International Journal of Renewable Energy, Vol. 4, No. 2, July 2009

Effect of Antioxidants on the Oxidative Stability of Waste Cooking Oil Based Biodiesel under Different Storage Conditions

Parncheewa Udomsap*, Nuwong Chollacoop*, Subongkoj Topaiboul* and Toshihiro Hirotsu**

*Bioenergy Laboratory, National Metal and Materials Technology Center (MTEC), Pathumthani, Thailand
**National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki, Japan
Tel: +66-2-5646500, Fax: +66-2-5646401, Email: buachuu@mtec.or.th

Abstract

In this study, the effects of antioxidant on biodiesel degradation characteristics with and without antioxidant under different storage temperatures were investigated. The oxidation stability of waste cooking oil methyl ester (WCOME) originated from soybean and canola oil was studied using different concentrations, ranging from 0 to 600 ppm, of BHT and BPH antioxidants. All mixtures were stored in glass containers at 20 and 40 oC storage temperatures for the testing period of 3 months. The samples were monitored in terms of oxidation stability, peroxide value, acid value, kinematic viscosity and water content. The results showed that both BHT and BPH could increase the oxidation resistance of biodiesel, especially at higher concentrations. The optimum concentration of both BHT and BPH antioxidants were 300 ppm in order to meet the requirement of European standard of oxidation stability, i.e., 6 hours. Due to their different chemical structure, BPH was more effective than BHT, while comparing at the same antioxidant concentration. The results also suggested that biodiesel degradation rate could become faster at higher storage temperature as detected by significant changes in oxidation stability, peroxide value and acid value. Consequently, the fuel quality could be worsened. Furthermore, the high level of unsaturated fatty acid methyl ester in WCOME composition was another factor that could contribute to higher rate of degradation.

Key Words Oxidative stability, Antioxidant, BHT, BPH, Biodiesel degradation, Biodiesel

1. Introduction

Biodiesel, defined as fatty acid alkyl ester, is derived from vegetable oil or animal fat through a transesterification reaction. It can be produced from various feedstocks such as palm oil, canola oil, soybean oil, coconut oil and jatropha oil. Different types of biodiesel feedstock contain different fatty acid compositions, which influence the properties of the crude oil as well as their methyl ester. Some critical properties of biodiesel such as oxidation stability, cetane number, iodine value and cold filter plugging point correlate with major fatty acid methyl ester composition in biodiesel, i.e., different types of fatty acids provide different degree of unsaturation and long chain saturated factor [1]. Since the presence of double bond in fatty acid molecule can make a high level of reactivity with the oxygen when exposed to the air during storage, the oxidation stability of biodiesel depends on the content of unsaturated fatty acid methyl ester in its composition and the storage conditions. A study from G. Knothe et, al. reported that the relative oxidation rate of esters of polyunsaturated fatty acids like linolenate and linoleate methyl esters are higher than that of monounsaturated fatty acid like oleate methyl esters [2]. Beside the presence of air, other parameters affecting the oxidation process of biodiesel include presence of light, heat, trace of metal, peroxide and the surface area between biodiesel and air [3]. Thus, storage and handling are also significant factors that can influence biodiesel oxidation. At a certain condition, the oxidation process begins with an initial chain reaction when highly active free radicals are formed by the influence of heat, light, or metal ions. Next step is the propagation phase, where these radicals quickly bind with the triplet-form oxygen in the air, resulting in unstable peroxides (ROOR) and hydroperoxides (ROOH). Finally, the termination phase results in a formation of stable oxidation products, such as aldehydes, which are further oxidized into acids and high molecular weight products [4]. The overall oxidation mechanism diagram is illustrated in Fig 1.

$$
\begin{array}{llcllll}
\text{Initial phase:} & & & \text{RH} & \rightarrow & \text{R}\bullet & \\
\text{Propagation phase:} & \text{R}\bullet & + & \text{O}_2 & \rightarrow & \text{ROO}\bullet & \\
 & \text{ROO}\bullet & + & \text{RH} & \rightarrow & \text{ROOH} + & \text{R}\bullet \\
\text{Termination phase:} & \text{R}\bullet & + & \text{R}\bullet & \rightarrow & \text{RR} & \\
 & \text{ROO}\bullet & + & \text{R}\bullet & \rightarrow & \text{ROOR} &
\end{array}
$$

Fig 1. Oxidation mechanism of biodiesel.

One approach for increasing oxidation resistance of biodiesel is to treat it with antioxidant. The general antioxidants currently used are monohydroxy or polyhydroxy phenol compounds with various ring substitutions. These antioxidant compounds have low activation energy to donate hydrogen in order to interrupt the propagation of the free radical chain. In other words, the compounds can delay the start and/or slow the reaction rate of oxidation. The resulting antioxidant free radicals do not initiate another free radical due to the stabilization of delocalization of radical electron, and it can also react with lipid free radicals to form stable complex compounds [5]. Not surprisingly, different antioxidants could show substantially different antioxidant effectiveness in different oils due to different molecular structures. Besides antioxidant effectiveness, the other factors such as off-odor, off-color, solubility and cost should also be considered. Oxidized biodiesel can have some negative effects on fuel quality, which results in negative effects to engine[6]. Therefore, various limits of oxidation stability have been specified in current biodiesel standard, as presented in Table 1.

