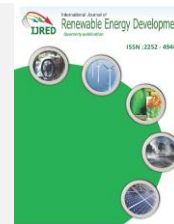




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Antioxidant Effect on Oxidation Stability of Blend Fish Oil Biodiesel with Vegetable Oil Biodiesel and Petroleum Diesel Fuel

M. Hossain^{a*}, S.M.A. Sujan^b and M.S. Jamal^b

^aBCSIR Laboratories, Dhaka, Bangladesh Council of Scientific and Industrial Research, BANGLADESH

^bInstitute of Fuel Research and Development, Bangladesh Council of Scientific and Industrial Research, Dhaka-1205, BANGLADESH

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ABSTRACT: Two different phenolic synthetic antioxidants were used to improve the oxidation stability of fish oil biodiesel blends with vegetable oil biodiesel and petroleum diesel. Butylhydroxytoluene (BHT) most effective for improvement of the oxidation stability of petro diesel, whereas tert-butylhydroquinone (TBHQ) showed good performance in fish oil biodiesel. Fish oil/Rapeseed oil biodiesel mixed showed some acceptable results in higher concentration of antioxidants. TBHQ showed better oxidation stability than BHT in B100 composition. In fish oil biodiesel/diesel mixed fuel, BHT was more effective antioxidant than TBHQ to increase oxidation stability because BHT is more soluble than TBHQ. The stability behavior of biodiesel/diesel blends with the employment of the modified Rancimat method (EN 15751). The performance of antioxidants was evaluated for treating fish oil biodiesel/Rapeseed oil biodiesel for B100, and blends with two type diesel fuel (deep sulfurization diesel and automotive ultra-low sulfur or zero sulfur diesels). The examined blends were in proportions of 5, 10, 15, and 20% by volume of fish oil biodiesel.

Keywords: antioxidants, blending, fish oil biodiesel, oxidation stability

1. Introduction

To meet the energy demand and reduce the global warming, biodiesel is able to attract the key attention as an alternative fuel source of renewable energy section which will be replacement of fossil fuel. In the concern of global warming green fuel can play main rule to reduce greenhouse gases emission. For the future fuel security and reduce greenhouse gases, biodiesel is an automatic choice. Generally biodiesel are produced through transesterification reaction derived from animal fat, waste cooking oil, different kinds of non-edible and edible oil source. Biodiesel from edible oil is difficult for food security that's why we generally chose non-edible oil source or waste materials. In this case fish oil from fish waste is the most acceptable alternative source as waste material in fish based country. Different parts of fish without meat are being used for oil production. Qualities of fish oil such as the

oxidation stability and cold flow properties are the most important factors for commercial utilization. Fish oil biodiesel consists large number of polyunsaturated carbon carbon double bonds which is prone to oxidation rapidly. Oxidative reactivity is determined by amount of and configuration of the olefinic unsaturation on the fatty acid chains. Methylene-interrupted fatty acids chain rather than conjugated are exist in many of the plant-derived fatty oils. As expected, fatty oils that contain more polyunsaturation are more prone to oxidation (Neff *et al.* 1994; Knothe *et al.* 2003). An early study (Gunstone *et al.* 1945) measured the relative rate of oxidation for the methyl esters of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids to be 1:12:25. More recent work has shown that the rate of oxidation of pure unsaturated fatty acids as measured by oxygen consumption in closed systems is proportional to the number of bis-allylic carbons present (Cosgrove *et al.* 1987; Neff *et al.* 1993).

*Corresponding Author: Tel: 8801741511376
Email: mhossain28@yahoo.com

In this experiment, we improved the oxidation stability of fish oil biodiesel using conventional method such as addition of antioxidant and blending with vegetable oil biodiesel and petroleum diesel. BHT and TBHQ antioxidants were used as anti oxidants because; BHT is more effective antioxidant for petroleum diesel and TBHQ for fish oil biodiesel (Hossain *et al.* 2010).

