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The Effect of Tertiary Butylhydroquinone Antioxidant on The Stability of Rubber Seed Biodiesel

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Abstract

This study aims to determine the effect of the addition of tertiary butylhydroquinone (TBHQ) antioxidants on the quality of biodiesel. Rubber seed biodiesel is synthesized through esterification and transesterification reactions, then biodiesel is characterized by different stages of adding TBHQ antioxidants before the esterification reaction and after the transesterification reaction. The usage of TBHQ antioxidants at the various stages of adding the process greatly affects the quality of biodiesel. The results showed that the addition of TBHQ 1000 ppm after transesterification was the most effective in slowing oxidative degradation by showing the lowest characteristics (acid number 0.64 mg KOH/g and peroxide value 33.91 meq O_2/kg) for 3 weeks. All rubber seed biodiesel samples had kinematic density and viscosity according to the Indonesian National Standard (SNI) for 3 weeks except for the acid number only lasted 0 weeks.

Keywords: biodiesel, biodiesel stability, TBHQ antioxidant

1. Introduction

The demand for diesel fuel continues to increase over time with the increase in industry, transportation, and Diesel Power Generation in Indonesia. Diesel engines use diesel as a fossil-based fuel. Fossil fuels are non-renewable fuels that can trigger the depletion of fossil oil and increase the price of diesel fuel. Therefore, an alternative to diesel fuel is biodiesel [1].

Biodiesel is a methyl ester product derived from the transesterification reaction between animal/vegetable oil and methanol with the help of a catalyst. The most widely used raw material for biodiesel production in Indonesia is palm kernel oil. The main content of rubber seed oil is unsaturated fatty linoleic acids along 40%, oleic acids along 42%, and saturated oil along 18% [2]. The fatty acid of rubber seeds is more than 2% causing saponification. Therefore, before the transesterification reaction, esterification is carried out. Esterification is the stage of converting free fatty acids with alcohol in an acidic state into esters [1]. In the reaction of making biodiesel, a catalyst is needed because the reaction tends to run slowly. The base catalyst in the transesterification reaction has several vital requirements so that the resulting FAME is optimal, including the alcohol used must be in an anhydrous state with a water content of < 0.1 – 0.5%-wt, and the oil used must have a free fatty acid content of < 0.5% [3].

Rubber seed oil and rubber seed biodiesel have a weakness that has the potential to reduce the quality of biodiesel, namely the occurrence of auto-oxidation reactions. One of the potentials for auto-oxidation reactions is high unsaturated fatty acids. The auto-oxidation reaction of biodiesel affects several basic properties such as viscosity, acid value, iodine value, peroxide value, and induction time. In addition, the reaction of alkenes and dienes also plays a role in the phenomenon of oxidation [4].

In the previous study, Raghuveer and Hammond observed in their experiment that there was a reduction in the stability of the oil during oxidation between 37°C and 50°C during the transesterification process as with antioxidants [5]. Antioxidants are compounds that delay, control or inhibit the auto-oxidation process of the substrate and reduce the yield of unwanted secondary products [6]. The requirement for a good antioxidant is to be soluble in oil and biodiesel. In the study of Ni et al. [7], the conventional antioxidant tertiary butylhydroquinone (TBHQ) had the best solubility compared to other conventional antioxidants, such as pyrogallic acid, gallic acid, and vitamin C. In other studies, the solubility of TBHQ was only soluble up to 1500 ppm. It showed that the addition of 1500 ppm TBHQ antioxidant was effective in inhibiting oxidative degradation by showing the value of kinematic viscosity, acid number, and acid number according to SNI [8].

Based on the above discussion, in this study, a characteristic test was carried out on the addition of TBHQ antioxidants with variations in the reaction stages before and after the reaction aimed at seeing the effect of physical and chemical properties on biodiesel. Antioxidant TBHQ 1000 ppm is expected to inhibit oxidative degradation so which qualifies the Indonesian National Standard (SNI).

