



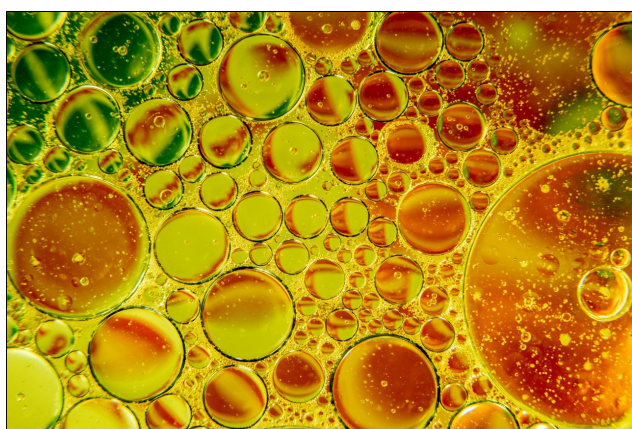
RESEARCH ARTICLE

Tertiary butylhydroquinone influence over oxidation stability of biodiesel from waste cooking oil

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OBJECTIVES This study observed the influence of tertiary butylhydroquinone (TBHQ), a synthetic antioxidant, on the oxidation stability of biodiesel. **METHODS** Biodiesel from WCO was produced by transesterification process at 60°C for one hour reaction time. Methanol was added in 4:1 (v/v) ratio of WCO with 2% potassium hydroxide as a catalyst. Tertiary butylhydroquinone (TBHQ) was used as an antioxidant agent to prevent biodiesel oxidation for such long-term storage. It was blended with biodiesel at various concentrations (0-1200 ppm). Samples were taken every week to measure the density, viscosity, acid value, iodine value (IV) and peroxide value (PV) during the storage process of the biodiesel blends which was conducted for 4 weeks. **RESULTS** An improvement in oxidation stability was achieved in all TBHQ concentrations. All parameters meet Indonesia's National Standards (SNI) for biodiesel added with TBHQ up to 1200 ppm. Biodiesel which was treated with 1200 ppm of TBHQ provided the best result, due to its density, viscosity, IV, and PV. **CONCLUSIONS** However, TBHQ addition was did not affect the free fatty acid and acid number for 4 weeks of storage.

KEYWORDS antioxidant; biodiesel; oxidation stability; waste cooking oil

1. INTRODUCTION

Biodiesel is an alternative diesel fuel which is derived from vegetable oil. Saturated and unsaturated fatty acids are transesterified into fatty acid methyl ester (FAME) to substitute

petroleum diesel fuel. Recently, Indonesia has produced B30 as diesel fuel which consists of 30% FAME in petrodiesel. For long-term storage and exposure to air, auto-oxidation can occur and degrade the quality of biodiesel. Some properties as density, kinematic viscosity, acid value and peroxide value are adversely affected. Maintaining the quality of biodiesel is important to increase the oxidation resistance. Some factors which affect the oxidation are the presence of lights, air, temperature and metal catalysts. Several approaches for increasing oxidation resistance were investigated, such as storage under nitrogen atmosphere, glass storage and treatment used oxidation inhibitors (Yaakob et al. 2014).

Waste cooking oil (WCO) is one of the potential biodiesel feedstocks in Indonesia. It is produced from the rest of the repeated frying process. It contains carcinogenic compounds, which occur during the frying process so that it can cause cancer in a long period of time. Thus, using WCO is environmentally friendly and known as the third generation of energy (Riadi et al. 2014). The WCO content is similar to palm oil, but in rather different composition on the fatty acids. Usually, it has higher water content which is generated from the fried materials.

