The Effect of Surfactant Addition towards Dispersion and Antioxidant Activity of *tert*-butylhydroquinone in Biodiesel

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Received: 01.08.2018 Accepted:10.09.2018

Abstract- Biodiesel is a renewable fuel as an alternative to fossil fuel. Currently, biodiesel is commercially used as a mixture of solar diesel. Biodiesel has many advantages. However, it has an instability issue towards oxidation which could lead to the low shelf life and quality degradation. Antioxidant additives such as tert-butylhydroquinone (TBHQ) is commonly used to prevent the oxidation. However, as an antioxidant additive, TBHQ has a low dispersion in biodiesel, thus it limits its antioxidant activity. Therefore, TBHQ is incorporated into biodiesel which was previously mixed with surfactant in order to increase its dispersion to increase its performance. In this research, three types of surfactants were used namely Sorbitan Monooleate, Glycerol Monostearate, and Polyglyceryl-4-isostearate to increase the solubility of TBHQ and its antioxidant activity. The functional group changes due to oxidation reaction product was confirmed by using FTIR. The solubility of the biodiesel mixtures was tested using UV-Vis Spectrophotometer. Result shows that the mixture of 100 ppm Polyglyceryl-4-isostearate with 2000 ppm TBHQ performed the most stable dispersion in biodiesel over one week observation followed by Glycerol Monostearate and Sorbitan Monooleate. The biodiesel quality in respect to acid number and iodine value were analyzed to evaluate the antioxidant performance of the additive-surfactant mixtures. The best improvement of oxidative stability of biodiesel over four-week storage time was performed by addition of 100 ppm Polyglyceryl-4-isostearate compared with other surfactants. These findings provide a potential use of surfactant, especially Polyglyceryl-4-isostearate, as a solubility enhancer as well as, more importantly, helping the antioxidant activity of phenolic additives in biodiesel.

Keywords Biodiesel; surfactant; dispersion; TBHQ, antioxidant.

1. Introduction

Biodiesel is renewable source of energy as an alternative to fossil fuel depletion. It is made from esterification reaction of free fatty acid and transesterification reaction of triglycerides which can be found in vegetable oils such as palm oil, jatropha, Nyamplung [1, 2], Pongamia pinnata seed [3], microalgae [4-6] and even cooking oil [7]. It has been used in many countries over the world as a blend with petroleum diesel [8]. Biodiesel is renewable and has many advantages especially due to its low emission. One of the major drawbacks is that biodiesel has low stability that it is susceptible to oxidation [9]. Since biodiesel is made from an esterification of both saturated and unsaturated fatty acid content from plant sources, it contains numbers of the unsaturated types. Unsaturated fatty acid is fatty acids that have at least one double bond (monounsaturated fatty acid) such as oleic acid, while linoleic acid and linolenic acid are polyunsaturated fatty acid, they have more than one double bonds whic are contained in most of biodiesels' original plants. The degree of oxidation increases as the number of double bond increase. Polyunsaturated fatty acid and its ester form contains at least one methylene hydrogen. It is the one that will be attacked by oxidation because it has the lowest breaking energy due to the resonance potential after the hydrogen abstraction froming primary and secondary products degrading biodiesels' quality and performance [10].

To mantain the quality and the potential of biodiesel as a renewable energy source, oxidation reaction on biodiesels' molecules must be prevented. The most common method is by the addition of antioxidant. TBHQ or tert-butylhydroquinone and pyrogallol are named to be the best antioxidants in many research. TBHQ was evaluated in this research because of its low environmental and health risk with higher availability [11]. TBHQ is an antioxidant which is commonly used in food industry. TBHQ is a phenolic-based antioxidants, which is insoluble in oil due to the gap of polarity. This causes serious problems where the antioxidant is not well dispersed in biodiesel, lowering its performance, the solid residue could block the engine nozzle.

To overcome this dispersion problem, research reported modification of phenolic molecule such as alkylation of pyrogallol to increase their solubility in biodiesel [12]. In the present research, surfactants were used to increase the dispersion of TBHQ in biodiesel. Surfactant has two molecular sides which have unique physical properties: has both hydrophobic and hydrophilic side in one molecule. It would act as a bridging agent which could carry more TBHQ in a nonpolar solution [13]. The surfactants used in this experiment is Sorbitan Monooleate, Glycerol Monostearate, and Polyglyceryl-4-isostearate. Their HLB ranging from 3-6 which is sufficient to stabilize a water in oil emulsion [14].