Table 1 Specified oxidation stability in current biodiesel standard.

Standard	Method	Oxidation stability	Units
ASTM D6751-08	BS EN 14112:2003	3	Hours
BS EN 14214:2003		6	
Thai standard		10	
JIS K 2390:2008		10	

Even though the oxidation stability limit of each standard is varied, one should be able to produce the biodiesel that passes all minimum requirements. An easy way to improve the stability is to add antioxidant into the oil. In general, BHT is used as an antioxidant for food, animal feed, petroleum products, synthetic rubbers, plastics, animal and vegetable oils, and soaps. It retards these materials from oxidation during prolonged storage, whereas BPH is mostly used in polymers industry as antioxidant and/or stabilizer, and in rubber industry as additives [7, 8]. The purpose of this study is to implement these antioxidants into biodiesel from waste cooking oil (waste cooking oil methyl ester: WCOME) and to investigate their effectiveness regarding the oil stability. The degradability characteristic of WCOME with and without antioxidant under 20 and 40 °C storage temperatures were determined throughout a storage time of 12 weeks. Oxidation stability, peroxide value, acid value, kinematic viscosity and water content were periodically recorded. This information will be useful for both biodiesel producers and users for designing their biodiesel storage system to maintain the quality of biodiesel.

2. Methodology

2.1 Materials

Waste cooking oil collected from an AIST center cafeteria in Japan was used as raw material to produce biodiesel in this study. This used oil is mainly composed of soybean and canola oil, which are generally used in Japan. Previous researchers have analyzed the fatty acid composition as presented in Table 2 [9]. Methanol, potassium hydroxide and purified glycerol were purchased from Wako Chemicals, Tokyo, Japan. All chemicals used for the transesterification process were analytical grade. Furthermore, two types of synthetic antioxidants used in this experiment were 2, 6-di-tert-butyl-p-cresol (BHT) and 6, 6'-di-tert-butyl-2, 2'-methylenedi-p-cresol (BPH). These chemicals were obtained from Baynox Plus, Germany. The chemical structure of BHT and BPH are shown in Fig 2(a) and 2(b), respectively.

Table 2 Fatty acid composition of soybean oil.[9]

Fatty acid profile	Canola oil (%wt.)	Soybean oil (%wt.)
Lauric acid (C12:0)	-	0.1
Myristic acid (C14:0)	-	0.1
Palmitic acid (C16:0)	3.5	10.2
Stearic acid (C18:0)	0.9	3.7
Total saturated	4.4	14.1
Oleic acid (C18:1)	64.4	22.8
Total monounsaturated	64.4	22.8
Linoleic acid (C18:2)	22.3	53.7
Linolenic acid (C18:3)	8.2	8.6
Total polyunsaturated	30.5	62.3

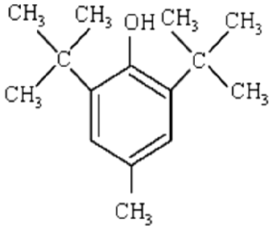
When dealing with biodiesel stability, unsaturated part of the molecular chain should be focused. From Table 2, it can be seen that different kinds of vegetable oils have different composition and the monounsaturated and polyunsaturated parts of oil reflect their stability. The higher the percentage of unsaturation, the higher is the possibility to be oxidized. The oxidation stability of refined canola oil and refined soybean oil are 8.29 and 3.17 hours, respectively [10]. Once these vegetable oils have been used, their oxidation stabilities are reduced due to heat and oxygen or the oxidation reaction. With this, it was expected that the blending of these oils after being used would be between 3-8 hours or less than 5.73 hours.

2.2 Experimental Procedure

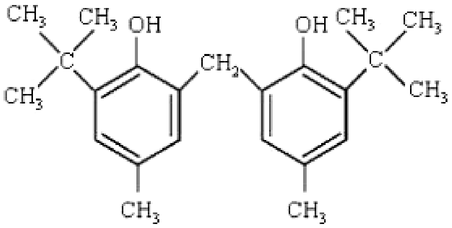
The transesterification reaction was carried out in a glass batch reactor filled with magnetic stirrer. Potassium hydroxide (1.67% by weight of oil) was completely dissolved in methanol (12.50% by weight of oil) prior to mixing with waste cooking oil preheated at 60 °C. The mixture was maintained in stirring condition for 1 hour to complete the reaction. Then the mixture was allowed to settle until two layers were separated. The upper layer mainly consisted of fatty acid methyl ester, and the lower layer was crude glycerol. Some of potassium hydroxide and methanol were dissolved in both layers, therefore, after the separation of the lower layer, the fatty acid methyl ester was washed with deionized water to remove the impurities. Finally, instead of heating the biodiesel, purified glycerol was added to absorb the trace amount of moisture to avoid the effect of heat on the biodiesel stability. After that, glycerol was separated. BHT and BPH antioxidants were added at various concentrations in thus obtained biodiesel. For BHT, the experiment was carried out at the concentrations of 100, 300 and 600 ppm while at 300 and 600 ppm for BPH. From economical point of view, antioxidant concentration should not exceed 1000 ppm; and it has been studied that the concentration of BHT around 200-250 ppm is suitable[11]. Therefore, the lower concentration of BHT was also analyzed. All samples were stored in closed bottles and were divided into two groups depending on the storage temperatures. First group was kept in closed shelf at 20 ^{o}C while the second group was kept in an incubator at 40 ^{o}C. During the storage time of 12 weeks, the samples were monitored periodically, i.e., oxidation stability was measured every 2 weeks, peroxide value and acid value were measured every 4 weeks, kinematic viscosity and water content were measured every 8 weeks.