Some compounds which act as oxidation inhibitors are antioxidants. Ideal antioxidants for biodiesel should have the following requirements: (1) no toxicity; (2) low volatility; (3) effective in low concentrations; (4) high thermal and light stability; (5) availability; (6) high solubility in biodiesel; (7) long shelf life; and (8) cheap Embuscado (2015). Synthetic antioxidants commonly used for biodiesel storage are tertiary butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), pyrogallol (PY), gallic acid (GA) and propyl gallate Yaakob et al. (2014). Antioxidants such as PY, TBHQ and GA were more effective due to their molecular structures compared to BHA and BHT. Most antioxidants have two hydroxyl groups, which are attached to the aromatic ring, but in the case of BHT and BHA, only one hydroxyl group is observed in the aromatic ring. Antioxidants such as TBHQ and PY provide more active sites for the development of a complex between the free radical of the sample and the antioxidant Karavalakis et al. (2011). TBHQ's thermal stability is slightly better than BHA and BHT. In addition, TBHQ forms a protective film coating that protects copper and carbon steel

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from corrosion reactions Almeida et al. (2011). TBHQ is a white and shaped crystalline solid which is soluble in fat/oil and slightly soluble in water. Molecular structure of TBHQ is shown on Figure 1.

Oxidation stability of biodiesel could be observed from two parameters, namely induction period (IP) or physical/chemical properties. Mostly research works analysed IP for determining biodiesel oxidation stability. A previous research studied oxidation stability using Rancimat test to analyse the Induction Period (IP) over soybean biodiesel Domingos et al. (2007). They studied any antioxidant (AO) effects such as TBHQ, BHA and BHT and compared them with controlled biodiesel (without AO). Another research have determined IP, acid number and kinematic viscosity for commercial biodiesel and compared between synthetic (TBHQ and PG) and natural AO (Mango leaf extract) Yuliarita et al. (2019). Several researches studied the effect of some AO to the biodiesel IP using Rancimat test on soybean and rapeseed biodiesel (Dunn 2005; Mittelbach and Schober 2003; Orives et al. 2014).

Some other methods were applied to provide TBHQ effect to biodiesel. They studied TBHQ impact to the copper corrosion which was immersed in biodiesel (Almeida et al. 2011) and also observed some AO including TBHQ to the indirect-injection diesel engine performance (Ryu 2009).

All of the researchers investigated oxidation stability of biodiesel on the IP using rancimat test. Physical and chemical properties of biodiesel, especially from waste WCO have not been studied yet. This work specifically observed those properties to predict the oxidation stability of WCO biodiesel. In Indonesia, biodiesel is still produced from palm oil which has similar content with WCO. Therefore, oxidation stability data of WCO biodiesel is important to estimate long-storage properties.

A short period observation is possible to examine oxidation stability of biodiesel. Jatropha Curcas biodiesel has been observed for 4 weeks with several antioxidants (Roliadi et al. 2012). Pyrogallol performance also observed weekly as a biodiesel antioxidant for 4 weeks (Yusri et al. 2020). In addition, other research stated that TBHQ is the best antioxidant compared with PG, BHA, BHT and tocoferol (Yang et al. 2013). This work observed biodiesel properties with TBHQ for 4 weeks, in expectation that the data could be used to predict oxidation stability for longer-term storage.

2. MATERIALS AND METHODS

2.1 Material

Waste cooking oil was supplied from a local market to be transesterified to FAME. Methanol (99.9 % purity Merck, Ger-

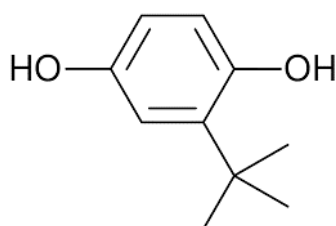


FIGURE 1. Tertiary butyl hydroquinon (TBHQ) molecular structure.