2. Material and Methods

2.1 Input data

Fish oil which contains higher number of poly unsaturated fatty acid was collected from Sanki Fish Oil Company, Japan. For B100 (100% biodiesel) blending, vegetable oil biodiesel such as rapeseed oil biodiesel were used because of the absence of natural antioxidant in rapeseed oil. The mixture of fish oil and rapeseed oil biodiesel were used to prepare B100 by using two different weight ratios of fish oil/rapeseed oil biodiesel 4:96 and 10:90 respectively. Making B5, B10, B15 and B20 fish oil biodiesel blends with two kinds of

petroleum diesel fuel (ultra-low sulfur or zero sulfur and deep sulfurization diesel) were used for this research. Butylhydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) antioxidant additives were purchased from WAKO Chemicals Company, Japan. All chemicals and reagents used in this research were analytical grade and purchased from WAKO Chemicals Company, Japan.

2.2 Methods

2.2.1 Transesterification

Fish oil biodiesel were produced by well known reaction transesterification (Fig.1 (a) and (b)). Transesterification reaction was carried out in the separable reaction flask with 10:3:0.5 weight ratio of fish oil, methanol, and KOH for 2 hours at 60°C. All biodiesel blend samples were analyzed according to EN 14214, published by the European Standard Organization (CEN). The main properties of fish oil biodiesel and the test methods used are shown in Table 1.



(a)



(b)

Fig. 1 Transesterification of fish oil (a); Fish oil biodiesel (b)

Tabel 1

Main properties of fish oil biodiesel

Parameters	Units	Results	Test method
Fatty acid methyl ester	Mass%	97.2	EN14103
Viscosity	mm ² /s	4.5	JIS K2283
Water content	ppm	480	JIS K2275
Oxidation stability	h	0.1	EN 14112
Acid value	mg KOH/g	0.28	JIS 2501
Peroxide value	meq/kg	15.2	1)
Iodine value		153	JIS K0070
Polyunsaturated FAME (≥4 double bonds)	mass%	25.2	EN14103
Pour point	(°C)	2	ASTM D6749-02
Cloud point	(°C)	3	ASTM D2500-05

1) JOCS standard methods for the analysis of fats, oils, and related materials

Tabel 2

Fatty acid composition of RME, FME and blends

FAME Component	RME	FME	FAME	
			FME/RME (4:96)	FME/RME (10:90)
C12:0	0	0.1	0	0
C14:0	0.1	4.5	1.1	1.9
C16:0	4.9	7.9	5.5	9.7
C16:1	0.3	7.1	2.2	3.4
C17:0	0.1	1.4	0.9	1.2
C18:0	1.8	4.7	1.9	2.3
C18:1	63.1	3.8	55.2	42.5
C18:2	19.8	3.3	14.2	12.1
C18:3	7.6	1.0	5.6	4.8
C18:4	0	1.5	0.3	0.5
C20:0	0.7	0.3	0.4	0.3
C20:1	1.2	5.9	2.3	3.1
C20:3	0	1.5	0.5	0.9
C20:5	0	8.0	2.5	3.2
C22:0	0.4	0.2	0.2	0.3
C22:5	0	2.4	1.1	1.6
C22:6	0	16.3	5.6	7.2
C24:0	0.1	0.2	0.1	0.1

2.2.2 Analysis of Biodiesel (FAME) Composition

GC-FID (Agilent 6890N, column: HP-1, length of column: 60m × 0.25mm × 0.25μm) was used for quantification and GC-MS (Agilent 6890N, column: HP-1, length of column: 50m × 0.2mm × 0.11μm) was used for identification of FAME composition. Fatty Acid Methyl Ester (FAME) composition of the fish oil biodiesel and rapeseed oil biodiesel and their blends is shown in Table 2.