2.3 Analytical methods

Oxidation stability of biodiesel expresses its susceptibility to be oxidized upon its exposure to the air. Metrohm 743 Rancimat was used to determinate the induction period. This procedure was developed according to EN 14112. For peroxide value, it can be expressed in the unit of milliequivalents of active oxygen per kilogram of fat or oil (meq/kg). This is determined by measuring the amount of iodine formed by the reaction of peroxides with iodide ion. In order to do that, Potentiometric titrado 809, Metrohm, was used to determine this value according to BS ISO 27107:2008. For acid value, the ASTM D664-07 was followed for measuring the amount of potassium hydroxide in milligrams that was necessary to neutralize free fatty acids contained in 1 gram of oil. In this study, the acid value was determined using GT-100 potentiometric automatic titrator from Mitsubishi Chemical Corporation. Kinematic viscosity is defined as resistance to flow of fluid under gravity and expressed in a unit of mm^2/s at a specific temperature. This parameter was determined by Yoshida kinematic viscosity bath model VB-X6 from Yoshida Kagaku Kikai Company. This procedure was developed according to ASTM D445-06. Water content was determined by using 831 Karl-Fischer (KF) coulometer from Metrohm, as per BS EN ISO12937.



(a)



(b)

Fig 2. Chemical structure of (a) BHT and (b) BPH.

3. Results and Discussions

3.1 Characteristics of WCOME

Waste cooking oil originated from soybean and canola was converted to waste cooking oil methyl ester (WCOME). Its properties are presented in Table 3. The properties of WCOME met all the requirement of JIS K2390:2008, EN 14214:2003 and ASTM D6751-08 standards in terms of peroxide value, acid value, kinematic viscosity and water content. However, the oxidation stability only met the requirement of ASTM D6751-08(i.e., the induction period at 110^{o}C of 3 hours) while it did not meet both EN 14214:2003 and JIS K2390:2008. These standards specify the induction period at 110^{o}C of 6 hours and 10 hours, respectively. As mentioned earlier, the low stability of oil occurs due to the high content of polyunsaturated fatty acid in its structure. It was expected that the oxidation stability of this waste cooking oil would be approximately less than 5.73 hours. After being converted to biodiesel, its ester is expected to have even less oxidation stability. In this study, the oxidation stability of WCOME was observed to be 5.22 hours (Table 3).

Table 3 Properties of waste cooking oil methyl ester (WCOME).

Properties	WCOME	Units
1.Oxidation stability	5.22	hours
2.Peroxide value	5.9	meq./kg
3.Acid value	0.15	mg KOH/g
4.Kinematic viscosity	4.4	mm^2/s
5.Water content	213.7	ppm

3.2 Effect of antioxidant

Fig 3 illustrates the effects of BHT and BPH antioxidants on oxidation stability of WCOME, while taking different antioxidant concentrations in the range 0 to 600 ppm. The results show that both BHT and BPH can increase the oxidation stability of WCOME, and the oxidation stability increases with increasing antioxidant concentration. However, BPH is more effective than BHT while comparing at the same concentration. Because of the different chemical structure, BPH can contribute two hydrogen atoms per molecule while BHT can contribute only one hydrogen atom per molecule to interrupt the free radical to break the oxidation process. The results from this figure can help to deduct how much antioxidant should be added into the WCOME, in order to meet the requirement the oxidation stability of both European and Japanese standards. The study has revealed that at least 300 ppm of BHT or BPH is necessary to meet European standard, whereas greater than 600 ppm of antioxidant must be added to achieve Japanese standard.