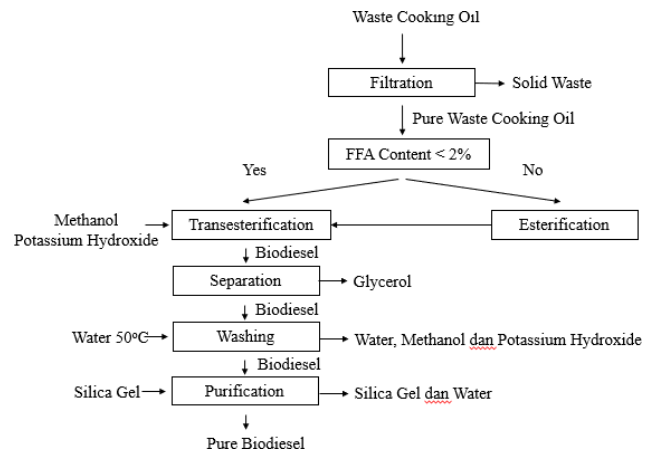


FIGURE 2. Trans-esterification method for producing WCO biodiesel.

many) and potassium hydroxide (85% purity Merck, Germany) were also used in this reaction. Tertiary butylhydroquinone (TBHQ) with a 97% purity was obtained from Sigma.

2.2 Procedures

Waste cooking oil was filtered to separate solid particles. Due to the low FFA contents (below 2%) of the WCO, it was straightly transesterified with methanol 1:4 (v/v) in the presence of 2% potassium hydroxide as a catalyst (Chai et al. 2014; NguyenThi et al. 2018). Biodiesel was purified by washing with warm water and using silica gel to adsorb the droplets. Washing is necessary to remove residual catalyst or soap (Oliveros et al. 2007). The detailed procedure is illustrated in Figure 2.

Biodiesel blends in various concentrations of TBHQ (0-1200 ppm) were kept in dark, sealed-glass bottles at room temperature. During a month of storage, samples were taken every week to measure the density, viscosity, acid value, iodine value and peroxide value. ASTM and AOCS methods were used to examine the physical and chemical properties of biodiesel. ASTM D-1298, ASTM D-445, ASTM D-664 were used to identify the density, viscosity and acid value of biodiesel, respectively. Then AOCS Cd-1-25 and AOCS Cd 8-53 were applied for iodine and peroxide values. This procedure is shown in Figure 3.

3. RESULTS AND DISCUSSION

Biodiesel properties were analyzed for 4 weeks of storage. Three levels of TBHQ concentration were observed for den-

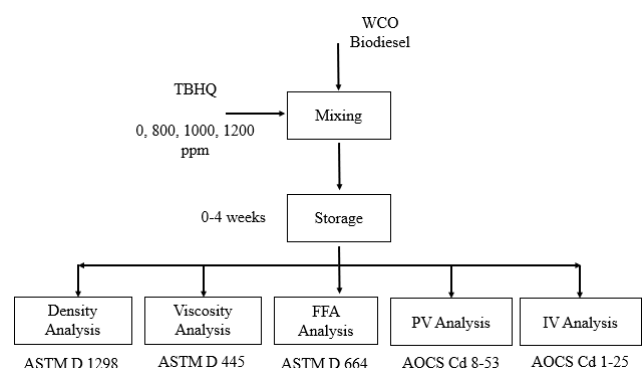


FIGURE 3. Biodiesel blending and analytical procedure.

sity, viscosity, %FFA, acid number and peroxide value. Iodine number was analyzed only for the lowest and highest concentration to observe the TBHQ effect.

3.1 Density

Density shows a comparison of mass per unit volume. Biodiesel with a high density value has low combustion capability in machine and shows high biodiesel conversion (Ebna Alam Fahd et al. 2014). Table 1 shows the biodiesel density after TBHQ adding and stored for 4 weeks. The density of pure biodiesel (without TBHQ) was higher than biodiesel with TBHQ, and more increasing especially after 3 weeks of storage, which was in accordance with previous research (Khalid et al. 2013). This indicates that pure biodiesel undergoes an oxidation process quickly and without hindrance compared to biodiesel with the addition of antioxidants.

At initial conditions, adding TBHQ of all concentrations increased biodiesel density a little bit higher than pure biodiesel, as shown in Table 1. This result was in accordance with previous research for biodiesel blends with 1000 ppm of TBHQ (Fattah et al. 2014).

