Binary Effect of Tertiary Butylhydroquinone and Butylated Hydroxytoluene Additives with The Addition of Glycerol Monostearate to Improve Oxidative Stability of Palm Oil-Based Biodiesel

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Abstract. Biodiesel is a renewable and environmentally friendly alternative to conventional diesel fuel. However, like any fuel, biodiesel is subject to oxidation, which can negatively impact its quality and performance when kept for long-term. The addition of binary antioxidants such as TBHQ:BHT had been proven to improve oxidation stability of biodiesel. Combining surfactant such as GMS into single antioxidant had been proven to solve its insolubility issue. However, the implementation of mixing binary antioxidants and surfactant has not been done yet. Therefore, this research analyzed the effect of single antioxidant, binary antioxidants, and binary antioxidants with GMS (100 ppm) addition into biodiesel and biodiesel blend B35. The effect was observed within 8 weeks storage period. The result showed that B35 did not have any significant impact. While in pure biodiesel samples, B100-bi and B100-bi+GMS had a slight difference in the results of oxidative parameters. B100-bi showed the best result in induction period and kinematic viscosity. Rancimat test showed 170 hours for B100-bi and 168 hours for B100-bi+GMS. While B100-bi+GMS indicated as the best additives in term of acid number, iodine value, and dispersion test. Hence, the addition of surfactant into binary antioxidants showed similar performance with B100-bi but with slightly better solubility.

1 Introduction

The reference scenario predicts the total energy consumption in the world is going to rise to 19.3 billion tons of oil equivalent in 2050. This increase is directly proportional to economic development and population growth [1]. In 2018, the world's total consumption of energy from fossil fuel sources is 84.7%; while the remaining comes from nuclear, hydropower, solar, wind, and other sources which are 15.3%. Fossil fuels cannot be continuously relied on to fulfil the energy demand. The current rate of production is predicted to result in the extinction of coal in 132 years, natural gas in 50.9 years, and oil in 50 years. In addition, the

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consumption of fossil fuels emits carbon dioxide (CO_2) into the air which affects greenhouse gas [2]. From 2020 levels, CO_2 emissions grew by roughly 2.1 Gt. This places 2021 ahead of 2010 in terms of the year-over-year increase in energy-related CO_2 emissions [3].

Therefore, the proposed scenario for net zero emissions (NZE) by 2050 lays out a restricted but feasible path for the global energy industry to reach net zero CO_2 emissions by 2050. To achieve this target, energy production from fossil fuels will be shifted to renewable energy sources. In addition, many investments in renewable energy technology and policies to support the realization of net zero emissions are being made [4].

In comparison to fossil fuels, renewable energy is cleaner since it does not release dangerous emissions like greenhouse gasses. Net zero emissions require support in critical technology areas such as improved batteries, low-carbon fuels, hydrogen electrolyzers, and direct air capture. One of the low-carbon fuels is a biofuel which might be the best-suited substitute for fossil fuel as a transportation fuel to reduce emissions [4].

Biofuel is a liquid or gaseous renewable fuel produced from biomass. Liquid bioethanol and biodiesel which are obtained from agriculture products or animal fats, are normally used as transport fuel [5]. To be compatible with the IEA Net Zero Scenario, biofuel consumption must almost double our main scenario or increase by more than 40% from the accelerated case. Liquid biofuels must be expanded under the Net Zero Scenario with the primary purpose of decreasing emissions from road transportation and, to a lesser extent, aviation and ships [6].

Biodiesel is a mono-alkyl ester of fatty acids from the transesterification process of triglyceride and alcohol. The safe alternative fuel biodiesel can be used in place of conventional petroleum diesel. It degrades rapidly in the environment and is non-toxic. It also burns cleanly and has many lubricities. It can protect the environment by reducing CO_2, SO_2, CO, and HC. The photosynthetic mechanism makes the biodiesel carbon cycle dynamic. More CO_2 is absorbed by plants than is released during the burning of biodiesel. The outcome is a positive energy balance [7].

Biodiesel that has just been acquired does not encounter any issues when used immediately and meets all the necessary standards, such as the use of biodiesel in car within days or weeks. Nevertheless, complications arise when biodiesel is stored for an extended period as biodiesel exhibits weaker oxidative stability compared to fossil diesel [8].

One of the most crucial characteristics of fatty acid methyl esters (FAME) is oxidation stability, which has an impact on biodiesel namely damaged fuel characteristics, reduced fuel quality, and decreased engine performance. In comparison to petroleum diesel, biodiesel is often less oxidation-resistant. Biodiesel can be oxidized easily because it has unsaturated bonds in the ester chain. Oxidation can happen when the biodiesel is in contact with air during storage time and undergoes too much heating process. This can result in sediment that might clog the engine and change the flash point [9].