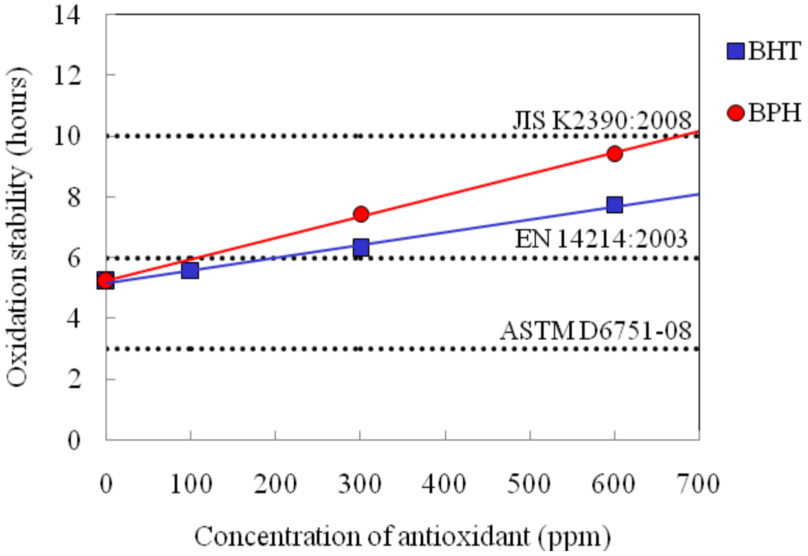
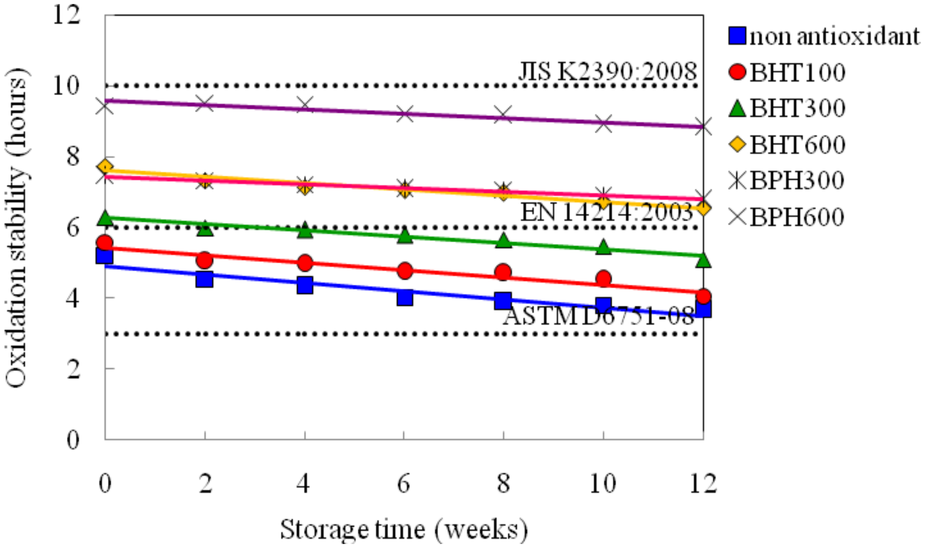


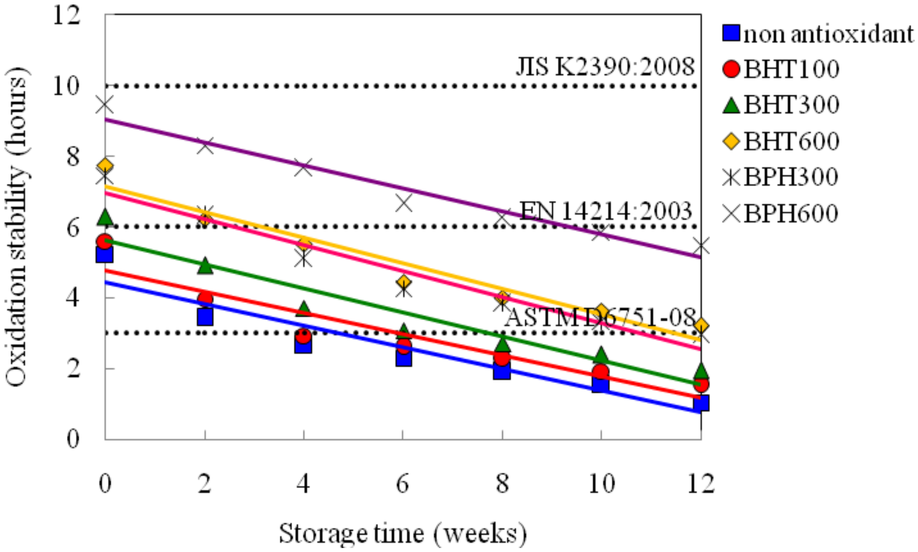
Fig 3. Effects of BHT and BPH antioxidant concentrations on oxidation stability of WCOME.

3.3 Effect of storage temperature

Fig 4-8 shows the degradation of WCOME with and without antioxidants under 20 and 40 ^{o}C storage temperatures for the 12-week testing period. Oxidation stability of all samples is decreased continuously with increasing storage period. However, the rate of decrease in oxidation stability is faster for the samples stored at the higher temperature of 40 ^{o}C is compared to those at 20 ^{o}C (Fig 4). Furthermore, similar to the results in Fig 3, BPH can delay the oxidation rate more effectively at the same concentration.