In this experiment, Sorbitan Monooleate, Glycerol Monostearate, and Polyglyceryl-4-isostearate were evaluated to stabilize the dispersion of TBHQ in a freshly made from palm oil biodiesel. UV-VIS Spectrophotometric method was used for the dispersion experiment. FTIR was used for the biodiesel oxidation confirmation. Antioxidant activity performance was performed over acid number and iodine value responses for four weeks storage period.

2. Experiment

2.1. Material and Instrument

Biodiesel was freshly made from palm oil. Solid Tert-Butylhydroquinone antioxidant from Merck Germany, Sorbitan Monooleate, Glycerol Monostearate, and Polyglyceryl-4-isostearate are in liquid form. Ethanol, Wijs solution, Chloroform, Sodium thiosulphate, starch solution, phenolphtalein indicator solution, Hexane, demineralized water, Potassium Iodide, and Potassium hydroxide. Solubility/dispersion test experiments used Agilent Technology™ Cary 60 UV/VIS Spectrophotometer, Thermo Scientific™ FT-IR Spectrometer Nicolet iS5, iD5 ATR Accessory. Thermo ScientificTM FT-IR Spectrometer Nicolet IS5 was used in the degradation quality of biodiesel experiment.

2.2. Methods

2.2.1. Sample preparation

Biodiesel solutions were prepared in five glass bottles. They are: pure biodiesel, biodiesel mixed with TBHQ, and the other three are biodiesel mixed with 3 different surfactants. The amount of TBHQ in each bottle was 2000 ppm (w/v) and the amount of surfactants were set to 100 ppm. The sample were stirred and stored in a controlled condition for 4 weeks with e weekly observation.

2.2.2. Dispersion test

The sample mixtures were diluted using n-hexane solvent. As much as 0.25 ml sample from the same depth distance from the surface was taken and 19.75 ml of hexane was added into a flask. The flask was shaken using a vortex mixer until they were homogenous. The solution further carried into Agilent Technology Cary 60 UV/VIS Spectrophotometer. The result was absorbance value of the solution in the 280nm wavelength.

2.2.3. Acid number analysis

Standard Test Method for Acid Number of Petroleum Products ASTM D 664 procedure was used for the acid number determination. 2.5 gram of biodiesel was put into a 250 ml erlenmeyer flask. Ethanol was added into thesolution followed by 5 phenolphtalein solution as an indicator. The sample was stirred until the solution is homogenous. The sample was titrated using KOH 0.01 N until the solution changed color from light color to pinkish. The same procedure was done to a blank sample containing 100 ml ethanol and 5 ml phenolphtalein. The resulting KOH titration volumes were used to calculate acid number.

2.2.4. Iodine vvalue analysis

The test for iodine value determination in the samples were performed by following the international standard procedure AOCS Official Method Cd 1-25. 0.15 gram of biodiesel was measured and put into a 500 ml erlenmeyer flask. 15 ml chloroform was added later into the flask. In the same flask, 25 ml of Wijs solution was added. The flask was sealed with aluminum foil and stored in a dark environment. After one hour, 20 ml of KI solution and 150 ml of demineralized water were added into the sample and then titrated using sodium thiosulphate 0.1 N solution while shaking the flask so that the sample stayed homogenous. When the solution changed color to light orange, 2 ml of starch solution was added and the titration was resumed. The titration was finished as the sample color turned clear. The same procedure was done to a blank sample which contained no biodiesel. The final titration volume of sodium thiosulphate was used to calculate iodine value.

2.2.5. Fourier Transform Infra-Red (FTIR) Analysis

The functional group analysis was carried out to study the changes in the biodiesel molecules before and after being stored for four weeks. The test was following ASTM E1252 standard procedure using Thermo Scientific™ Nicolet iS5 FT-IR Spectrometer. FTIR measurement was taken using wavenumber range 4000 – 500 cm^{-1}.

3. Result and Discussion

3.1. Dispersion test

The effect of surfactant to the dispersion of TBHQ in biodiesel was measured using the dispersion test. The UV/VIS spectrophotometer method was used to determine the dispersion level of a solution based on the absorbance values [15]. Three different surfactants were evaluated namely Sorbitan Monooleate (SMO), Glycerol Monostearate (GMS), and Polyglyceryl-4-isostearate (PG4IS). The concentration of TBHQ was set to 2000 ppm. As the comparison the absorbance of TBHQ in biodiesel without surfactant was also measured. The result of the dispersion test is shown in Table 1. Absorbance of the samples were decreased during one week storage time. This showed that the concentration of TBHQ in the sampling spot was decreasing because of the polarity difference that caused both biodiesel and TBHQ to not dissolve to each other. The undissolved TBHQ, being denser than biodiesel, sunk to the bottom of the flask within the time.