A study observed the effect of long-term storage of biodiesel in 18 weeks period which shows biodiesel storage with a condition that is dark and in a closed container [10]. Both types experience increases in kinematic viscosity, acid number, density, total glycerol, and peroxide value as well as decrease in FAMEs. Others indicator for oxidation process could be decrease in induction period and iodine value These changes can result in the production of peroxides and hydroperoxides that can then be broken down into shorter-chain compounds including alcohol, ketones, aldehydes, and oligomers [11]

In Indonesia, B35 has been implemented nationally starting on February 1, 2023 [12]. Indonesia is a country that excels in biodiesel development with the highest blend currently, other largest biodiesel-producing countries apply lower blends, for example, the US and Brazil apply the highest B20 and B12 respectively [13]. This gradual increase in the blend is a form of the government's commitment to overcoming the climate crisis to achieve Net Zero

Emissions [12].A higher transitional biodiesel blend means that it is more prone to oxidation, which requires a solution to the problem of long-term storage.

Addition of antioxidant has been the primary focus of research among scientists to improve the oxidative stability [14]. Antioxidants inhibit the oxidation process and have an extensive record of usage in controlling biodiesel oxidation. Antioxidant chemicals are added to biodiesel in order to increase its oxidative stability. Antioxidants function as a barrier that stops the process of oxidations, causing the antioxidant to react with free radicals first. The widely used synthetic antioxidants are TBHQ, BHT, BHA, PG, and PY[15]. Synthetic antioxidants in food industry are preferred as it has higher stability and performance, low cost and widely available [16].

Studies by Ajie et al. (2020) and Naufal et al. (2020) show that some binary effect at the right proportion has better oxidative stability compared to a single antioxidant [11,17]. One example is the TBHQ:BHT (3:1) combination which has 24.19 hours induction period which is 7.5% and 24.1% higher in comparison to TBHQ and BHT alone at the same concentration.

TBHQ and BHT are both phenolic substances. TBHQ is soluble in both oil and slightly in water. TBHQ is recognized as the most powerful antioxidant in biodiesel [18]. It is better at enhancing oxidative stability due to its partial solubility, which makes it more efficient at decreasing free radicals on the oil-air surface. Although TBHQ has been shown to prevent oxidation, it is still not completely soluble in oil and may result in sediment formation. On the other hand, BHT is very soluble in oil. It is suitable for biodiesel blends that contain low concentrations of biodiesel. The combination of TBHQ and BHT creates a synergistic effect and is able to enhance the oxidative stability of biodiesel [19]. The addition by binary antioxidants could outperformed single antioxidants in terms of induction time [11,20,21].

Solving the solubility issue can be done by altering the antioxidant’s molecular structure to increase oxidative stability. Besides that, surfactant addition may also be able to answer the issue. Due to the unique property of the substance, the surfactant functions as a medium. Its non- polar side will contact with oil, and its polar side will interact with an antioxidant. As a result, adding surfactants makes the antioxidant more soluble in biodiesel and boosts the fuel's oxidative stability [22]. Glycerol monostearate (GMS) is one of the effective surfactants to increase the dispersion of antioxidants [23].

A mixture of TBHQ and BHT additives and GMS as the surfactant will be added to palm oil-based biodiesel samples to achieve synergism of both antioxidants and higher solubility of antioxidants in biodiesel. Theoretically the quality of biodiesel could be improved further to SNI level, as the TBHQ and BHT combination has a synergistic binary effect, and the addition of surfactant both antioxidants could increase the solubility to both antioxidants.

2 Materials, Equipment and Method

2.1 Materials and Equipment

The chemicals that were used in this experiment for the sample are Tert-butylhydroquinone (TBHQ) and Butylated hydroxytoluene (BHT) as biodiesel antioxidants, Glycerol Monostearate (GMS) as surfactant, and commercially produced biodiesel in Indonesia. The antioxidants and surfactant were obtained from commercial store. The pure biodiesel was obtained from Sinarmas while biodiesel B35 was obtained from commercially sold biodiesel.

The chemicals that were used for the antioxidant activity test are Phenolphtalein indicator solution; Potassium Hydroxide (KOH) and ethanol for acid number test, chloroform; Wijs solution; Potassium Iodide (KI); Sodium thiosulphate ($Na_2S_2O_3$); starch solution and demineralized water for iodine value test. N-hexane was used as a solvent for dispersion test. All the chemical were from Merck.

The mass scale used was WANT Electronic Balance with precision of 0.1 mg. While T60 UV VIS Spectrophotometer was used for spectrophotometry.

2.2 Design of Experiment

The fresh biodiesel obtained was used as the samples, one without fossil-fuel blend while another with B35 blend. After that, the samples were further divided into three categories which were added with nothing, antioxidant(s), and antioxidants with surfactant. A total of ten samples, as can be seen in Table 1, were prepared for oxidative stability test through iodine test, acidity test, viscosity test and Rancimat test to find out if there was any oxidation occurring that decrease the product quality.

Table 1. The samples list

No.	Sample
1	Biodiesel B35
2	Biodiesel B35 + TBHQ (2000 ppm)
3	Biodiesel B35 + BHT (2000 ppm)
4	Biodiesel B35 + TBHQ:BHT (3:1 2000 ppm)
5	Biodiesel B35 + TBHQ:BHT(3:1 2000 ppm) + GMS (100 ppm)
6	Biodiesel B100
7	Biodiesel B100 + TBHQ (2000 ppm)
8	Biodiesel B100 + BHT (2000 ppm)
9	Biodiesel B100 + TBHQ:BHT (3:1 2000 ppm)
10	Biodiesel B100 + TBHQ:BHT (3:1 2000 ppm) + GMS (100 ppm)

Acidity test and iodine test were being conducted duplo in the laboratory every two weeks for two months while Rancimat and kinematic viscosity test were tested on trusted analysis company that was done once in the beginning and the end of the observation period. After finding out the result from acidity and iodine test, the best two samples of mixed B100 along with pure B100 were selected for Rancimat test. The viscosity test and Rancimat test were done in an operating condition of 40 °C. The dispersion test was also done to find out the dispersion of the antioxidants.