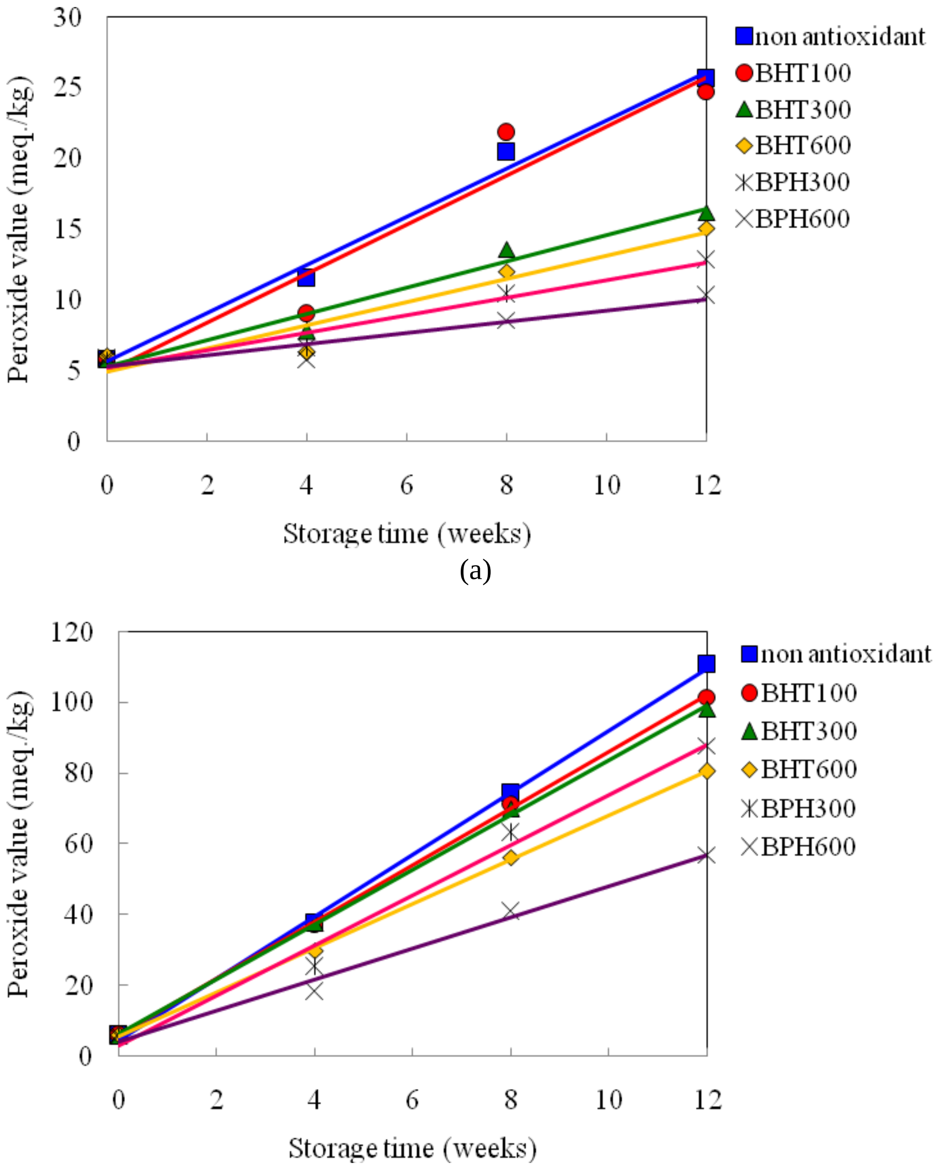
(a)



(b)

Fig 4. Changes of the oxidation stability of samples during the 12-week storage time at (a) 20 and (b) 40 ^{o}C storage temperatures.

The oxidation reaction has affected the many parameters of biodiesel fuel qualitysuch as peroxide value, acid value and kinematic viscosity. Although peroxide value is not specified in the current biodiesel fuel standard, this parameter shows negative compatibility effects with plastic and elastomer parts in engine such as swelling and ageing [12]. Fig 5 shows the change of peroxide value of samples under different storage temperatures over storage time. The results show that peroxide value of all samples is increased over time, with faster rate at higher temperature because of higher rate of oxidation and it is expected that the acid value should be increased as well. Even though the higher peroxide value indicates the potential for lower fuel stability, it should be noted that peroxide formed during oxidation can increase the fuel's cetane number and enhance combustion in engine [12].

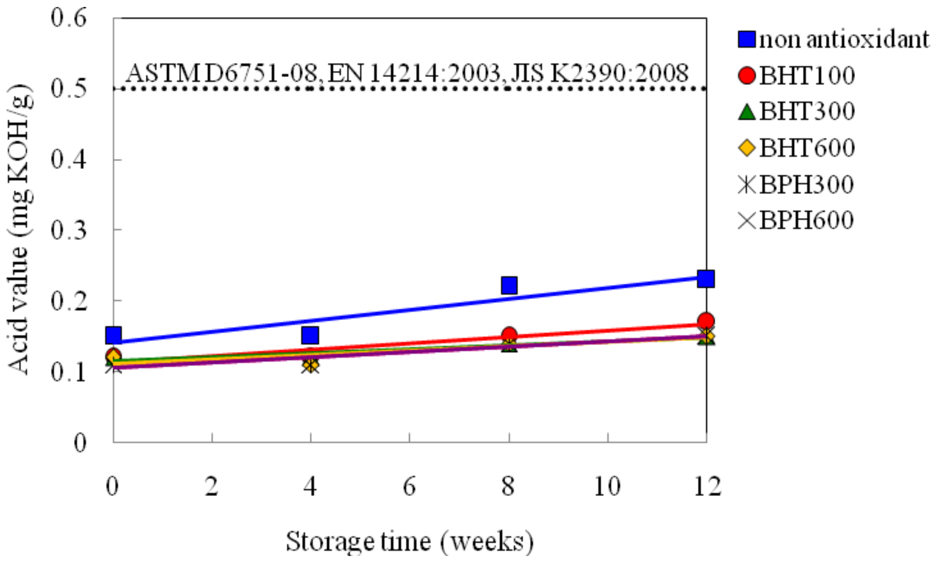


(a)