2. Materials and Method

The materials used in this study were NaOH, H_2SO_4, chloroform, TBHQ antioxidant, n-hexane, methanol, and aquadest. The materials were purchased from Merck and Chemical Suppliers. Rubber seeds were taken from PTPN VIII Mira Mare Garden, Karya Mukten Village, Cibalog District, Garut Regency, West Java.

This research includes the process of making biodiesel by transesterification, characterization of biodiesel, and observing the effect of adding TBHQ antioxidants with various treatments.

2.1 Introduction stage

a. Rubber seed oil isolation

The rubber seeds are peeled, then the rubber seeds are cleaned and dried in the sun for a day and then dried in an oven for one hour at 100°C to reduce the moisture content. Rubber seeds ± 90 grams were extracted with n-hexane as much as ± 390 mL for 4 hours using Soxhlet equipment. The mixture was cooled, and the n-hexane was evaporated using a rotary evaporator at 60°C.

b. Esterification

The 200 grams of rubber oil obtained in step (a) was esterified to reduce the acid value. The rubber seed oil was poured into the flask and heated to 50°C. 174 mL of methanol was added to the heated rubber seed oil and stirred at 800 rpm for several minutes. 0.5% concentrated sulfuric acid (v/w of the sample) was also added to the mixture. Heating and stirring were continued for 60 minutes at atmospheric pressure. The product is poured into a separatory funnel for a day to separate the alcohol phase. Excess alcohol, sulfuric acid, and impurities move to the top surface. The bottom layer is separated to be tested for acid value and processed by transesterification. If the gum cannot be separated, the sample is centrifuged to separate the sample from the gum and alcohol.

c. Transesterification

The esterification product of 200 grams from step (b) is heated to the required reaction temperature of 50°C in a flask. The NaOH 0.5% w/w of the sample was also dissolved in 58 mL of methanol. The mixture was added with heated rubber seed oil and stirred at 800 rpm for 90 minutes. The resulting product is allowed to stand for 24 hours until the product separates into two layers. The bottom layer, containing glycerol and NaOH is taken, and esters remain in the top layer. The methyl ester was washed to remove the trapped catalyst and glycerol with hot demineralized water (10% by volume) was sprayed onto the surface of the ester and stirred slowly to pH 7. The bottom layer was removed and the yellow color layer (known as biodiesel) was separated, after which the biodiesel product was characterized. 1000 ppm antioxidant was added as a sample treatment. Finally, biodiesel was characterized and analyzed for its physical and chemical properties.

2.2 Quality test of rubber seed biodiesel and rubber seed oil

Biodiesel that has been transesterified in step (c) is stored indoors for a month. Every week the physical and chemical properties of the acid number, peroxide value, and kinematic viscosity were checked.

a. Acid numbers (AOCS CA 30-63 or ASTM D-664)

A total of 1 g of the oil sample was weighed and put into a 250 mL erlenmeyer. Add 10 mL of a mixture of diethyl ether and 95% ethanol solvent which has been neutralized in a ratio of 1: 1, then the PP indicator is added to the erlenmeyer. Stir and then titrated with 0.1 N KOH solution until pink color is formed. The pink color should last at least 15 seconds. The titrant volume was recorded. The acid number is calculated using Equation 1.

$$\text{Acid Number} = \frac{\text{V x N x 56,1056 } {}^{g}/_{mol}}{\text{W}} \qquad (1)$$

where:
V: Volume of KOH for titration
N: Normality of KOH (N)
W: Weight of oil sample (g)

b. Density (AOAC 969.17)

The pycnometer was washed first, then the empty pycnometer was weighed and continued by weighing the mass of the pycnometer containing the sample which had been heated at 40°C. Sample density can be calculated by Equation 2.

$$\text{Density } (40^{\circ}\text{C}) = \frac{(B-A)\ g}{(volume\ pynometer)mL} \qquad (2)$$

where:
B: Mass of the pycnometer containing the sample
A: Mass of empty pycnometer

c. Peroxide value (SNI 3741:2013)