In the first week of storage, all of the biodiesel added with TBHQ have lower densities until 2 weeks except for 800 ppm TBHQ added. Their densities then increased and almost constant until 4 weeks of storage. It showed that TBHQ improved the oxidation stability after 3 weeks of storage. However, all of these biodiesel densities were still appropriate for Indonesian Standard of biodiesel (SNI).

3.2 Viscosity

Figure 4 shows the viscosity changing for a month of storage. In the first week, all biodiesel samples had relatively the same viscosity. Without adding TBHQ, biodiesel viscosities were relatively constant until the second week, and start to decrease on the third week of storage. At that time, the polymer began to degrade and forming compounds with shorter chains and lower molecular weight (Zuleta et al. 2012). After the second week of storage, the addition of TBHQ caused a decrease in viscosity significantly for all concentrations. It continued until the third week before they started to raise again at the fourth week. However, biodiesel viscosity with 800 ppm TBHQ started to increase early on the second week than others which is not good indication.

Viscosity tended to be higher after 4 weeks of storage (Figure 4). This is due to intensive oxidation, which forms free radicals which polymerize to form compounds with longer chain bonds and higher molecular weight. If it was compared between all concentrations, 1200 ppm TBHQ was the lowest viscosity, which indicated the best result. However, it might be justified that 1200 ppm of TBHQ was not enough to prevent viscosity from increasing after 3 weeks of storage. For

commercial biodiesel, using 3000 ppm of TBHQ provided the best result (Yang et al. 2013). At the addition of 1000 and 1200 ppm TBHQ, the increase in viscosity began to appear at week 3. There was a tendency that the higher TBHQ concentration, the increase in viscosity could be prevented for longer shelf life. Controlled biodiesel (without TBHQ) has a higher viscosity than blended biodiesel with TBHQ for up to 4 weeks, indicating that using TBHQ can inhibit oxidation which degrades biodiesel, thereby reducing the intensity of the polymerization of the degradation products.

3.3 Free fatty acid (FFA) and acid number (AN)

The free fatty acids test aims to determine the content of free fatty acids contained in biodiesel. FFA content in biodiesel shows the level of biodiesel damage due to fatty acid oxidation. In this study, FFA content in all samples were almost constant (Figure 5). Whether blended with TBHQ or not, FFA contents still did not change for 4 weeks of storage. Even the addition of TBHQ up to 1200 ppm had no effect on FFA contents. The formation of free fatty acids in the form of carboxylic acids could be minimized in a closed vessel with no air-contact and controlled temperature. The addition of TBHQ enhanced the oxidative stability of biodiesel at higher temperature (Banu et al. 2016). In lower temperature, the fatty acid composition tends to remain unchanged. The FFA test in this work was carried out at room temperature so that there was a tendency that the fatty acid levels did not change. PUFA and MUFA turned into SFA on heating process. WCO biodiesel, the majority of fatty acids contained are SFA, so it was already stable and almost unchanged. However, it was possible that FFA contents may change after 4 weeks. This is in line with previous research which showed that the addition of synthetic antioxidants results in an increase in FFA levels after 2 months (Tang et al. 2008) and even one year of storage (Yang et al. 2013).

Figure 6 shows the acid number (AN) of all variants. There were no changes of acid number either on controlled biodiesel or added with TBHQ. It has similar tendencies with FFA contents. All biodiesel with TBHQ concentrations of 800, 1000, and 1200 ppm still have good performance in inhibiting the oxidation reaction up to the fourth week, therefore the acid number tends to be constant. Furthermore, the acid numbers of biodiesel, either controlled or with TBHQ, were

TABLE 1. Biodiesel densities (g/cm^3) for 4 weeks of storage.

