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Home > Archives > **Vol 13, No 2 (2023)**

Vol 13, No 2 (2023)

June

Table of Contents

Articles

Biodiesel Additive Performance from Tertiary Butylhydroquinone and Surfactant Glycerol Monostearate

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Abstract- As the world moves towards cleaner energy sources to replace the conventional use of fossil fuels, biodiesel has emerged as a promising alternative for the transport sector. Biodiesel is produced from vegetable oils through the process of transesterification, however this process presents some problems due to unsaturation in the ester chains, which makes them oxidatively unstable. To overcome this issue, the addition of phenolic antioxidants and surfactants is often necessary. Previous research has demonstrated that tertiary butylhydroquinone (TBHQ) and glycerol monostearate (GMS) were effective as antioxidant additives in biodiesel by improving its oxidative stability. However, the complete parameter of its performance has not yet been thoroughly evaluated. This research aims to analyze the performance of TBHQ and GMS mixture based on four parameters – acid number, iodine value, kinematic viscosity at 40ºC, and induction period – in both pure biodiesel (B100) and commercial blended biodiesel (B30) made from crude palm oil (CPO). These parameters were assessed according to the Indonesian standards. Within the span of four weeks results shows that addition of additives TBHQ and GMS significantly improved the oxidative stability of biodiesel in terms of acid number, iodine value, and induction period. Although the viscosity increased with the addition of TBHQ, GMS was able to inhibit this rise. Nevertheless, all the results complied under Indonesian standards for biodiesel.

Keywords Biodiesel Additives, antioxidant, Tertiary Butylhydroquinone, Glycerol Monostearate, oxidative stability of biodiesel

1. Introduction

The International Energy Agency (IEA) reported that, as of 2019, the global electricity demand has increased by 0.9% which is less than half of the growth rate in 2018. This number is well below the average rate since 2010. This recession was due to generally slower global economic growth. Although the energy demand declined in 2019, fossil fuel still contributes up to 80% in world energy consumption. According to the Energy Information Administration (EIA), the energy demand outlook in the near future (2040) is expected to continue to grow by nearly half worldwide. In addition, the demand for fossil fuel was forecasted to grow by 38% [1].

The consumption of fossil fuel has proven to cause negative environmental impact as the burning of fossil fuel emits a great amount of CO_2 into the atmosphere which is one of the main causes of global warming and climate change [2-3]. As the demand and usage of fossil fuel continues to increase so will the CO_2 emissions worldwide [4]. Several countries have made their pledges in contributing to the reduction of CO_2 emissions [5].

For centuries burning fossil fuels has been one of the dominant sources of energy to in various sectors including the transport sector which is one of the most energy demanding sectors. There are various renewable alternatives to slowly replace fossil fuel for transport and one of the more promising ones being biodiesel [6-9].

Biodiesel, a type of biofuel, can be made from a variety of raw materials through the process of transesterification [10-11]. They are a composition of mono-alkyl esters of long fatty-acids which can usually be found in vegetable oils and animal fats [12-15]. The clear advantages of biodiesel are that most of the biodiesel currently uses readily available biowaste resources and the production of biodiesel has been described as "carbon neutral" which means it does not produce net CO_2. Furthermore, biodiesel is biodegradable and completely non-toxic making it much more environmentally friendly [16-17].

However, there are several challenges in the production of biodiesel, mainly its oxidative behaviour. Due to the fact that they consist of long chain fatty acids, biodiesel fuels are most likely to oxidize when interacting with different environments such as oxygen, temperature and storage conditions therefore making biodiesel low in stability [18-21]. Interactions with different environments causes sediment formation as well as higher viscous oil. A solution to this problem has been developed by using external additives such as antioxidants into the biodiesel. Antioxidants are natural or synthetic chemicals that can inhibit oxidation. Previous studies show that phenolic antioxidants such as TBHQ, Pyrogallol (PY), and Propyl Gallate (PG), are most effective in increasing the stability of biodiesel [20-21]. In addition, the usage of antioxidants also decreases the formation of NOx during engine operation [22].