2.3 Acid Number Test

The Standard Test Method for Acid Number of Petroleum Products ASTM D 664 protocol was used to measure the acid number with the modification of reducing the quantity of materials by half. In the Erlenmeyer flask, 50 ml of ethanol and around 10 drops of phenolphthalein were combined to create a blank sample. Then, ethanol and each sample weighing around 1.5 grams was added to an Erlenmeyer flask. The flask was filled with an indicator solution— 10 drops of phenolphthalein—and swirled until the indicator solution reached homogeneous state. KOH 0.01 N was used to titrate the solution until the color turned pinkish. The acid number was determined using Equation (1) by measuring the KOH titration volume [22].

$$Acid\ Number\ \left(mg\,\frac{KOH}{g\ sample}\right) = \frac{(V_{blank} - V_{titrant}) * N_{KOH} * M_{KOH}}{mass\ of\ sample\ (g)} \tag{1}$$

where: V is the volume, N_{KOH} is the normality of the selected titrant in mol/L, M_{KOH} is the molecular weight of KOH which is 56.11 g/mol.

2.4 Iodine Value Test

International Standard Procedure AOCS Official Method Cd 1-25, which was adapted from was used to measure the iodine value. The sample was placed in a 500 ml Erlenmeyer flask after being weighed at about 0.15 grams. Then, 25 ml of Wijs solution was added to the solution, followed by 15 ml of chloroform. The flask was sealed with aluminum, and it was kept in a dark location for an hour. 100 ml of demineralized water and 20 ml of 10% KI solution was then added to the sample. The solution was titrated using sodium thiosulfate solution of 0.1 N, and the flask was shaken as the reducing agent was introduced to the solution. When the color turned light orange, approximately 1 ml of starch solution was added, and the titration process was continued until the solution turns clear. The same process was used to create a blank sample that does not contain any biodiesel [22]. To determine the iodine value, the volume of sodium thiosulphate was measured using Equation (2).

$$Iodine\ Value = \frac{(V_{blank} - V_{titrant}) * N_{Na2S2O3} * 12.69}{mass\ of\ the\ sample\ (g)} \tag{2}$$

where: V is the volume in ml, $N_{Na2S2O3}$ is sodium thiosulphate normality.

2.5 Kinematic Viscosity at 40° C Test

The prepared samples B100 were further by PETROLAB which located in East Jakarta using ASTM D 445 method.

2.6 Rancimat Test

Pure biodiesel along with two best samples were analyzed by using EN 15751 method by BRIN (Badan Riset dan Inovasi Nasional). The purpose of this analysis was to find information about induction period.

2.7 Dispersion Test

n-hexane was used as a solvent to dilute the sample combinations. A 0.25 ml sample was taken from the same depth distance from the surface, and 19.75 ml of hexane was put to a flask. A vortex mixer was used to agitate the flask until the contents were homogeneous. The solution was then passed through the T60 UV VIS Spectrophotometer. The solution's absorbance was measured at 290nm and 278nm wavelengths [22].

3 Result and Discussion

3.1 Effect of Various Additives Addition to Acid Number During Storage

The acid number is a measurement used to quantify the carboxylic acid groups within a sample, indicating the amount of acid present in the fuel. In the process of oxidation, hydroperoxides (ROOH) typically form when peroxide radicals attack the hydrocarbon chain. As the propagation of oxidation progresses, the accumulation of hydroperoxides increases over time. Subsequently, the oxidation process facilitates complex reactions of hydroperoxides, leading to the formation of aldehydes, which are further oxidized into acids [24]. When that happens, the acid number increases.

3.1.1 Effect of Antioxidant Additives to Acid Number of Pure Biodiesel

The acid number during 8 weeks period was observed. Pure biodiesel's acid number increased which indicated that there was an oxidation process happening as can be seen in Figure 1. The increase in acid number was significant as p value < 0.05. A study from Wahyono et al. (2022) also showed that palm oil biodiesel gets oxidized over time [10].

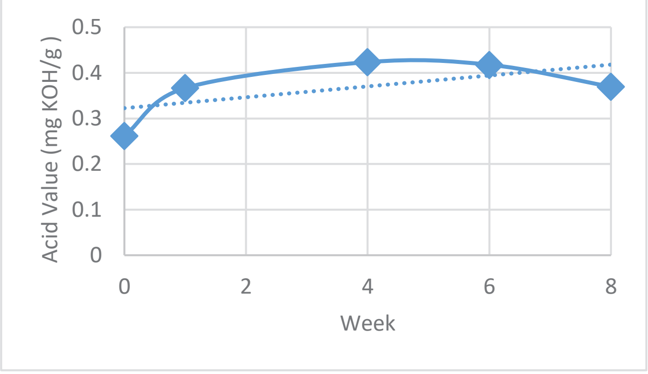

Fig. 1. Acid number of pure biodiesel for 8 weeks

Afterwards, there were four kinds of additive being added into pure biodiesel which were TBHQ, BHT, binary, binary with GMS.