The 1 g sample was put into a 250 mL erlenmeyer, then 10 mL of a mixture of glacial acetic acid and chloroform in a ratio of 3:2 was added and stirred. A total of 0.5 mL of potassium iodide was added and kept in a dark place for a minute. Then 30 mL of CO_2-free distilled water was added and 0.5 mL of 1% starch indicator was added and then titrated with 0.1 N sodium thiosulfate standard solution. The blank was also determined. The peroxide value is calculated using Equation 3.

$$\text{Peroxide Value} = \frac{(A-B)xNx1000}{mass\ of\ sample\ (gram)} \qquad (3)$$

where:
A: Number of mL $Na_2S_2O_3$ for sample
B: Number of mL $Na_2S_2O_3$ for blank

d. Kinematic viscosity (ASTM D-445)

Oswalt viscosity was washed with water and acetone, then placed in a bath and allowed to stand until the temperature of the bath water and liquid was the same (40°C ± 0.02°C). The oil sample is pumped into the capillary and allowed to descend and the time required for the sample flow to the bottom calibration mark is calculated. Kinematic viscosity is determined by Equation 4.

$$v = C \times t \qquad (4)$$

where:
v: Kinematic viscosity (mm^2/s)
C: Calibration of miniature viscosity constant U (mm^2/s^2)
t: flow time (s)

3. Results and Discussion

3.1 Characteristics of rubber seed oil and rubber seed biodiesel

Table 1. Characteristics of rubber seed oil

Characteristic	Value	Unit
Density	0.92	g/mL
Kinematic Viscosity	27.62	cSt
Acid number	24.44	mg KOH/g

The total rubber seed oil obtained from the extraction was 717 mL from 2 kg of rubber core meat (yield 35.87%). According to reference [9], rubber seed yields 40-50% oil. Different yields may occur due to different sources of rubber seed varieties so the resulting oil yields are different. The color of the rubber seed oil produced is yellow. It can be seen from Table 1 that the characterization of rubber oil is not in accordance with the biodiesel standard.

Density, acid number, and kinematic viscosity higher than SNI may damage the diesel engine, so a transesterification step is needed in order to reduce the density and viscosity according to SNI 7182:2015. The high acid number (more than 2.0 mg KOH/g sample) causes a saponification reaction during transesterification, so biodiesel is difficult to separate from the methanol phase [10]. For this reason, the next step is needed, namely the esterification stage. The acid number of rubber seed oil after esterification was 0.64 mg KOH/g sample.

The samples with an acid number of less than 2 mg KOH/g were then transesterified to convert triglycerides into methyl esters. The results of this study showed a decrease in density, viscosity, and acid number. The decrease in density, kinematic viscosity, and acid number is thought to be due to the conversion of triglycerides into methyl esters with smaller molecules. Table 2 shows the characterization of biodiesel according to the biodiesel standard as follows.

Table 2. Characteristics of biodiesel rubber seed oil

Characteristics	Value	SNI 7182:2015	Unit
Density	0.881	0.85-0.89	g/mL
Kinematic Viscosity	3.13	2.0-6.0	cSt
Acid Number	0.48	Max 0.5	mg KOH/g
Peroxide Value	18.19	-	meq O_2/kg

3.2 Characteristics of biodiesel in the addition of TBHQ to biodiesel stability

The transesterified samples were then tested with density, viscosity, acid number, and peroxide value. This test is carried out to see the stability of biodiesel when stored for 3 weeks and is tested every 7 days. Biodiesel is stored in a closed room and stored at room temperature (ambient). The results of the characterization can be seen in Table 3.

a. Density

Density was tested by AOAC 969.17 method. The fuel density parameter is important for the fogging process in diesel engines [11]. In Table 3 and Figure 1, it can be seen that all the results of biodiesel samples with various stages of adding TBHQ antioxidants experienced an increase in the density pattern from time to time. Density itself is influenced by molecular weight and molecular density. As long as biodiesel is stored, an oxidation reaction will occur and produce oxidation by-products in the form of monomers and polymers which can increase the density [11]. The highest density yield was obtained by biodiesel with the addition of the TBHQ after the certification reaction of 0.889 g/mL after 3 weeks. This is because the TBHQ molecule has an –OH group that attracts each other electrostatically with the O atom of the ester causing hydrogen bonds to occur. Hydrogen bonding is the distance between the molecules close together so that the molecular density increases as shown in Figure 2.