Table 1. Delta absorbance of biodiesel samples

Sample	Average Absorbance		
	Week 0	Week 1	Delta Abs
Biodiesel + TBHQ 2000 ppm	1.5827	1.3988	0.1839 ±0.0001[d]
Biodiesel + TBHQ 2000 ppm + GMS 100 ppm	1.4630	1.4390	0.0240 ±0.0030[b]
Biodiesel + TBHQ 2000 ppm + SMO 100 ppm	1.5493	1.4960	0.0533 ±0.0000[c]
Biodiesel + TBHQ 2000 ppm + PG4IS 100 ppm	1.7582	1.7484	0.0098 ±0.0002[a]

The gap of absorbance difference was used as the indication of the number of TBHQ exits the solution as a solid. The absorbance difference of the sample that contains TBHQ and surfactants was smaller than the one with TBHQ only. This happened because the TBHQ of the sample with surfactant was dispersed better in the biodiesel than the one without surfactant. The best surfactant in dispersing TBHQ in biodiesel was 100 ppm PG4IS followed by GMS and SMO with the same concentration. PG4IS only lost 0.0098 of the initial absorbance compared to other surfactants which had much higher decreasing gaps as shown in table 1. The delta absorbance of each sample were significant different ($p < 0.05$) analyzed using one-way ANOVA.

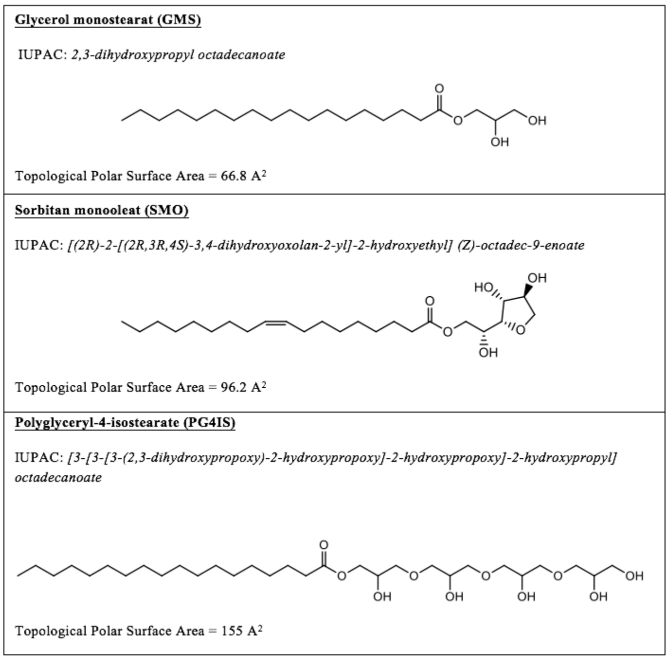

Fig. 1. Chemical Structure of surfactants [16-18]

PG4IS performed the best dispersion compare to other surfactants. From the chemical structure analysis as shown in Fig 1, all surfactants have the same length of fatty acid group which is C18. The main difference is on the alkyl ester end of the molecule. This part is the one which will distinguish their chemical property towards TBHQ and biodiesel. The C-18 end of the surfactant molecules is the one which interacts with biodiesel solution due to its hydrophobic property. The opposite end or the alkyl ester part is the polar or hydrophilic side, it binds TBHQ by creating hydrogen bonds. As can be seen from fig 1, PG4IS has polyglyceryl group which is 4 times the number of glycerol in GMS, more numbers of hydroxyl groups and available electron donors from oxygen atoms from PG4IS would results a bigger chance to create hydrogen bonds with TBHQ. The same explanation can be applied to PG4IS when compared with the dispersion ability of SMO. The strength of the surfactants' ability to disperse TBHQ is by using the analysis of the Topological Polar Surface Area (TPSA), it is the sum of the surface areas of polar atoms in a molecule [19]. From the three surfactants used in this experiment, PG4IS has the highest TPSA value 155 A^2 [16], higher than GMS and MSO which have 66.8 A^2 [17] and 96.2 A^2 [18] respectively.