2.2.3 Oxidation Stability Determination

The oxidation stability of methyl ester as biodiesel and their blends with vegetable oil biodiesel and petroleum diesel were quantified by Rancimat in the term of induction period (IP). The IP of pure biodiesel was evaluated according to the Rancimat method EN 14112 and the modified Rancimat method EN 15751 for the biodiesel blends. All stability measurements were carried out on a Metrohm 783 Biodiesel Rancimat instrument. Samples of 3 g of pure biodiesel and 7.5 g of biodiesel blends were analyzed under a heating block temperature 110°C, with a temperature correction factor ΔT to be set to 1.5, constant air flow of 10 L/h, passing through the fuel and into a vessel containing distilled water. As soon as volatile organic acids (mainly acetic and formic acids) are formed in the sample, an increase in conductivity in the measuring vessel is indicated. The time that elapses until the secondary oxidation products are detected is known as the induction period. Oxidation stability as induction period was detected when the secondary oxidation products (such as low molecular organic acids) were formed and conductivity increased rapidly in measuring vessel.

2.2.4 Quantification of Solubility of TBHQ and BHT

Antioxidants are usually polar compounds. It is predicted that more polar antioxidants can hardly dissolve in less polar solvent such as petroleum diesel (main components are paraffins and aromatic hydrocarbons). On the basis of this hypothesis, solubility of antioxidant may have influence on the oxidation stability of fish oil methyl ester (FME)/diesel mixture. To clarify the relationship between solubility of antioxidant and oxidation stability of FME/diesel mixture, solubility of TBHQ and BHT were quantified by GC. Since the identification of antioxidants peak contained FAME/diesel mixture in GC chart is too difficult, so tetradecane was used as a model diesel instead of real diesel. Calibration curve for TBHQ was prepared using different concentration of TBHQ solution. Butylhydroxyanisole (BHA) used as an internal standard and pyridine as a solvent. Then FME blended with model diesel tetradecane and made five different blended samples (B0, B5, B10, B20, and B100). Added TBHQ in the blended sample and run into the GC-FID (Agilent 6890N, column: HP-1, length of column: 60m × 0.25mm × 0.25μm) for quantification.

3. Result and Discussion

From Fig. 2, it can be seen that solubility of TBHQ in B0 (tetradecane) is only 24.6 % and this percentage is increasing with increasing of FAME amount in tetradecane. FAME is more polar compound than diesel fuel. Because FAME contains ester functional group has a C=O bond similar character to the ketone and aldehyde functional group. On the other hand TBHQ has two hydroxyl (OH) groups which are more polar than BHT. Solubility of TBHQ increased with increasing FAME concentration because the polarity of the FAME/diesel mixture increased by addition of FAME.

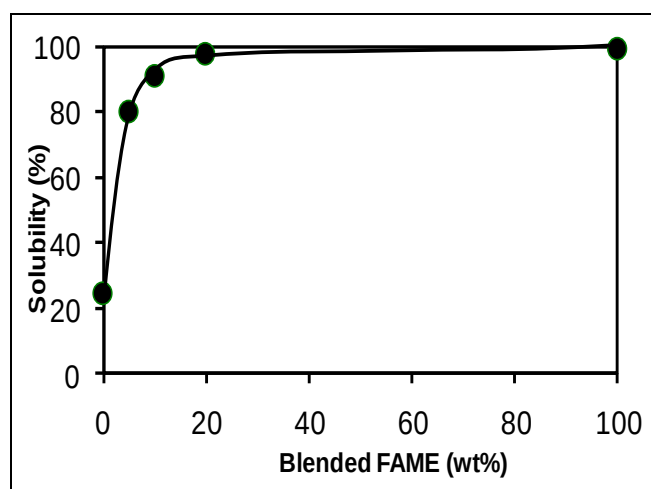
**Fig. 2** Solubility percentage of TBHQ in blended FAME

Fig. 3, shows the solubility of BHT in tetradecane. BHT dissolved very well in any weight percent of FAME because BHT has only one hydroxyl OH⁻ group and is less polar than TBHQ. Therefore, BHT is suitable for improvement of oxidation stability of less FAME blended diesel.