According to SNI 7182:2015, each other the density is between 0.850-0.890 g/mL. In Table 3 it can be seen that all biodiesel samples with various variations of the addition of TBHQ antioxidants still suitable SNI 7182:2015.

Table 3. Effect of the addition of TBHQ antioxidants for 3 weeks

Addition of Antioxidant TBHQ		Density (g/mL)	Kinematic Viscosity	Acid Number	Peroxide Value
Volume	Week		(cSt)	(mg KOH/g)	(meq O_2/kg)
0 ppm	0	0.881	3.13	0.48	18.19
	1	0.883	3.18	0.59	24.28
	2	0.886	3.22	0.69	36.62
	3	0.887	3.26	0.73	50.86
1000 ppm before esterification	0	0.880	3.16	0.46	13.58
	1	0.883	3.28	0.58	21.17
	2	0.885	3.33	0.62	35.12
	3	0.888	3.48	0.68	47.98
1000 ppm after transesterification	0	0.882	3.52	0.48	17.46
	1	0.885	3.64	0.59	22.09
	2	0.887	3.64	0.61	25.63
	3	0.889	3.72	0.64	33.91

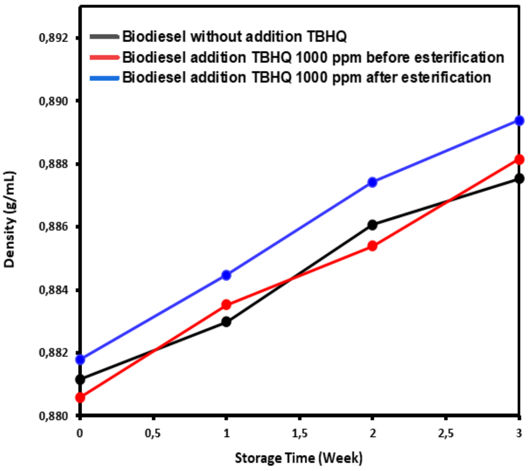

Figure 1. Biodiesel density chart for 3 weeks

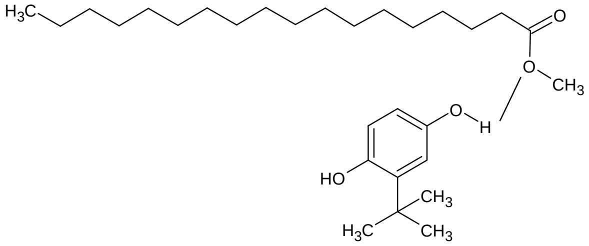

Figure 2. Hydrogen bonding between biodiesel and the antioxidant TBHQ

b. Kinematic Viscosity

From Figure 3 it can be seen that it has the same tendency as density. Where the highest kinematic viscosity condition was obtained from biodiesel with the addition of 1000 ppm TBHQ after the transesterification reaction of 3.72 cSt. followed by biodiesel with the addition of 1000 ppm TBHQ before the esterification reaction of 3.48 cSt. Then biodiesel without the addition of TBHQ of 3.26 cSt.