Table 2. Acid number slope difference of pure biodiesel with four different kinds of additive(s)

Sample	Slope
B100-TBHQ	0.0087
B100-BHT	0.0116
B100-bi	0.0108
B100-bi+GMS	0.0020

The added additives were compared using their individual linear slope values to observe the difference between one with another. Some acid number increased quickly as biodiesel oxidized. From Table 2, B100-BHT was shown to have the fastest rate of oxidation. B100-bi turned out to have better performance than B100-BHT, however, had a higher slope compared to B100-TBHQ. While B100-bi+GMS had the best performance compared to other kinds of additives. Among all additive types, they were statistically did not show any significant difference (p value > 0.05), however, the addition of binary antioxidant with surfactant had the least increasing slope in acid number, it might indicate to have a better biodiesel antioxidation performance.

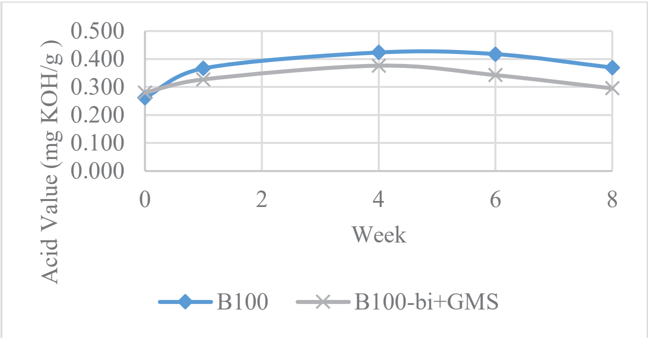

Fig. 2. Acid number of pure biodiesel and biodiesel with binary antioxidants and surfactant for 8 weeks

Figure 2 shows when acid number of biodiesel with binary antioxidants and surfactant was compared to the acid number of pure biodiesel only, the one with additives addition showed better performance because it has smaller increase compared to no addition of additives. T test < 0.05 which indicated it was significant different. Similar result in a study by Hery Sutanto et al. (2018) where the combination of TBHQ + GMS (100 ppm) was proven to have a better performance compared to pure biodiesel only [22]. Therefore, in this acid number test of pure biodiesel, the addition of TBHQ:BHT(3:1) + GMS also proven to reduce the rate of oxidation as the additives could prevent the attack of oxidation directly to the fuel.

3.1.2 Effect of Antioxidant Additives to Acid Number of Blended Biodiesel (B35)

The acid number of B35 during 8 weeks period was also observed. Biodiesel blend's acid number slope was near zero as can be seen in Figure 3. Statistically, it was significant different since the p value < 0.05. However, the difference between week 8 and week 0 was very thin which they can be concluded biodiesel B35 was rather stable. This incident could be explained as petroleum diesel dominated the whole fuel.

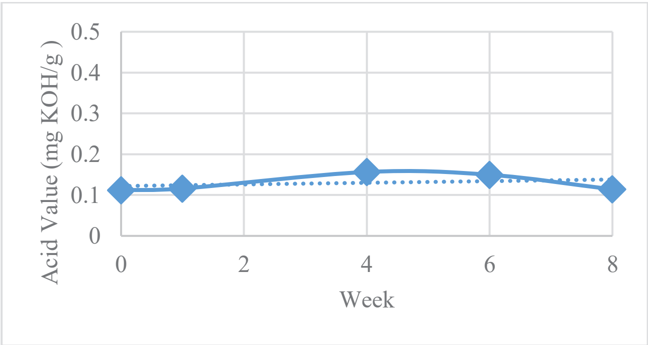

Fig. 3. Biodiesel B35 acid number for 8 weeks

Table 3. Acid number slope difference of biodiesel B35 with four different kinds of additive(s)

Sample	Slope
B35-TBHQ	-0.0027
B35-BHT	0.0043
B35-bi	-0.0010
B35-bi+GMS	-0.0007

Table 3 shows the slope differences between four additive(s) into biodiesel blend were not significant (p value > 0.05). However, when similar approach was implemented, it was rather difficult to choose the best performance. The slope which indicated an increase only showed by BHT additive, while the remaining has negative slope. This can be explained in Figure 4 that the numbers fluctuated a bit that resulted in negative slopes. Despite that, at a glance the trend showed a stable acid number for 8 weeks. Hence, no conclusion could be made about which additives had the best performance.