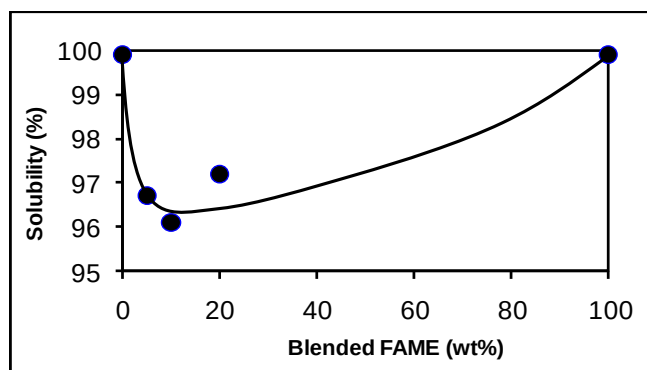


Fig. 3 Solubility percentage of BHT in blended FAME

3.1 Improvement of Oxidation Stability of FME Blended with Other FAME (B100)

To prepare FME mixed biodiesel with relatively high oxidation stability, it might be useful for the mixing of FME with other biodiesel which shows high oxidation stability. In this experiment, rapeseed oil methyl ester (RME) was chosen as a feedstock. Rapeseed oil methyl ester (RME) was blended with FME in two different weight ratios specified as follows; FME/RME; 4:96 and 10:90. Analysis data were given in Table 3 and Table 4. Table 3 shows that oxidation stability of 4wt%FME/RME was 3.0 h. Compared with FME oxidation stability (induction period =0.1 h), it is increased but not enough to reach the target value. Then, antioxidants were added to increase oxidation stability. BHT and TBHQ showed close results in 1000 ppm. But in 2500 ppm, TBHQ was given four times higher oxidation stability than BHT. Very similar results were found in 10wt%FME/RME shown in Table 4.

Tabel 3

Oxidation stability of blended FME (4 wt %) /RME mixture with and without antioxidant

Antioxidant Concentration (ppm)	Induction period (h)	
	BHT	TBHQ
0	3.0	3.0
1000	6.2	7.2
2500	9.4	36.8
5000	12.2	>48.0

Tabel 4

Oxidation stability of blended FME (10 wt %) /RME mixture with and without antioxidant

Antioxidant Concentration (ppm)	Induction period (h)	
	BHT	TBHQ
0	2.5	2.5
1000	5.7	6.2
2500	8.1	23.0
5000	11.2	>24.0

3.2 Effect of Antioxidant on Oxidation Stability of FME Blended with Petroleum Diesel

Table 5, shows the results of oxidation stability as an induction period of 5wt% FME/diesel (B5) which could not meet the biodiesel blended standard oxidation stability (Induction period=20 h (EU temporary), 6 h (ASTM-D7467-09A)) because of the presence of polyunsaturated compounds of FME. The present results confirmed the observation that small amounts of more highly unsaturated FAME have serious influence on oxidation stability of mixed diesel. 100 ppm or above concentration of BHT, enable to realize the more than 20 h oxidation stability of B5 mixed diesel. Interesting result was found in between in FME/sulfur free diesel and FME/ deep sulfurization diesel with BHT. FME/deep sulfurization diesel showed higher induction period due to antioxidant property of sulfur. On the contrary, induction period of FME/ deep sulfurization diesel was less than sulfur free diesel in the case of TBHQ. In addition, lower induction period were found than BHT.

From table 6, TBHQ shows better performance than BHT from the low concentration in 10 wt% FME/diesel (B10). More than 20 h induction period was found in above 250 ppm of BHT and TBHQ. It was noted that TBHQ showed better induction period in FME/sulfur free diesel but lower in deep sulfurization diesel.