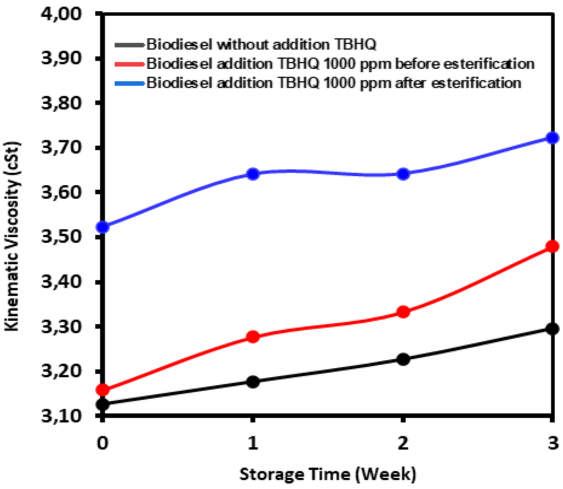

Figure 3. Kinematic viscosity biodiesel chart for 3 weeks

In storage conditions for 3 weeks, there was an upward trend. Liu and Chiu [13] said that during oxidation molecular weight increased along with storage time which resulted in increased kinematic viscosity to form polymers. The formation of polymers can cause the liquid to become more viscous due to the joining of monomers. Final products auto-oxidation aldehydes and ketones can act as aldol condensation to form sediments that are insoluble in biodiesel [12]. Indirectly, the kinematic viscosity and density have similarities to Figure 1 and Figure 3. All biodiesel samples have kinematic viscosity values according to SNI 7182:2015.

c. Peroxide value

The peroxide value is not used as a biodiesel standard. but the peroxide value influences oxidative stability because peroxide value is an indication of the formation of milligram equivalent hydroperoxide compounds due to the oxidation process in biodiesel. It can be seen in Table 3 and Figure 4 that the longer the sample is stored, the higher the peroxide value.

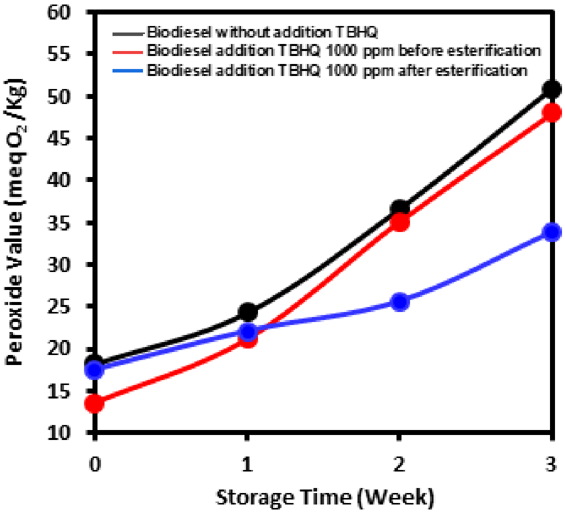

Figure 4. Peroxide value biodiesel chart for 3 weeks

Adding antioxidant TBHQ 1000 ppm after transesterification has a sloping pattern compared to added antioxidant TBHQ 1000 ppm before esterification and without the addition of TBHQ. This is because new antioxidants can inhibit free lipid radicals by donating H radicals after being stored for a long time [6]. It can be seen in Figure 4 that biodiesel with the addition of antioxidants has a more sloping pattern.

Biodiesel with 1000 ppm TBHQ before esterification at week 0 had a lower peroxide value of 13.58 meq O_2/Kg compared to the peroxide value of biodiesel without TBHQ addition of 18.19 meq O_2/Kg and biodiesel with 1000 ppm TBHQ addition of 17.46 meq O_2/Kg. This is because the addition of antioxidants before esterification causes the sample to be resistant to oxidation degradation. Oxidative degradation occurs due to environmental factors such as air and temperature. So that during the esterification and transesterification treatment, biodiesel added with antioxidants before esterification experienced less oxidative degradation. From week 1 to week 3, the peroxide number pattern increased quite sharply in the sample with the addition of 1000 ppm TBHQ antioxidants before esterification. The antioxidants might have formed stable antioxidant radicals due to the esterification and transesterification steps. Another factor is that TBHQ is very volatile causing TBHQ in the sample to resist the oxidation reaction in biodiesel. In research by Liu and Chiu [13] TBHQ can withstand oxidation degradation in oil up to a temperature of 80°C. Biodiesel without the addition of TBHQ experienced the highest oxidative damage which can be seen in the Table 3 and Figure 4. This is due to the absence of antioxidant inhibitors so that the double bonds in lipids react with oxygen to form lipid radicals continuously. Then the lipid radicals react with oxygen to form peroxide compounds. The TBHQ mechanism as an antioxidant can be seen in Figure 5.