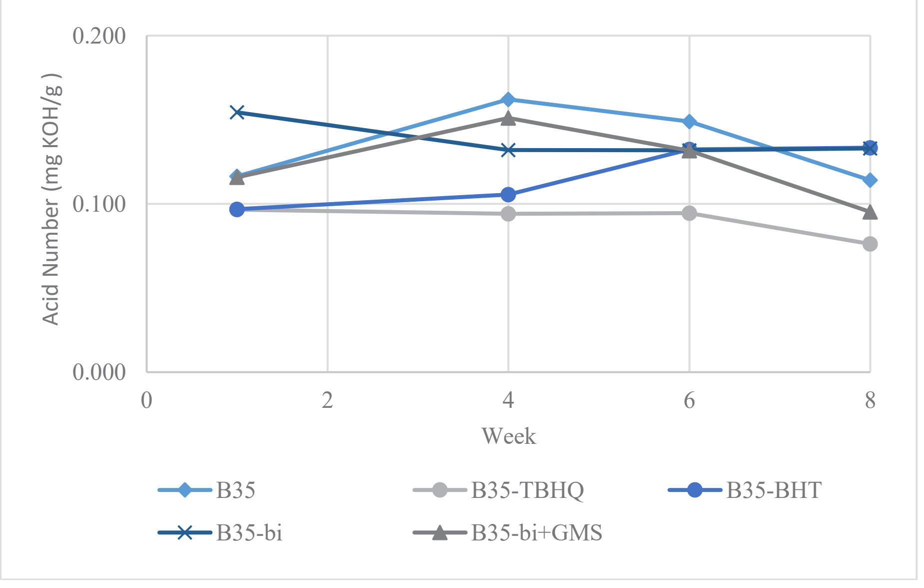

Fig. 4. Biodiesel B35 with additive(s) acid number trend for 8 weeks

During 8 weeks period of storage, all B100 and B35 samples still fulfilled the SNI standard of acid number, which has 0.5 mg KOH/g as the upper limit with pure biodiesel without additives taking the lead. Biodiesel without additives had the highest acid number because oxidation occurs directly in the fuel, while in the presence of antioxidants, antioxidants can replace oxidation attacks by themselves.

3.2 Effect of various additive addition to iodine number during storage

The iodine value (IV) is employed as a means to assess the degree of unsaturation within a sample. It specifically indicates the number of double bonds present in the sample, with a larger IV suggesting a bigger number of double bonds. A higher IV value indicates that the biodiesel is more prone to oxidation. As the double bonds undergo oxidation, the molecular chains are broken, resulting in the conversion of double bonds to single bonds. Consequently, this leads to a decrease in the IV value compared to its initial measurement [24].

3.2.1 Effect of Antioxidant Additives to Iodine Value of Pure Biodiesel

In the initial week, Figure 5 showed the IV was at 56.65 g I_2/100g which indicated it had many unsaturated fatty acid esters. Hery Sutanto et al. (2018) also had a similar starting point of IV in his research [22]. Biodiesel that has higher IV is more prone to oxidation. P value test was conducted to see if the data was significant different or not. The result showed $p < 0.05$ which concluded that the data was. There was a difference from initial week and the final week which was 3.444 g I_2/100g. The number might indicate there was an oxidation happening on double bonds.

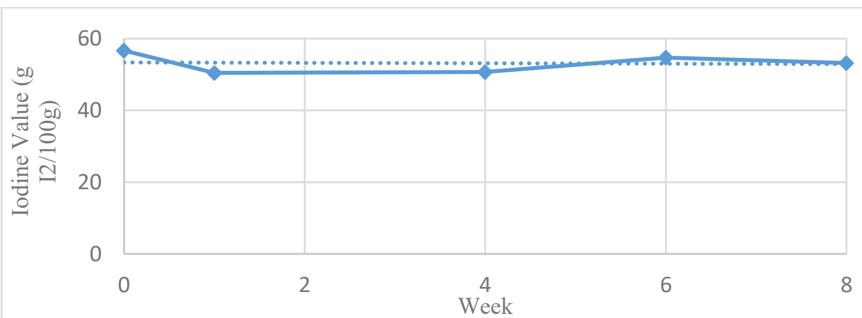

Fig. 5. Pure Biodiesel Iodine value for 8 weeks

While the pure biodiesel slope was close to zero, the slopes between four different kinds of additive(s) were observed. A similar case as acid number happened, the data did not tell that it was significant. However, in Table 4 showed that the best performance was obtained by biodiesel with the addition of binary antioxidants and GMS, slightly better than the addition of binary antioxidants.

Table 4. Iodine value slope difference of pure biodiesel with four different kinds of additive(s)

Sample	Slope
B100-TBHQ	-0.3696
B100-BHT	-0.3865
B100-bi	-0.1856
B100-bi+GMS	-0.1389

Iodine value of each sample decreased from its starting point which indicated the samples were oxidized. The slope between pure biodiesel and biodiesel were compared to see whether it was significant or not. Figure 6 compared both of the slopes. While being tested with t test, the value > 0.05 indicating it was not significant to each other.

The IV cannot determine whether the hydrogens adjacent to the double bonds are allylic or bis-allylic, a crucial factor in assessing the oxidizability of biodiesel. The stability of biodiesel is not solely determined by the overall count of double bonds indicated by the IV but rather relies on the presence and location of bis-allylic methylene groups neighboring the double bonds. Therefore, in this research the addition of TBHQ:BHT (3:1) and GMS to pure biodiesel did not have any significant difference on its iodine value.