TBHQ (ppm)	Week				
	0	1	2	3	4
0	0.8512	0.8512	0.8510	0.8526	0.8532
800	0.8515	0.8532	0.8493	0.8517	0.8518
1000	0.8515	0.8510	0.8495	0.8518	0.8518
1200	0.8515	0.8503	0.8519	0.8519	0.8524

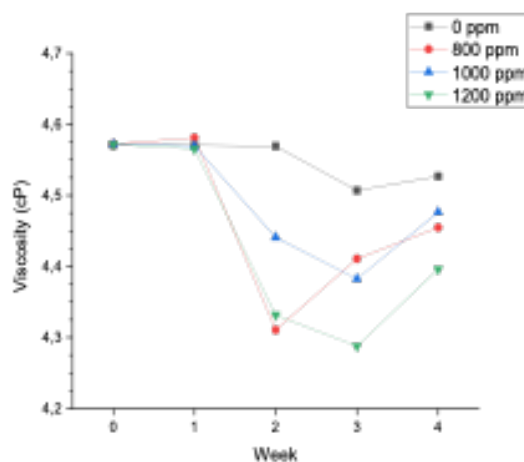


FIGURE 4. Viscosities of biodiesel in 4 weeks storage.

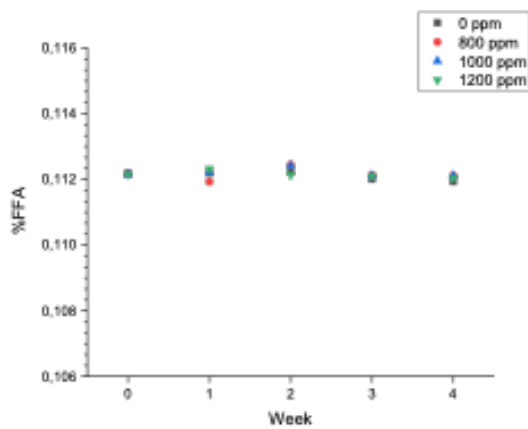


FIGURE 5. FFA contents of biodiesel in 4 weeks storage.

in the range of 0.244-0.246 mg KOH/g. When they were compared to the acid number requirement according to SNI of <0.5 mg KOH/g, all biodiesel variants still meet the standard. Different results were provided by previous research, which obtained higher and increasing AN for 4 weeks of storage (Yusri et al. 2020). The differences probably due to the fatty acid compositions of the biodiesel feedstock. While Yusri et al. (2020) used palm cooking oil which is high composition of unsaturated fatty acid, this work employed waste cooking oil which has major component of saturated fatty acid. Another possibility is due to storage condition. Carbon double bond in fatty acid is more susceptible to oxidation which will produce more FFA in supportive condition. In this work, the influence of light was avoided by using dark-sealed bottle to prevent an oxidation reaction.

3.4 Peroxide value (PV)

At initial conditions, the peroxide value in biodiesel treated with antioxidants decreased compared to controlled biodiesel. This shows that adding antioxidants such as TBHQ can reduce the peroxide number (Mittelbach and Schober 2003). Based on the experimental results, the initial conditions indicate that higher concentration of TBHQ provided smaller peroxide number (Figure 7).

In the first week, all peroxide numbers of biodiesel blended with TBHQ decreased significantly. This antioxidant that has been in contact for one week, scavenge free radicals

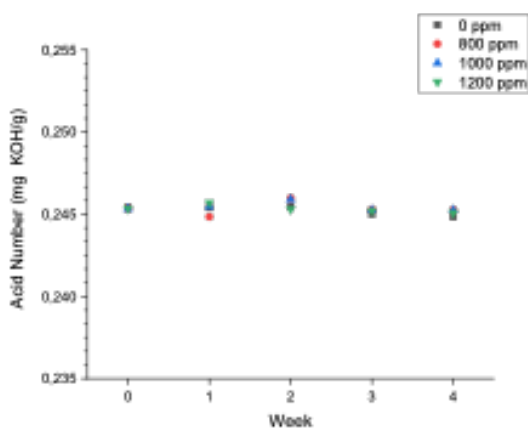


FIGURE 6. Acid number of biodiesel in 4 weeks storage.