3.2. *Acid number*

Acid number is one of the parameters which could directly indicate oil degradation occurrence. Acidic compounds are produced during oxidation of oil samples. The formation of both long or shorter free fatty acids and other organic acids after secondary oxidation is very common which initiated by the formation of hydroxyperoxide compounds due to radical oxidation [9]. In this research the acid number was determined using a simple acid base titration method following the ASTM D 664 standard procedure. The result of acid number determination is shown in the fig 2.

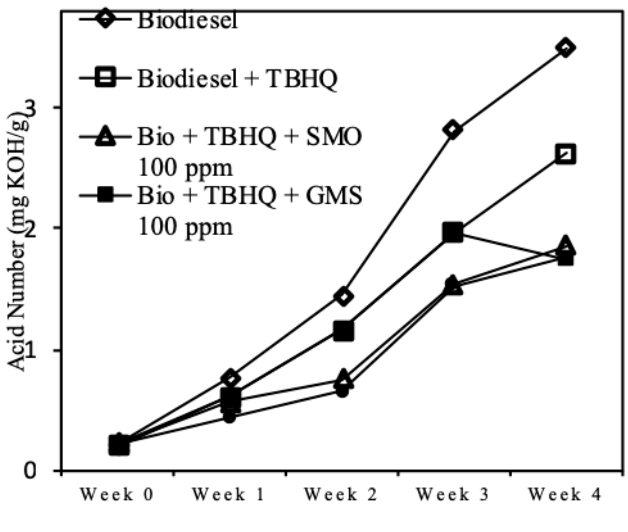

Fig. 2. Acid number of biodiesel samples

Figure 2 shows that acid number of the samples were increased for all samples over four weeks storage time. A sample of biodiesel without TBHQ shows the highest acid number increase every week. The other biodiesel samples which contains TBHQ was found to be effective in maintaining the acid number every week compared to biodiesel without TBHQ. Three out of five samples contained surfactant SMO, GMS, and PG4IS. The performance of GMS surfactant was the same with TBHQ without surfactant until week 3, however at week 4, it lowered the acid number significantly while the sample with TBHQ only was keep increasing. SMO and PG4IS performed better than GMS where they always maintained the acid number low every week. A significant highlight of this result is that the mixture of TBHQ and PG4IS was able to maintain the acid value below the American and European Union Standard Specification for Biodiesel Fuel Blend Stock ASTM D6751-12 and EN 14214:2012 for liquid petroleum products which is 0.5 mg KOH/g [20] up to two weeks while the other samples exceeding the standard within two weeks. To evaluate the performance trends for all sample, the slope of their linear regression equation were calculated. The slope values of samples: biodiesel only, biodiesel with TBHQ, biodiesel with TBHQ added by SMO surfactant, biodiesel with TBHQ added by GMS surfactant, and biodiesel with TBHQ added by PG4IS surfactant were 0.8603, 0.6158, 0.4255, 0.4330, and 0.4170 respectively. These slope values suggested that TBHQ added with PG4IS had the best performance in increasing biodiesel stability over acid number parameters. This finding is in correlation with the dispersion experiment result which stated that PG4IS possessed the best dispersion performance to dissolve TBHQ. The more TBHQ molecules dispersed in the biodiesel solution increases the availability of TBHQ as the radical scavenger molecule to protect the fatty acid methyl esters of biodiesel from being oxidized [21].

TBHQ is a phenolic compound that contain two hydroxyl groups bonded to a benzene ring. Phenolic compounds are known to have the property to reduce the oxidation rates of organic matter due to its reactivity as a hydrogen or electron donating agent from the hydroxyl group to the chain-carrying free radicals [22], which in order to stop the chain propagation step during the process of oxidation.

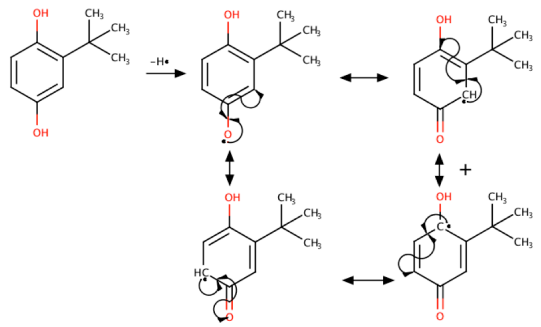

Fig. 3. Radical stabilization by TBHQ

The antioxidant property of phenolic compounds is also related to their ability to delocalize or stabilize the resulting phenoxyl radical within their structures [23]. The reaction mechanism of TBHQ as antioxidant against reactive oxygen species (ROS) or radical molecules are shown on Figure 9. TBHQ as a phenolic compound donates a hydrogen atom from its phenol –OH group to the free radical, thus reducing number of free radical molecules [24]. TBHQ, just like the other phenolic molecules has the ability to stabilize the radical within its structure by performing a resonance stabilization (Figure 3). This unique property of TBHQ and other phenolic antioxidant is very important in protecting the biodiesel molecules. Without antioxidant, biodiesel molecules will be susceptible to oxidation especially towards the unsaturated fatty acid methyl esters [9].