FME/diesel mixture with BHT and TBHQ shows lower induction period in 15 wt% FME/diesel (B15) than B5 and B10 (Table 7). FME/diesel mixture with BHT and TBHQ shows lower induction period than B5 and B10 (Table 7). It is clear that BHT in B15 could not meet EN temporary standard value of oxidation stability in the concentration below 250ppm but over the 250ppm antioxidant concentration easily reached the target value.

FME/diesel mixture with BHT and TBHQ shows lower induction period in 20 wt% FME/diesel (B20) than B5, B10 and B15 (Table 8). It is clear that BHT in B20 could not meet EN temporary standard value of oxidation stability in any concentration within the experimental doses limit. In case of TBHQ, only 1000 ppm reached the target value.

From all the experiments, it is clear that better performance was shown in lower amount FME blended by BHT and in higher amount FME blended by TBHQ.

Tabel 5

Oxidation stability of 5wt% FME blended diesel (B5) with antioxidants BHT and TBHQ

Antioxidant concentration (ppm)	Induction Period (h)			
	BHT		TBHQ	
	FME/Sulfur free diesel	FME/440 ppm sulfur diesel	FME/Sulfur free diesel	FME/440 ppm sulfur diesel
0	1.4	1.8	1.4	1.8
100	24.3	28.2	13.7	11.9
250	45.8	>48.0	25.9	21.2
500	>48	>48	46.9	36.0
1000	>48	>48	>48	>48

Tabel 6

Oxidation stability of 10wt% FME blended diesel (B10) with antioxidants BHT and TBHQ

Antioxidant concentration (ppm)	Induction Period (h)			
	BHT		TBHQ	
	FME/Sulfur free diesel	FME/440 ppm sulfur diesel	FME/Sulfur free diesel	FME/440 ppm sulfur diesel
0	1.2	1.5	1.2	1.5
100	10.6	10.8	12.3	9.8
250	21.0	23.3	24.3	18.7
500	35.6	41.6	39.0	31.7
1000	>48	>48	>48	>48

Tabel 7

Oxidation stability of 15wt% FME blended diesel (B15) with antioxidants BHT and TBHQ

Antioxidant concentration (ppm)	Induction Period (h)			
	BHT		TBHQ	
	FME/Sulfur free diesel	FME/440 ppm sulfur diesel	FME/Sulfur free diesel	FME/440 ppm sulfur diesel
0	1.0	1.2	1.0	1.2
100	4.9	6.2	7.5	6.2
250	9.7	12.4	15.4	16.3
500	21.2	24.7	32.3	34.7
1000	38.5	45.1	>48	>48

Tabel 8

Oxidation stability of 20wt% FME blended diesel (B20) with antioxidants BHT and TBHQ

Antioxidant concentration (ppm)	Induction Period (h)			
	BHT		TBHQ	
	FME/Sulfur free diesel	FME/440 ppm sulfur diesel	FME/Sulfur free diesel	FME/440 ppm sulfur diesel
0	0.7	0.9	0.7	0.9
100	2.6	2.7	4.8	4.2
250	5.5	5.8	10.9	9.4
500	10.3	11.1	19.2	18.0
1000	17.7	19.2	38.1	33.9

4. Conclusion

Oxidation stability of 4wt% FME/RME was 3.0 h which is 300 times greater than FME (0.1h) but not reach enough to meet the standard value. 1000 ppm concentration of BHT and TBHQ antioxidant showed close results whereas in 2500 ppm, TBHQ was given four times higher oxidation stability than BHT in 4wt% FME/RME. Very similar results, TBHQ showed better performance than BHT that was found in 10wt%

FME/RME. Oxidation stability not increased remarkably in blended FME/diesel without antioxidant. In B5, 100ppm and above concentration of BHT are effective for improvement of oxidation stability to achieve the target value according to standard. TBHQ did not show better results than BHT in B5. 250ppm of BHT and TBHQ are needed for getting standard oxidation stability value in B10. B15 is also showed nice results in the concentration 500ppm of BHT and TBHQ. About 1000

ppm concentration antioxidants are effective for improvement of oxidation stability of B20.

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