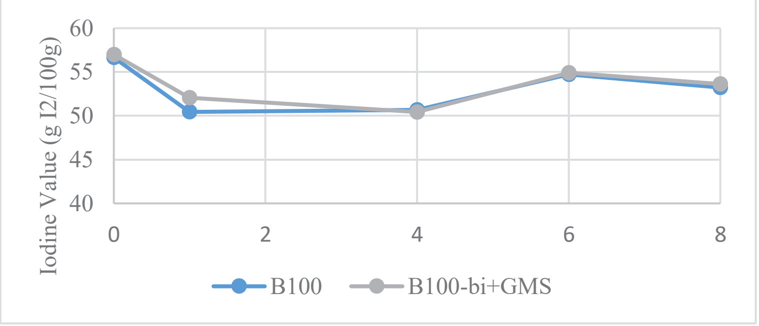

Fig. 6. Iodine value of pure biodiesel and biodiesel with binary antioxidants and surfactant for 8 weeks

3.2.2 Effect of Antioxidant Additives to Iodine Value of Blended Biodiesel (B35)

In the initial week, the iodine value was 32.96 g I_2/100g which was lower in comparison to B100 IV as can be seen in Figure 7. B35 Biodiesel blend consisted of 35% of biodiesel, which meant the remaining share was from fossil fuel. The IV value counts the existence of double bond that originated from biodiesel since diesel in general is a chain of single bond of carbon. In week 8, there was a significant drop of IV which the fixed cause was not determined. The drop was not experienced by biodiesel blend only, the other samples mixed with B35 also experienced similar decrease.

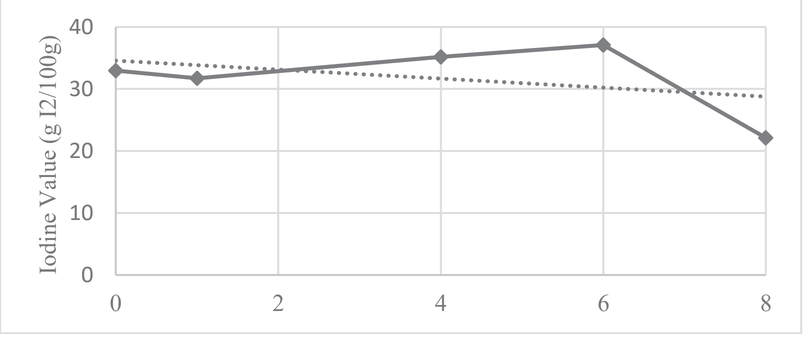

Fig. 7. Biodiesel B35 iodine value for 8 weeks

There might be an influence of storage condition that cause the double bond oxidized faster than usual. While pure biodiesel did not experience similar drop in the same storage condition, there might be other cause that could explain this drop. The biodiesel blend might have other components since it was obtained commercially, it might have a reaction with the added additive(s) at a certain period. As a result, more research might be conducted to determine what causes this drop by pinpointing what ingredients are included in the blend.

Table 5. Iodine value slope difference of biodiesel B35 with four different kinds of additive(s)

Sample	Slope
B100-TBHQ	-0.8797
B100-BHT	-0.7908
B100-bi	-0.9272
B100-bi+GMS	-0.5544

The slope decrease of four different added additives can be seen in Table 5, it had p value > 0.05, however, the slope with the least decrease was biodiesel B35 with binary and GMS. With similar approach as previous, the best performance was compared to the one without any additives. As shown in Figure 8, both graphs had similar pattern where the difference cannot be observed when compared to biodiesel B35. It was supported by the p value > 0.05 which explained the data was not significant. Therefore, between the four additive(s), there was no conclusion could be made.

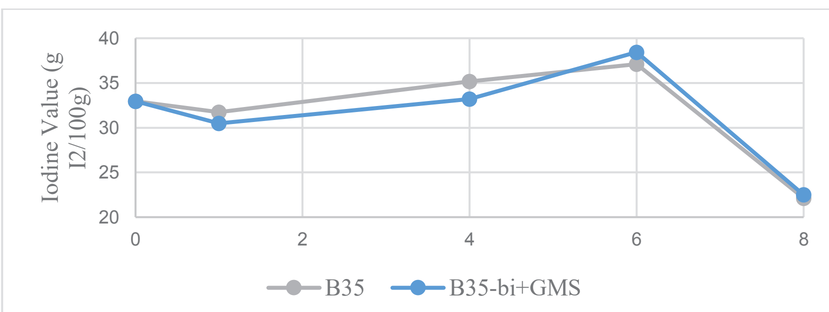

Fig. 8. Iodine value of biodiesel B35 and biodiesel B35 with binary antioxidants and surfactant for 8 weeks.

The SNI 7182 standard indicates that the maximal IV that can be tolerated is 115 g I_2 per 100 g of material. All the samples had IV that were lower than the required, therefore it fulfilled the standard.

The predictive capability of the iodine value regarding the oxidation stability of a particular sample is limited. This is because the IV solely considers the quantity of double bonds present in the sample while disregarding their distribution throughout the molecular structure. It is feasible for two samples with identical IV values to exhibit different oxidation stabilities and characteristics. Relying solely on the IV value as an indicator of oxidative stability is inadequate as it does not provide insight into the degree of unsaturation [24].

3.3 Effect of various additive addition to kinematic viscosity at 40 °C during storage

Another variable that corresponds to acid number is kinematic viscosity. Because the acid number and kinematic viscosity both climb as oxidation progresses, both of these measurements are routinely used to assess the quality of fuel samples. Under normal circumstances, the acid number and kinematic viscosity will continue to rise until the sample's induction time zeroes out. They will then grow faster in the future. The formation of acids in the system is proportional to the increase in sample viscosity [24].