3.3. Iodine value

Iodine value is one of the parameters which could directly indicate oil degradation occurrence. Iodine value represents the number of double bond or degree of saturation in olefinic solution such as biodiesel. Unsaturated bonds are susceptible to oxidation. One of the unsaturated oils' oxidation products is the decreasing of its degree of saturation. Thus, the iodine solution which is added to biodiesel reacts with C-C double bond via addition reaction. It could indicate the oxidation occurrence [23]. Results of the iodine value experiment are shown in the fig 3.

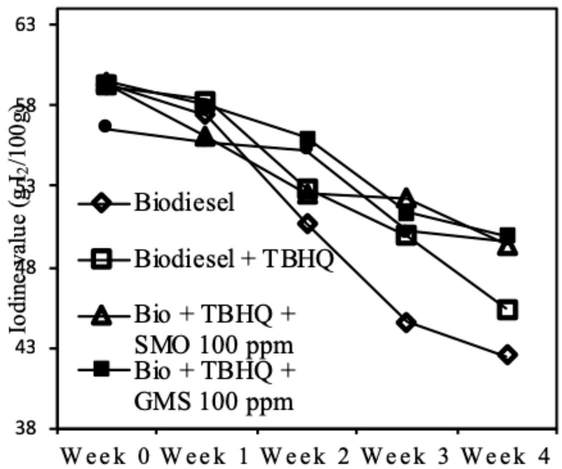

Fig. 4. Iodine value of biodiesel samples

Consistent with the result from acid number experiment, samples with TBHQ added with PG4IS claimed the best mixture. As can be seen in fig 4, all sample actually could not maintain iodine value during four weeks storage, however the values are still acceptable according to US and EU Biodiesel Specifications ASTM D6751-12 and EN 14214:2012 which is 120 g I2/100 g sample [20]. Unlike in the acid number experiment result, the declining patterns are random with several intersections between the curves. However, to gain a better conclusion, the slope test was analyzed. The slope values of samples: biodiesel only, biodiesel with TBHQ, biodiesel with TBHQ added by SMO surfactant, biodiesel with TBHQ added by GMS surfactant, and biodiesel with TBHQ added by PG4IS surfactant were -4.6472, -3.6154, -2.4015, -2.5843, and -1.947 respectively. The negative sign indicates the declining curve pattern, the lower the slope value the worse it is as an antioxidant. The most positive slope value was from sample biodiesel with TBHQ added by PG4IS surfactant. This finding again proved that iodine value is correlated with dispersion ability of the antioxidant.

3.4. FTIR

The infrared absorbance spectrum of the freshly made biodiesel sample was performed using FTIR instrument. Comparison of the biodiesels' spectrum between before and after four weeks storage period were analyzed. In this experiment, the changes in the biodiesel molecule observed based on the changes of the absorbance peaks detected by the spectrometer were within the wavenumber range 500-4000 cm-1. The absorbance of carbonyl (C=O), (C-O), (C-H) and (O-H) functional groups as the identity of biodiesel molecule and the oxidized products are the main interest in the discussion. Figure 5 is the result from the FTIR instrument.

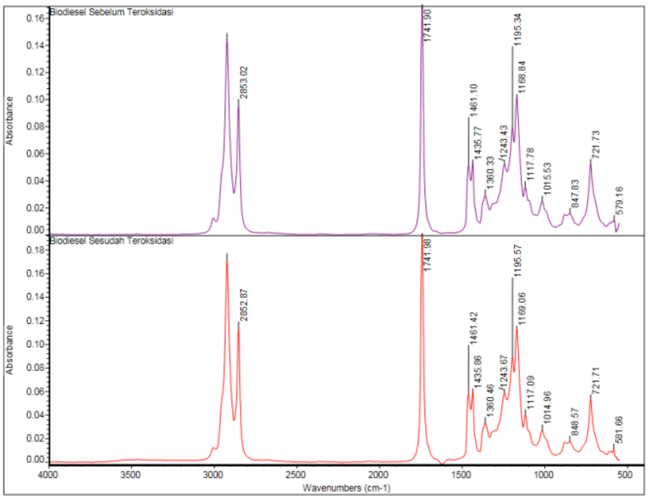

Fig.5. Infrared spectrum of biodiesel before (top) and after storage time (bottom)