The addition of antioxidant into biodiesel may prevent the formation of products that could potentially degrade the quality of biodiesel. The shorter chain of carboxylic acids, polymer, and sediment are the primary byproducts that resulted from biodiesel oxidation. In order to assess the oxidation, it is necessary to measure the physical and chemical properties of biodiesel, such as acid value and kinematic viscosity to determine the presence of carboxylic acids and to detect the formation of polymer respectively [23]. Biodiesel with added phenolic antioxidants content such as TBHQ and Propyl Gallate (PG) exhibit greater stability in terms of acid value and viscosity than biodiesel without antioxidants. After a 12-week storage period, the acid value of palm oil-based biodiesel containing TBHQ only increased by 2.86%, while that containing PG increased by 11.43%. Nevertheless, even with these increases, the values were still lower than those of biodiesel without antioxidants, where acid value increased by up to 37.14% [24]. Another research study examined how phenolic antioxidants (such as Pyrogallol, Butylated Hydroxy Toluene, and Butylated Hydroxyanisole) affected the kinematic viscosity of biodiesel. The study found that when the antioxidants were added at lower concentrations (500 ppm), the kinematic viscosity of biodiesel decreased. However, at higher concentrations (1000 ppm), the kinematic viscosity increased slightly, though still less than the viscosity of pure biodiesel [25].

Although using antioxidants fixes the issue of stability, another problem arises as antioxidants are naturally polar while in contrast, biodiesel is non-polar. The solubility problem of phenolic antioxidants in biodiesel can be solved by using surfactant, a bridging agent. Studies have proved glycerol monostearate (GMS) as a promising surfactant [26]. Previous combinations of antioxidants and surfactants have been studied in pure biodiesel made from used cooking oil. The surfactant used in the study were Polyglyceryl-4-isostearate (PG4IS), Sorbitan Monooleate (SMO), and Glycerol. This evaluation was performed on two types of antioxidants, namely pyrogallol (PY) and TBHQ, however the testing parameter was limited to solubility, acid number, and iodine value. Compared to the other surfactants, GMS showed superior performance in enhancing the solubility of both antioxidants in biodiesel, especially for Pyrogallol. In addition, the combination of those antioxidants with GMS successfully improved its ability in preventing oxidation in biodiesel in terms of acid number and iodine during four weeks of storage period [21,26]. This research focused on the combination of TBHQ and GMS as the antioxidant and surfactant mixture to obtain the complete parameter of their effects in pure biodiesel and blended biodiesel B30.

2. Materials and Methodology

The antioxidant performance of the biodiesel additive antioxidant TBHQ and surfactant GMS mixture was tested in pure biodiesel B100 and commercial blended biodiesel B30 in four oxidative stability parameters; acid number, iodine value, kinematic viscosity, and induction period. The experimental design of this research can be seen in Fig. 1.

2.1. Materials and Equipment

The materials used for this research were pure palm oil biodiesel and commercial blended biodiesel B30. Both biodiesel samples were not made during the experiment instead it was purchased from biodiesel producer company in Indonesia. Commercial blended biodiesel B30 was obtained from company X (one of the biggest biodiesel retailer in Indonesia), while the pure biodiesel was sourced from company Y (biodiesel supplier of company X). Antioxidant tert-butylhydroquinone in solid form from Merck, Germany. Surfactant glycerol monostearate in solid form. Additional chemicals and materials used includes ethanol, demineralized water, potassium iodide, potassium hydroxide, chloroform, Wijs solution, sodium thiosulphate, starch solution, hexane, and phenolphthalein as indicator solution. The equipment used for this thesis includes a titration equipment set (burette and Erlenmeyer flask), a viscometer, and Rancimat instrument. Furthermore, the statistical analysis was done using paired t-test method.

2.2. Sample Preparation

Performance analysis of the antioxidant additive was divided into 2 stages, where the first stage was carried out for pure biodiesel (B100) and the second stage was for commercial blended biodiesel (B30). A total of 4 samples were prepared for both stages and each filled with different solution. The composition of the samples was: i) pure biodiesel (B100); ii) pure biodiesel with addition of antioxidant TBHQ and surfactant GMS (B-AD); iii) blended

biodiesel (B30); and blended biodiesel (B30) with addition of antioxidant TBHQ and surfactant GMS (B30-AD). The concentration of TBHQ and GMS were set to 2000 ppm (w/v) and 100 ppm respectively, stirred and stored in
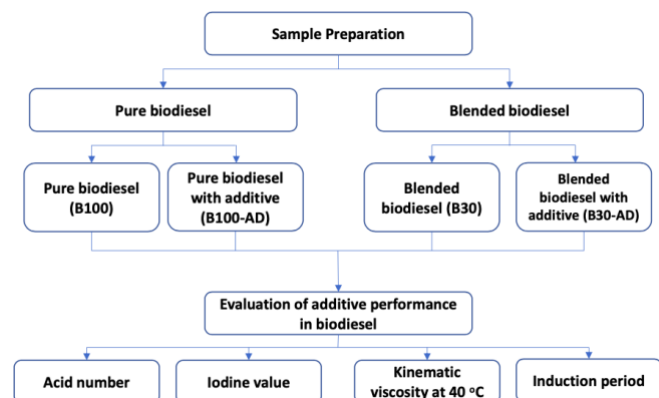
Fig. 1. Experimental design of TBHQ & GMS performance analysis in biodiesel

controlled condition. A sample of pure biodiesel with addition of 2000 ppm of TBHQ (B-TBHQ) was prepared to evaluate the effect of surfactant GMS to biodiesel's viscosity and induction period. The samples were observed within 4 weeks of storage.