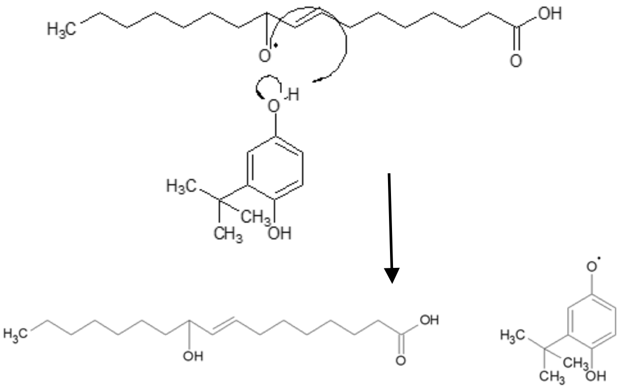

Figure 5. TBHQ mechanism of action as antioxidant

d. Acid number

Based on Table 3 and Figure 6, all biodiesel sample results have increased acid numbers from time to time. The longer the storage, the higher the acid number because it undergoes an oxidation reaction for a long time.

The biodiesel sample at week 0 did not have a significant difference in acid number. It is possible that a new oxidation reaction occurred so that it did not produce short-chain acid compounds. Furthermore, at week 2, it was clear that the difference in acid numbers was due to the addition of the antioxidant TBHQ. The addition of TBHQ antioxidants (before and after the reaction) shows a sloping pattern in Figure 6, which shows a slowdown in oxidation. The oxidation can be slowed down by donating antioxidant H radicals to lipid radicals so that no acidic compound products are formed [4]. At week 3 the addition of 100 ppm TBHQ antioxidant after transesterification was most effective to inhibit and slow down oxidative degradation of 0.61 mg KOH/g. The acid number without the addition of TBHQ was highest because there was no inhibition from antioxidants. Furthermore, based on SNI 7182:2015, the limit of acid number is 0.5 mg KOH/g. Table 3 shows that all biodiesel samples at week 0 only suitable biodiesel standards.

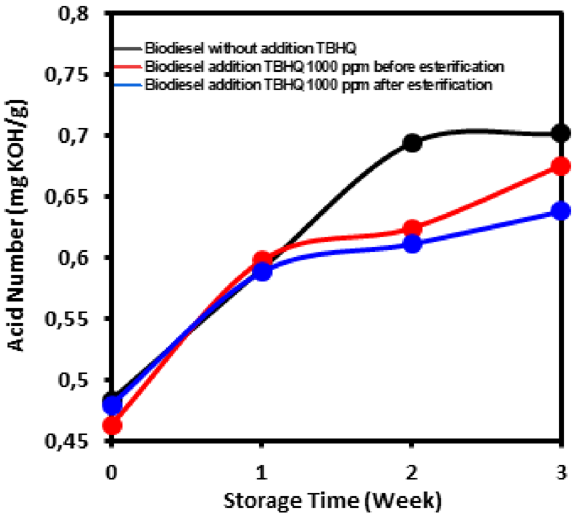

Figure 6. Biodiesel acid number chart for 3 weeks

4. Conclusions

Based on the results of the study, it can be concluded that the addition of 1000 ppm TBHQ antioxidants in rubber seed biodiesel could not fulfill SNI because the acid numbers of all treatment samples exceeded the SNI threshold in the third week. Biodiesel with the addition of the antioxidant TBHQ 1000 ppm (after trans-esterification) was most effective in inhibiting oxidative degradation (by showing an acid number of 0.6379 mg KOH/Kg and a peroxide number of 33.9056 meq O_2/Kg). Because antioxidants do not undergo heating during the esterification and transesterification stages.

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