From Fig 4 it can be seen that both spectrums show similar patterns to confirm the qualitative biodiesel structure characteristics. Peaks at 2920 and 2850 cm-1 indicate biodiesels' long chain aliphatic group. Peaks at 1741 cm-1 and 1435 cm-1 show the carbonyl group (C=O) and methylester (-O-CH3) respectively. The differences are on their absorbance intensity between before and after storage period.

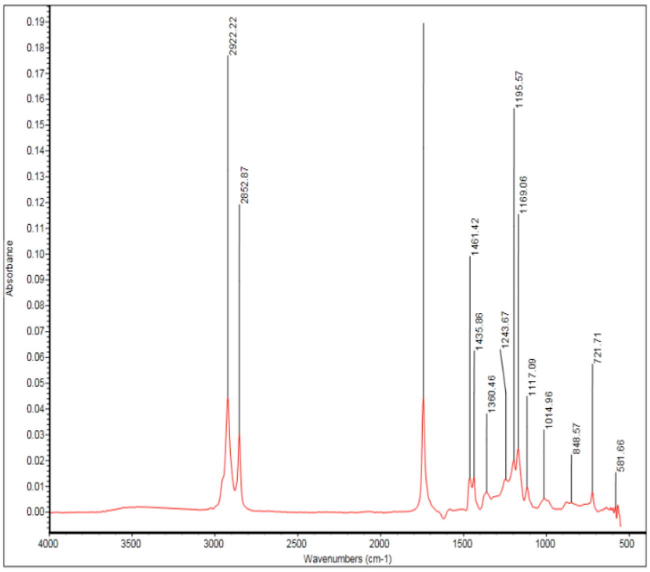

Fig. 6. Subtracted Infrared Spectrum of Biodiesel

Figure 6 shows the subtraction of FTIR spectrum before and after storage period to see the difference of the absorbance values. There are several changes detected from the spectrum which indicate the oxidation reaction occurrence. These result show that several functional groups were changed both increased or decreased concentration due to the oxidation reaction [25, 26]. The increase of absorbance intensity at the wavelength of 1700 – 1750 cm-1 shows that the concentration of the hydroperoxide radical decomposition product had increased forming aldehyde and ketone by-products [27]. There was an increase of absorbance intensity at the wavelength of 3400 – 3500 cm-1 shows that there were an increase in concentration of hydroperoxide (ROOH). Formation of lipid peroxides is an indication of unsaturated oil oxidation reaction. This can be further analyzed by the determination of peroxide and iodine values. Peroxide value will increase and iodine value as the marker of the number of C=C bond decreases [23]. The decreasing of C=C group indicated by the changes of concentration at 1600-1680 dan 3000-3100 cm-1 The FTIR result proves the biodiesel oxidation reaction occurs during storage due to the interaction with pro-oxidant species which exist in the air. It also suggested that new compounds were formed.

4. Conclusion

The dispersion test showed that the addition of surfactant to the TBHQ increases the dispersion of TBHQ in biodiesel. The mixture of 100 ppm Polyglyceryl-4-isostearate with 2000 ppm TBHQ performed the most stable dispersion in biodiesel over one week observation followed by Glycerol Monostearate and Sorbitan Monooleate with the same concentration. The high TBHQ dispersion with the help of Polyglyceryl-4-isostearate contributes to its best performance in increasing biodiesel stability over acid number and iodine value responses. FTIR confirms the oxidation reaction of biodiesel, the changes cover decreasing intensity in the main functional groups of fatty acid methyl ester and the increasing intensity of oxidation products. This results suggest to incorporate PG4IS surfactant to increase the dispersion and its antioxidant activity of TBHQ additive. It is important to increase the dispersion of antioxidant additive to ensure its optimum activity in preventing oxidation degradation towards biodiesel during storage period.

Acknowledgements

Authors would like to thank Hibah Doktor UI (1355/2018) and the Biodiesels' research members: Reza Adhitya, Woro Bismo, and Iva Raudyatuzzahra for the significant contribution in this research.

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