2.3. Acid Number Analysis

The acid number of the biodiesel was determined using the American Society for testing Materials (ASTM) D664 procedure. [26]. First, 100 ml of ethanol and 5 drops of phenolphthalein indicator solution were added into 2.5 grams of biodiesel inside a 250 Erlenmeyer flask. The solution was stirred until it reached a homogenous state. Then, the solution was titrated by gradually adding 0.01 N KOH until it reached a point where its color turned pinkish. The same procedure was applied to a blank sample containing 100 mL of ethanol and 5 drops of phenolphthalein, which was titrated accordingly. The acid number was determined by calculating the resulting KOH volume from the titration.

2.4. Iodine Value Analysis

The iodine value of the biodiesel was determined using the American Oil Chemists' Society (AOCS) official method Cd 1-25. [26]. 0.15 grams of biodiesel was placed into a 500 ml Erlenmeyer flask, followed by the addition of 15 ml of chloroform. 25 ml of Wijs solution was later added into the previous flask. Next, the flask was sealed with aluminum foil and stored in a dark environment. After one hour of incubation, 20 ml of KI solution and 150 ml of demineralized water were added, and the mixture was titrated using 0.1 N of sodium thiosulphate. The flask was slightly swayed around during titration to ensure homogeneity. When the color changed to a light orange, 2 ml of starch solution were added, and titration continued until the color became clear. The blank sample was also analyzed using the same method. The iodine value was calculated using the final titration volume of sodium thiosulphate.

2.5. Kinematic Viscosity Analysis

This experiment used the standard kinematic viscosity measurement at 40ºC procedure according to the Indonesian standard SNI of Biodiesel 7182:2015 [27].

2.6. Kinematic Viscosity Analysis

This analysis was carried out according to the SNI 7182:2015 standard method to measure induction period using a biodiesel Rancimat method. The biodiesel sample was placed in a closed vessel and was in contact with oxygen at temperature 110ºC. The biodiesel was heated to speed up oxidation in biodiesel [28].

3. Result and Discussion

3.1 Antioxidant Additive Performance in Pure Biodiesel

3.1.1 Acid Number Analysis

The acid value is one of the main parameters that could indicate oxidation as it naturally produces acidic compounds in oil samples. The oxidation of esters forms peroxides which will then form aldehydes and will further oxidize into acids [29]. Furthermore, biodiesel tends to be more corrosive compared to conventional diesel which is caused by their naturally present water content and fatty acids. During oxidation, the methyl esters in the fatty acids quickly forms radical and links with oxygen in the air [30]. The acid value test was conducted using the standard acid base titration method according to ASTM D 664 procedure within the span of four weeks beginning from week zero. The comparison of acid value of pure biodiesel (B100) and biodiesel with addition of antioxidant TBHQ and surfactant GMS can be seen in Fig.2.
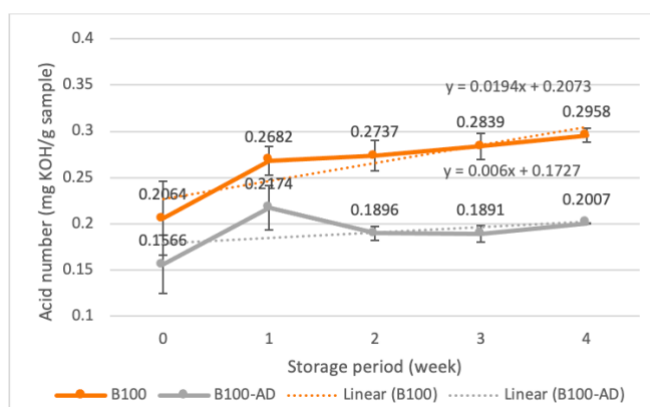

Fig. 2. Experimental design of TBHQ & GMS performance analysis in biodiesel

Fig.2 shows that there is an increase in acid number over the weeks from week zero to week four. This result supports the statement that as biodiesel is stored for a longer period of time, acids can be formed due to degradation from oxidation. However, the comparison between the two samples can be seen with the plot of a linear regression line to obtain the slope which are 0.0194 for pure B100 and 0.006 for B100 with additives. A higher slope value indicates a higher rate of acid formation which indicates faster oxidation. The observed rise in acid value over a four-week period also provided evidence that the additives were effective in retarding oxidation. The increase in acid value was 43.41% for pure biodiesel and only 28.16% for biodiesel with the additive (B100-AD). This implies that incorporating TBHQ and GMS enhances the oxidative stability of biodiesel in terms of the acid parameter. And interesting note is that the Indonesian standards of biodiesel for acid value is anywhere below 0.6 mg KOH/g samples, in this case both B100 samples complied with the standards.