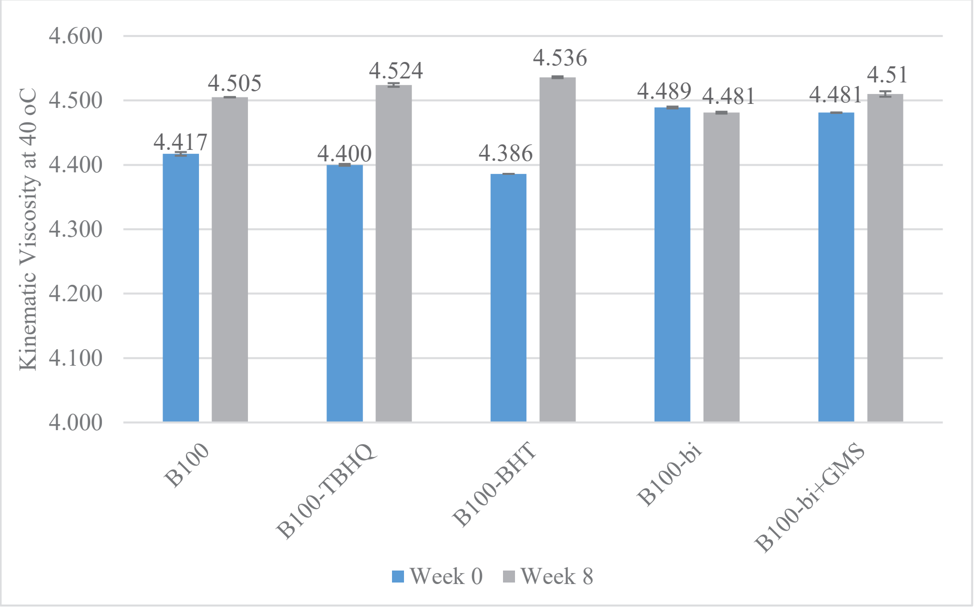

Fig. 9. Kinematic viscosity at 40 °C during 8 weeks storage

The initial and final value of kinematic viscosity during 8 weeks of storage were under the maximum requirement of SNI 7182 which is 6 mm^2/s. As can be seen in Figure 9, most samples had an increase in its value. The starting point of B100-bi and B100-bi+GMS were already higher compared to other samples, however, they showed a stable viscosity after 8 weeks. While B100, B100+TBHQ, and B100+BHT had significant increase in 8 weeks period.

The gap between 8 weeks could be further seen in Figure 10 to see the difference clearer. P value < 0.05 indicated that it was significant difference. Although the starting value of B100-bi and B100-bi+GMS were higher than the others, the samples with the least increase were biodiesel with binary and the combination of binary and GMS. Therefore, the addition of binary antioxidants proved its ability to reduce oxidation the best, followed by the addition of GMS.

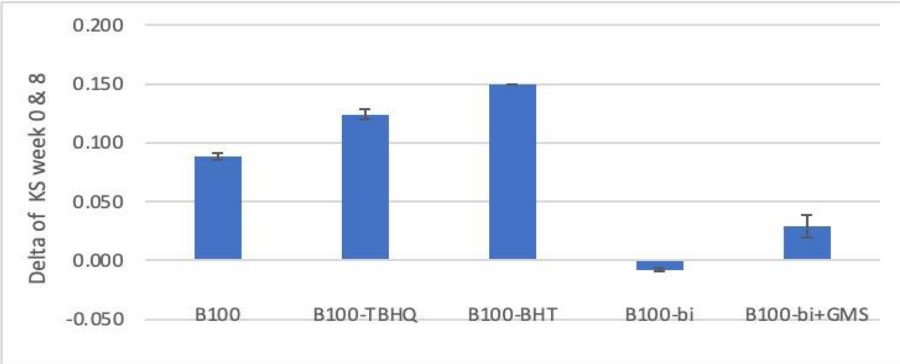

Fig. 10. Kinematic viscosity at 40 °C difference

3.4 Effect of various additive addition to induction period at 40 °C during storage

As the process of oxidation progresses, oxidation stability decreases as a result of the unsaturated ester concentration in biodiesel promoting the attack of radicals. As a result, strict standards have been set up to guarantee the fuel's quality. According to ASTM D6751, EN 14214, and SNI 7182 biodiesel has a minimum oxidation stability of 3 hours, 6 hours, and 6 hours, respectively [24]

Ajie et al. (2020) had previously conducted Rancimat test for TBHQ, BHT, and TBHQ:BHT individually. The performance of TBHQ:BHT(3:1) showed a better result compared to the addition of antioxidant individually [17]. Hence, in this research the Rancimat test of TBHQ:BHT (3:1) along with the addition of GMS was done.