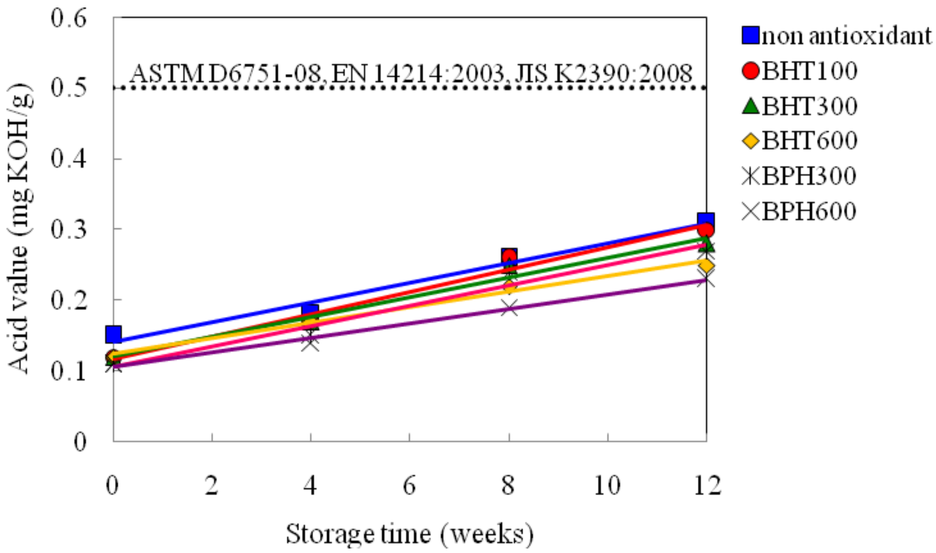
(b)

Fig 5. Changes of the peroxide value of samples during the 12-week storage time at (a) 20 and (b) 40 °C storage temperatures.

As previously discussed, oxdiation mechanism will eventually give rise to acid value from the increasing peroxide. Acids formed can cause corrosion on metal components in engine. Fig 6 shows the change of acid value during storage period. The result shows acid values of all samples increases over time with faster rate at higher temperature as a result of higher degradation rate. Acid can be formed through the oxidation reaction and hydrolysis reaction when exposed to oxygen and moisture in the air, respectively. Furthermore, water in oil itself can cause hydrolysis of the esters and turn it into alcohol and acids, therefore, the water content in biodiesel should be minimized. However, from the test results, the acid value of all samples after 12-week period was found to be still below the limits of all standards.



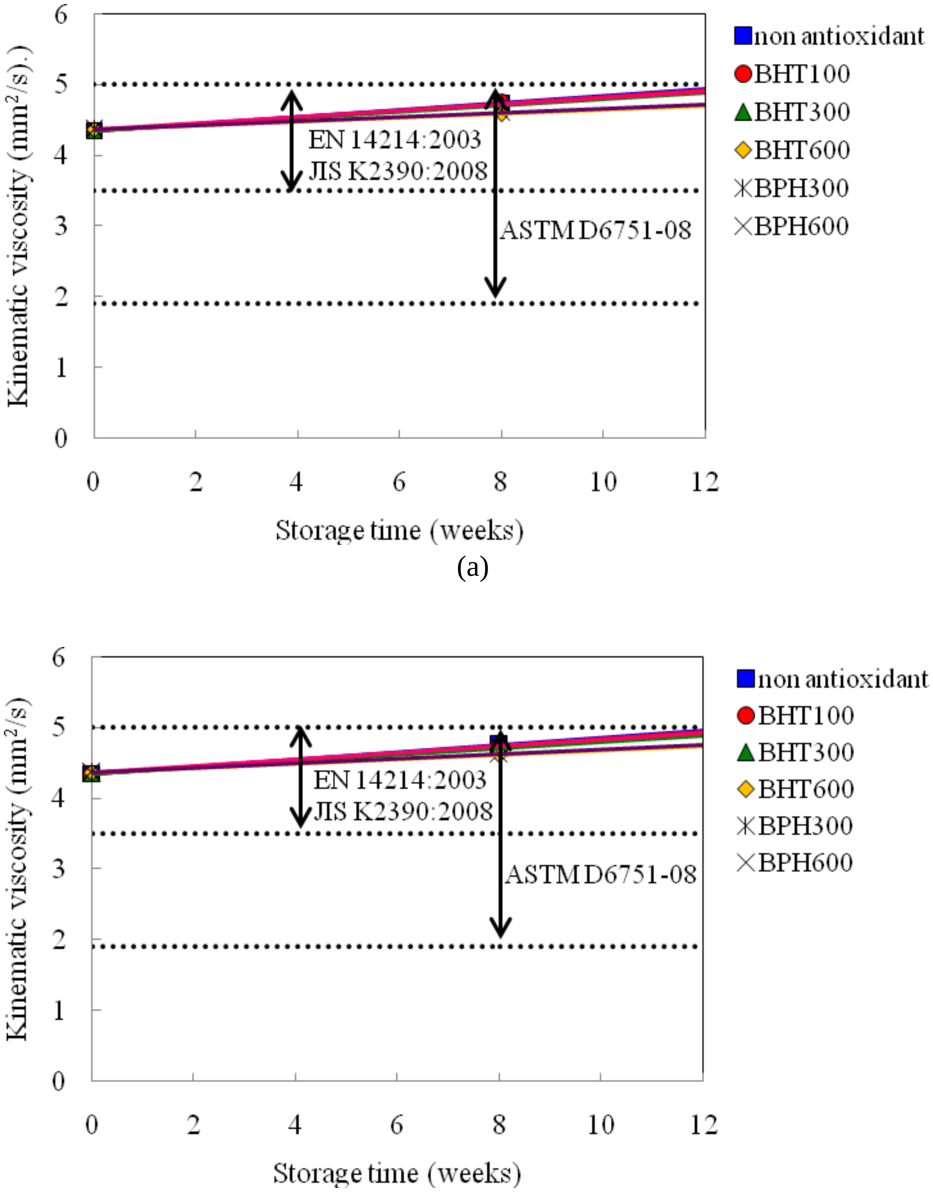
(a)



