The RIPs of DPOME with and without antioxidant were shown in Fig. 2 and Table 3.

Results obtained show that α-T can be used as antioxidant to improve the oxidative stability of DPOME. The RIP of DPOME was increased gradually from 3.52 h to 6.42 and 11.2 h when 1000 and 3000 ppm α-T was added respectively (Fig. 2). Thus, approximately 0.1% of α-T sufficed to meet the European biodiesel specification in terms of oxidative stability of 6 h.

BHT offers better antioxidant properties than α-T for DPOME (Fig. 2) as lower dosage was needed to achieved the same RIP. Result shows that low dosage i.e. 50 ppm (wt/wt) of BHT is able to improve the oxidative stability of DPOME from 3.52 to 6.17 h. Thus, only 50 ppm of BHT was needed to enhance the RIP to above 6 h as required by the european biodiesel standard. The RIP of DPOME was further increased linearly to 7.75, 13.10 and 16.60 h when the dosage of BHT was increased to 100, 500 ppm and finally, 1000 ppm.

TBHQ offered the best performance by increasing the RIP of DPOME significantly although it was used in a small amount as compared to α-T and BHT. A dosage of 50 ppm (wt/wt) of TBHQ improved the RIP of DPOME by more than 5 h, from 3.52 to 8.85 h. RIP of 12.1 and 30.2 h were recorded when 100 and 500 ppm (wt/wt) of TBHQ was engaged, respectively (Fig. 2 and Table 3). Using dosage of 1000 ppm and above, DPOME became stable against oxidation with RIP greater than 48 h.

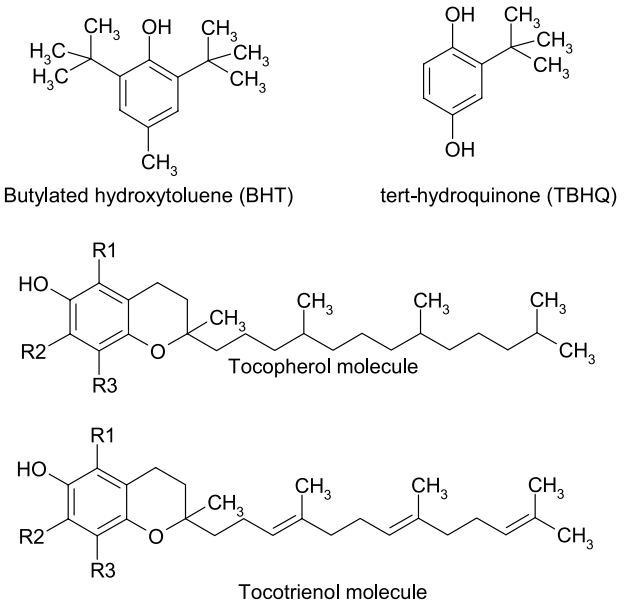

Fig. 1. Chemical structures of antioxidants.

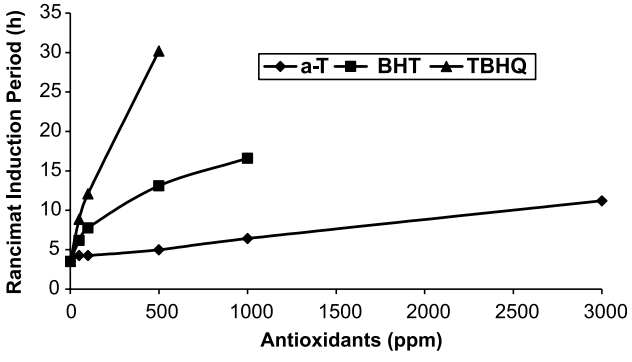

Fig. 2. Oxidative stability of distilled palm oil methyl ester (DPOME) at 110 °C. α-T: α-Tocopherol, BHT, butylated hydroxyltoluene; TBHQ, tert-butyl hydroquinone. Test condition: temperature at 110 °C, flow rate of air at 10 L/h.

TABLE 3
Effect of natural and synthetic antioxidants on oxidative stability of palm oil methyl esters (palm diesel)

Palm diesel sample	Vitamin E (ppm)	Dosage of antioxidants (ppm)			Rancimat induction period (h)
		α-T	BHT	TBHQ	
CPOME	644[a]	–	–	–	25.70
	0	–	–	–	3.52
DPOME	0	1000	–	–	6.17
	0	–	50	–	6.42
	0	–	–	50	8.85

CPOME, crude palm oil methyl esters; DPOME, distilled palm oil methyl esters; α-T, α-Tocopherol; α-T3, α-tocotrienol; γ-T3, γ-tocotrienol; δ-T3, δ-tocotrienol; BHT, butylated hydroxyltoluene; TBHQ, tert-butyl hydroquinone.

[a] α-T, 119 pm; α-T3, 113 ppm; γ-T3, 352 ppm; δ-T3, 70 ppm.