For a more conclusive look on the conclusion drawn above, a paired t-test was conducted to compare the two sets of data for pure biodiesel B100 and pure biodiesel B100 with additives. The result shows a p-value lower than 0.05 therefore indicates that there is a significant difference between the two result and thus confirming the conclusion that the addition of additives improves oxidative stability in terms of the acid number.

3.1.2 Iodine Value Analysis

The iodine value in biodiesel indicates the level of unsaturated alkyl esters, in other words the number of double bonds present. One mole of iodine (I_2) reacts with one pair of double bonds and therefore can be defined and measured as the number of grams or milligrams of iodine which reacts with 100 grams of the alkyl esters, as can be illustrated in Fig.3.

The higher the number of double bonds the easier it is for the biofuel to oxidize. The iodine solution added reacts with the double bond through addition reactions and therefore could indicate oxidation. However, it is important to note that the iodine value does not directly indicate oxidation as it does show the exact number of double bond distribution within the ester. The iodine value measurement serves as a rough indicator for oxidative stability. The general principle is that the higher the number of double bonds the higher the probability of oxidation. The results from the iodine measurements are shown in the table and Fig.4.
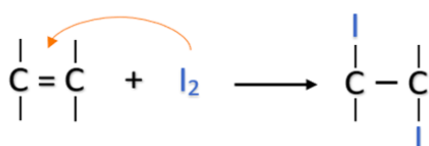
Fig. 3. Addition of iodine in double bonds
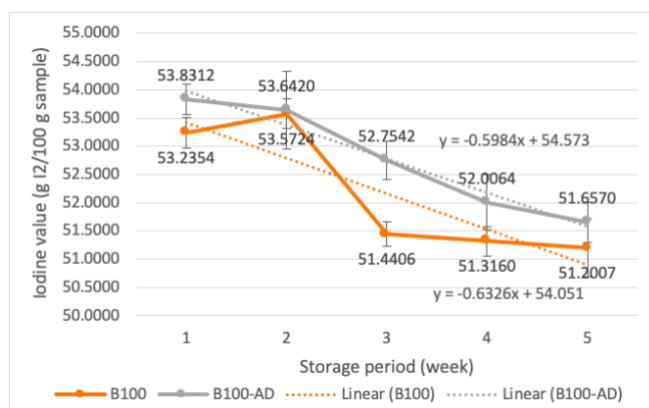
Fig. 4. Iodine value analysis for pure biodiesel (B100)

As seen in the Fig.4, both line graphs for B100 and B100-AD are declining over storage time. The iodine value of pure biodiesel decreased from 53.8312 to 51.6570 g I_2/100g sample, whereas for biodiesel with additive, this value reduced from 53.2354 to 51.2007 g I_2/100g sample. The slope was plotted to get a better conclusion for the result; pure biodiesel (B100) showed a slope of -0.6326, and biodiesel with the addition of additives showed a slope of -0.5924. The negative sign represents the reclining pattern of the curves, and the slope that shows a higher decreasing value has a lower antioxidant performance as it means that the faster the rate of iodine decreasing which correlates to higher number of double bonds present therefore a higher rate of unsaturation. Here, consistent with acid number, indicates that biodiesel with the addition of surfactants shows a better performance in terms of the iodine value. Furthermore, there was a slight increase for iodine value for B100 in week one, which could be due to measurements issues, followed by a significant drop in the following week. An interesting note is that just like in the acid number analysis, both samples were in week one still shows the acceptable iodine value according to both the European standards and the Indonesian standards which are below 120 and 115 g I_2/100g sample respectively.

The significance of additives in the pure biodiesel can be seen better after a paired t-test was conducted. Similar to the acid number, the p value is lower than 0.05 which further concludes that the addition of additives TBHQ and GMS gave a significant improvement in oxidative stability in B100 in terms of iodine value.