(b)

Fig 6. Changes of the acid value of samples during the 12-week storage time at (a) 20 and (b) 40 ^{o}C storage temperatures.

Apart from peroxides and acidity, the oxidized biodiesel can affect the viscosity to increase. During storage, the viscosity of the methyl esters is increased by the formation of more polar, oxygen-containing molecules and also by the formation of oxidized polymeric compounds, possibly leading to the formation of gums and sediments that may potentially clog fuel line. In this study, all samples stored under 20 ^{o}C and 40 ^{o}C storage temperatures show a slight increase in viscosity over the storage period (Fig 7).

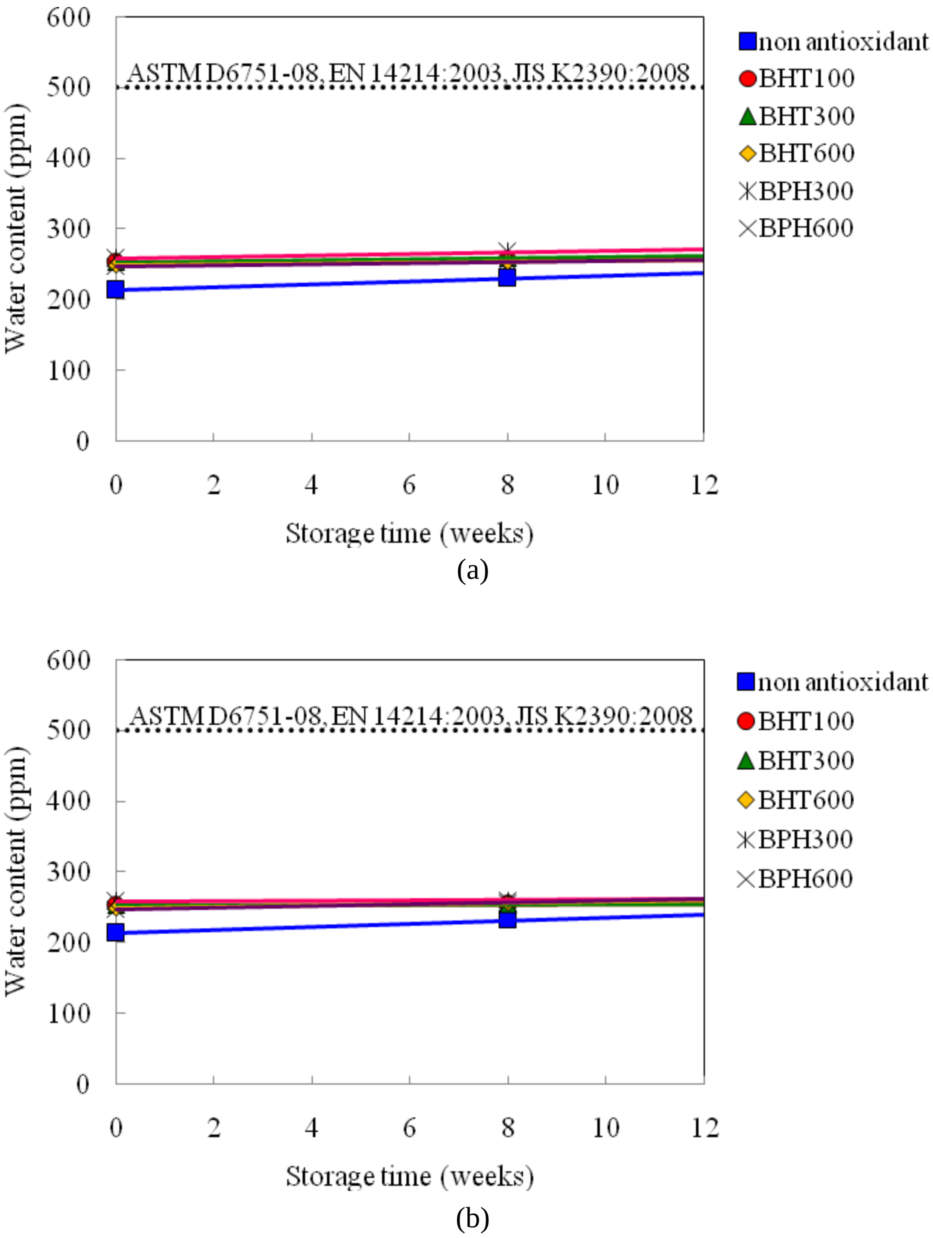


(a)

(b)

Fig 7. Changes of the kinematic viscosity of samples during the 12-week storage time at (a) 20 and (b) 40 ^{o}C storage temperatures.