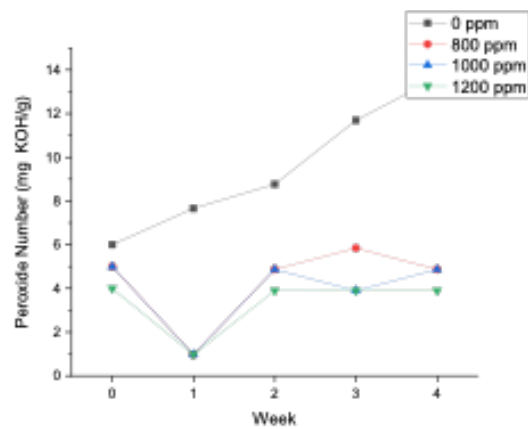


FIGURE 7. Peroxide value of biodiesel in 4 weeks storage.

in biodiesel. However, controlled biodiesel had increased peroxide value started from initial conditions until 4 weeks of storage. This result was in accordance with the previous research (Abramovič and Abram 2005). From week 1 to 2, all blended biodiesel’s PV increased significantly. After that period, PV tended to be constant until 4 weeks of storage. The black curve of Figure 7 described the actual difference of PV between controlled and blended biodiesel. The addition of TBHQ enhanced the oxidation stability since the first week of storage. Biodiesel with 1200 ppm of TBHQ provided the lowest PV since 0 until 4 weeks, which indicated it as the best concentration.

3.5 Iodine (IV)

Viscosity and PV data showed that 1200 ppm of TBHQ resulted the best oxidation stability of WCO biodiesel. Therefore, iodine value (IV) analysis observed only the lowest and the highest concentrations of TBHQ. Figure 8 compared iodine value between controlled and blended biodiesel with 1200 ppm of TBHQ. For the first 2 weeks, biodiesel added with TBHQ provided lower IV. However, after 2 weeks, they both showed the similar IV.

The biodiesel IV either controlled or with antioxidants ranged from 5.076 to 19.198 g I₂/100 g. Compared to the requirements for iodine number according to SNI of a maximum of 115 g I₂/100 g, all biodiesel samples met the requirements. However, the highest concentration of TBHQ could

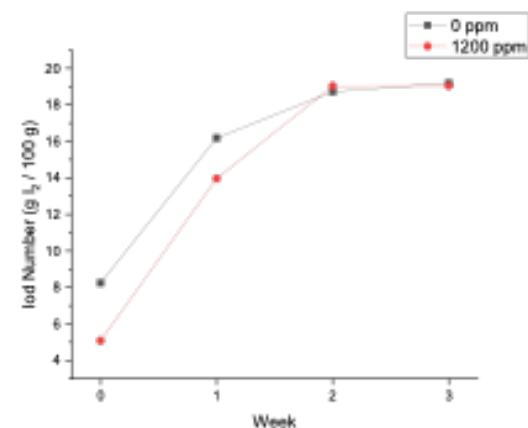


FIGURE 8. Iodine value of biodiesel in 4 weeks storage.

decrease IV only until 2 weeks of storage. After that, WCO biodiesel with TBHQ obtained similar IV with the controlled biodiesel. Biodiesel that undergoes oxidation is indicated by IV decreasing. Figure 8 shows that biodiesel oxidation start to stop after 2 weeks of storage. It indicated good condition because higher IV is susceptible to oxidation. IV was significantly influenced by the storage time and the presence of antioxidants in the biodiesel. Lower iodine number was provided by the biodiesel which was treated with antioxidants. Iodine value increased along with longer storage time (Zuleta et al. 2012).

4. CONCLUSIONS

All parameters tested on biodiesel from WCO with various concentrations of antioxidant of TBHQ for 4 weeks meet Indonesia's National Standards (SNI) for biodiesel. Biodiesel which was treated with 1200 ppm of TBHQ provided the best result, due to its density, viscosity, PV and IV. Meanwhile, TBHQ addition was not affected the FFA and acid number for 4 weeks of storage.

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