In the present study, synthetic antioxidant BHT and TBHQ shown better antioxidant property than natural antioxidant α-tocopherol. When compared BHT with TBHQ, TBHQ was found to display better effectiveness on enhancing the RIP of DPOME. Antioxidant is a chemical that delays the start or slows the rate of lipid oxidation reaction. It inhibits the formation of free radicals or interrupts the propagation of free radical and hence contributes to the stabilisation of the lipid sample. The antioxidant property of TBHQ is greater than BHT. This can be explained based on their molecular structures, which the former possesses two OH groups attached to the aromatic ring while the latter possesses only one OH group attached to the aromatic ring. Thus, TBHQ offers more sites for the formation of complex between free radical and antioxidant radical for lipid stabilisation purpose. Hence, TBHQ is more effective compared to BHT at the same dosage.

4. Conclusion

CPOME containing not less than 600 ppm of vitamin E were found to exhibit oxidative stability of more than 6 h and thus, conform to the specification of the European standard for biodiesel (EN 14214). While DPOME need to be treated with antioxidants in order to meet the specification. Synthetic antioxidants, namely BHT and TBHQ are found to be more effective than natural antioxidant, α-T in terms of their performance to enhance the RIP of DPOME. The RIP of DPOME increases drastically with small increments of the amount of TBHQ used (less than 0.1%). It can be concluded that the efficiency of antioxidants investigated in the present study was as follows: TBHQ > BHT > α-tocopherol.

Acknowledgements

The authors wish to thank JJ-Degussa Chemicals (M) Sdn. Bhd. and SUKA Chemicals (M) Sdn. Bhd. for their complimentary of BHT and TBHQ samples, respectively. Thanks are also given to the staff of processing group for their technical assistance.

References

[1] Ali Y, Hanna MA, Cuppett SL. Fuel properties of tallow and soybean oil esters. J Am Oil Chem Soc 1995;72:1557–64.
[2] Choo YM, Ma AN, Basiron Yusof. Preparation and evaluation of palm oil Methyl esters as diesel substitute. ELAEIS 1995;15:22. Special Issue.
[3] Clark SJ, Wagner L, Schrock MD, Piennaar PG. Methyl and Ethyl soybean esters as renewable fuels for diesel engines. J Am Oil Chem Soc 1984;61:1632–8.
[4] Drown DC, Harper K, Frame E. Screening vegetable oil alcohol esters as fuel lubricity enhancers. J Am Oil Chem Soc 2001;78:579–84.
[5] Chang DYZ, Gerpen JHV. Fuel properties and emissions of soybean oil esters as diesel fuel. J Am Oil Chem Soc 1996;73:1549–55.
[6] Du Plessis LM, De Villers JBM, Van der Walt WH. Stability studies on Methyl and Ethyl fatty acid esters of sunflower oil. J Am Oil Chem Soc 1985;62:748–52.
[7] Bondioli P, Gasparoli A, Lanzani A, Fedeli E. Storage stability of biodiesel. J Am Oil Chem Soc 1995;72:699–702.
[8] Mittelbach M, Gangl S. Long storage stability of biodiesel made from rapeseed and used frying oil. J Am Oil Chem Soc 2001;78:573–7.
[9] Dunn RO. Effect of oxidation under accelerated conditions on fuel properties of Methyl soyate (biodiesel). J Am Oil Chem Soc 2002;79: 915–20.
[10] Bondioli P, Gasparoli A, Bella LD, Taglibue S. Evaluation of biodiesel storage stability using reference methods. Eur J Lipid Sci Technol 2002; 104:777–84.
[11] Bockey D. Biodiesel Production and Marketing in Germany: The Situation and Perspective. Union Zur Föderung Von Oel-Und Proteinpflanzen E.V. 2002.
[12] Mittelbach M, Schober S. The influence of antioxidants on the oxidation stability of biodiesel. J Am Oil Chem Soc 2003;80:817–23.
[13] Lacoste F, Lagardere L. Quality parameters evolution during biodiesel oxidation using rancemat test. Eur J Lipid Sci Technol 2003;105:149–55.
[14] Bondioli P, Gasparoli A, Bella LD. Biodiesel stability under commercial storage conditions over one tear. Eur J Lipid Sci Technol 2003;105: 735–41.
[15] Schober S, Mittelbach M. The impact of antioxidants on biodiesel oxidation stability. Eur J Lipid Sci Technol 2004;106:382–9.
[16] Choo YM. Transesterification of palm oil: effect of reaction parameters. J Oil Palm Res 2004;16:1–11.
[17] Malaysian Palm Oil Board (MPOB). Determination of fatty acid composition (FAC) as their Methyl esters by capillary column gas chromatography. MPOB Test Method 2005;310–7.
[18] Malaysian Palm Oil Board (MPOB). Determination of carotene content. MPOB Test Method 2005;194–7.
[19] Malaysian Palm Oil Promotion Council. An Endorsement on Health, Nutrition and Palm Oil. 2000.