Rancimat test was done twice on each sample to see the difference of induction period (IP) between 4 weeks. As can be seen in Figure 11, the induction period of pure biodiesel in the latter week dropped 29% from the initial week, from 23.68 hours to 16.81 hours. If within 4 weeks the decrease was 6.87 hours, it would take approximately 10 weeks until it would not fulfil the SNI standard. Although the biodiesel samples with the addition of binary antioxidants experienced a slight increase in week 8, both showed greater performance compared to no additive(s) addition. Related laboratory analysis claimed that precision calculations are not covered by the EN 15751 method precision provisions because they exceeded 48 hours. This might answer the increase of induction period of B100-bi and B100-bi+GMS since the IP exceeded 48 hours. Despite all that, the addition of binary proved significance effect on biodiesel, with biodiesel with binary antioxidants took the lead by little difference in comparison to B100-bi+GMS. According to a study by Hamdani et al. (2020), the formation of a heterodimer interaction between two antioxidants results in the generation of a more effective and superior antioxidant compound [20].

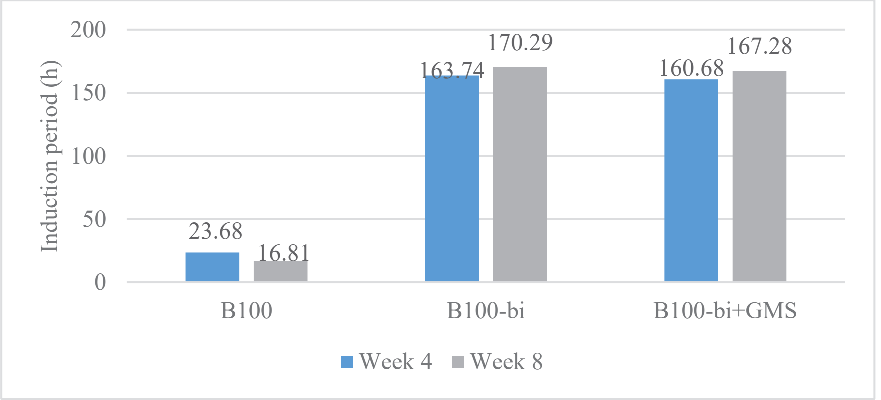

Fig. 11. Induction period in hours of pure biodiesel with none, binary antioxidants, and binary antioxidants & GMS

3.5 Effect of various additive addition to induction period at 40 °C during storage

The dispersion test was performed to assess a surfactant's effect on the dispersion of antioxidant(s) in biodiesel. Based on the absorbance measurements, the dispersion level of a solution was calculated using the UV/VIS spectrophotometer method. The wavelength at 290 nm was used as TBHQ has a peak at that level, while 278 nm was used as BHT has a peak at that level. The height was taken 10% from the surface level for each measurement in this research.

Table 6. The average of absorbance of each sample at 290nm and 278nm wavelength in the initial week

Sample	290 nm	278 nm
B100-TBHQ	0.4415	-
B100-BHT	-	0.174
B100-bi	0.3240	0.179
B100-bi+GMS	0.3325	0.193

In the beginning of the UV/VIS spectrophotometry analysis, it could be seen that the measurement at 290 nm wavelength can be used to detect the dispersion of TBHQ, whereas wavelength at 278 nm used to detect BHT. Since the addition of TBHQ in binary accounted 75% from 2000 ppm, the absorbance of B100-bi and B100-bi+GMS were lower compared to B100-TBHQ (see Table 6). The data at 290 nm wavelength has a p value < 0.05 while the data at 278 nm had a p value > 0.05, meaning it was significant and not significant respectively.

In order to see how the performance of surfactant works, the dispersion difference during four weeks was observed as can be seen in Table 7. TBHQ has the tendency to gather at the surface layer due to gap polarity. With the addition of GMS, the delta difference was slightly lower compared to B100-binary which indicated that the dispersion of TBHQ in biodiesel was more even and lesser antioxidant fell to the bottom. A study by Hery Sutanto et al. (2018)

also showed that the addition of GMS could distribute the dispersion of TBHQ more even by having smaller gap difference between duration of one week [22].

Table 7. Delta absorbance at 290 nm and 278 nm wavelength between four weeks

Sample	Delta Abs 290 nm	Delta Abs 278 nm
B100-TBHQ	0.0870	-
B100-BHT	-	0.0535
B100-bi	0.0830	0.0720
B100-bi+GMS	0.0665	0.0545

The absorbance difference at 278 nm wavelength showed similar pattern as the gap polarity at 290 nm wavelength which B100-bi+GMS had smaller gap compared to B100-bi. This might indicate the addition of GMS could solve the problem of insolubility of antioxidant which could fall on the bottom. On the other hand, B100-bi+GMS did not indicate better oxidative stability when induction period and kinematic viscosity were taken into consideration, as discussed previously.

4 Conclusion

In this research, there was no significant effect found on B35 in its acid number and iodine value. While on B100, the addition of surfactant and binary antioxidant have significant effect on oxidative stability based on kinematic viscosity and induction period results between the four parameters used. The mixture with binary antioxidants took a lead as the best additive, followed by the addition of GMS with slight difference. The induction period of B100-bi and B100-bi+GMS in the final week were 170 hours and 167 hours respectively. Although there was no boost effect of the addition GMS, the involvement of GMS into biodiesel could disperse the TBHQ more throughout the fuel because the gap polarity of GMS involved was smaller than without GMS addition. Therefore, the addition of a surfactant to binary antioxidants produced results comparable to B100-bi but with improved solubility.

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