Although the oxidation process and inhibition of oxidation by antioxidants do not produce water, the water content in biodiesel was also determined in this experiment. The water content is insignificantly changed with increasing storage time(Fig 8). It slightly increases because the methyl ester can quickly absorb moisture when storage container is opened. However, both the kinematic viscosity and water content of all samples are still below all the standard values for the whole testing period.



(a)

(b)

Fig. 8 Changes of the water content of samples during the 12-week storage time at (a) 20 and (b) 40 °C storage temperatures.

The results of this investigation can indicate that higher storage temperature leads to the faster rate of degradation of biodiesel and may change fuel quality by adversely affecting properties such as oxidation stability, peroxide value and acid value. However, antioxidant can increase the oxidation resistance of biodiesel. 600 ppm of BPH was the most effective antioxidant screened in this study. Furthermore, combustion characteristics and exhaust emissions in diesel engine were not influenced by the addition of antioxidants in biodiesel.

4. Conclusions

The oxidation stability of biodiesel depends on the unsaturated fatty acid content and the storage conditions. Oxidation rate of all sample groups increases when increasing the storage temperature, which can be seen from significant change of oxidation stability, peroxide value and acid value. It was found that poor stability characteristics could be noticed when the samples were stored at 40 ^{o}C. Therefore, the storage temperature should be less than that to preserve the biodiesel stability for long term storage. But, some biodiesels do not initially have high stability sufficient to pass the standard requirements. Adding antioxidant is an easy way to delay the rate of oxidation. From the results, BPH was more effective than BHT and could be used as a antioxidant. However, the optimum antioxidant concentration depends on type of biodiesel and biodiesel production process as well.

5. Acknowledgements

This study is supported by New Energy Foundation (NEF) under the Asia Biomass Researcher Invitation Program 2008 and as a part of on-going collaboration between Research Center for New Fuels and Vehicle Technology (NFV) at the National Institute of Advanced Industrial Science and Technology (AIST), Japan and Bioenergy Laboratory at the National Metal and Materials Technology Center (MTEC), Thailand.

References

[1] Ramos, M. J., Fernandez, C. M., Casas, A., Rodriguez, L., and Perez, A., (2009). *Influence of fatty acid composition of raw materials on biodiesel properties*. Bioresource Technology, Vol. 100, pp. 261-268.

[2] Knothe, G., Gerpen, J. V., and Krahl, J., (2005). *Oxidation stability*. The biodiesel handbook. AOCS press, Champaign, IL.

[3] Knothe, G., (2007). *Some aspects of biodiesel oxidation stability*. Fuel Processing Technology, Vol. 88, pp. 669-677.

[4] Bouaid, A., Martinez, M., and Aracil, J., (2007). *Long storage stability of biodiesel from vegetable and used frying oils*. Fuel, Vol. 86, pp. 2596-2602.

[5] Mittelbach, M., and Schober, S., (2003). *Influence of antioxidants on the oxidation stability of biodiesel*. Journal of American Oil Chemist's Society, Vol. 80, pp. 817-823.

[6] Yamane, K., Kawasaki, K., Sone, K., Hara, T., and Prakoso, T., (2007). *Oxidation stability of biodiesel and its effects on diesel combustion and emission characteristics*. International Journal of Engine Research, Vol. 8, pp. 307-319.

[7] Screening Information Data Set, *2, 6-di-tert-butyl-p-cresol*. SIDs Initial Assessment Report for SIAM14, Paris, France, 26-28 March 2002, UNEP Publication.

[8] Screening Information Data Set, *6, 6'-di-tert-butyl-2,2'-methylenedi-p-cresol*. SIDs Initial Assessment Report for SIAM14, Paris, France, 26-28 March 2002, UNEP Publication.

[9] Ma, F., and Hanna, A. M., (1999). *Biodiesel production*. Bioresource Technology, Vol. 70, pp. 1-15.

[10] Farhoosh, R., Einafshar, S., and Sharayei, P., (2009). *The effect of commercial refining steps on the rancidity measures of soybean and canola oils*. Food Chemistry, Vol. 115, pp. 933-938.

[11] Dunn, R. O., (2005). *Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel)*. Fuel Processing Technology, Vol. 86, pp. 1071-1085.

[12] Leung, D. Y. C., Koo, B. C. P., and Gua, Y., (2006). *Degradation of biodiesel under different storage conditions*. Bioresource Technology, Vol. 97, pp. 250-256.