3.1.3 Kinematic Viscosity Analysis

The kinematic viscosity is the product of the measured flow time multiplied by the constant viscometer calibration and it measures the formation of polymeric secondary products during oxidation. The hydroperoxides formed after initial oxidation progresses and begins to deteriorate and inter-react. This causes fatty acid chains to link together to form polymeric species. These secondary products increase the viscosity of the fuel which can result in the formation of sediments that can damage engines. This analysis was done withing the span of two weeks and the results can be seen in Fig.5.
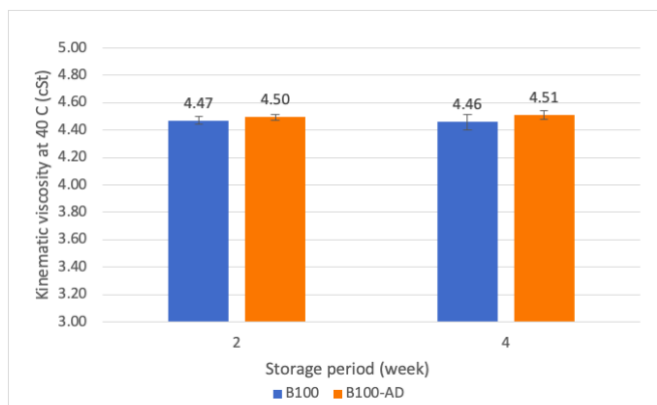
Fig. 5. Kinematic viscosity analysis for pure biodiesel (B100)

Comparing between pure biodiesel B100 and pure biodiesel B100 with the addition of TBHQ and GMS, Fig.5 shows the one with the addition of additives has a slightly higher viscosity. Previous studies about the effect if antioxidants on biodiesel characteristics reports that an increase in viscosity due to antioxidants is possible because of the chemical structure of the antioxidants. Furthermore, at higher concentrations it is also possible that there could be some crosslinks formation and hydrogen bonds between the FAME and the antioxidants. For TBHQ, the increase in viscosity could possibly be related to its two hydroxyl groups in its chemical structure, making it much more prone to form hydrogen bonds with the FAME and therefore increasing its viscosity [31]. A solubility gap between phenolic antioxidants and biodiesel is also another possible reason.

To show if the addition of additives significantly affects the increase in viscosity, a paired t-test was conducted, and the result shows that the p value is higher than 0.05, in this case, there is no significant difference in kinematic viscosity between pure biodiesel B100 and pure biodiesel B100 with the addition of additives. However, it is still important to take into account the effects of TBHQ in viscosity at a higher concentration in biodiesel, or when the biodiesel has a relatively high viscosity (near the standards limit).
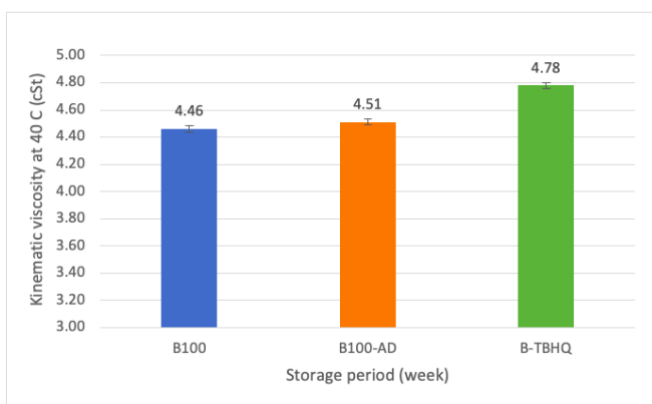
Moreover, kinematic viscosity value in Fig.6 indicates that the addition of surfactants, such as GMS in this case, retards the increase in viscosity to some extent as the result shows that pure biodiesel B100 with only TBHQ shows the highest kinematic viscosity value. This suggests that it is possible to consider the addition of surfactants with antioxidants to control the rise in viscosity, especially when the rise is significant. Nevertheless, from the results, both biodiesel samples were able to comply within the Indonesian standard range for kinematic viscosity between 2.3-6.0 cSt.

3.1.4 Induction Period

The Rancimat method is one of the most important parameters in determining biodiesel oxidative stability as it measures the storage lifetime of the fuel, how long can it last before oxidation. This measurement was also done within the span of two weeks and the result can be seen in Fig.7.

The result shows that there is a significant drop in the induction period from B100 compared to B100 with the addition of TBHQ and GMS. During the two-weeks observation, the induction period declined due to the biodiesel's oxidation. A shorter induction period indicates lower oxidative stability of biodiesel. However, the addition of antioxidant additives prevented the oxidation process. TBHQ, which is a phenolic antioxidant with two hydroxyl groups, was able to prevent oxidation by donating its hydrogen or electron from the hydroxyl group to the free radical, thereby delaying the oxidation process in biodiesel. GMS as a mixture in the additive improved the dispersion of TBHQ in biodiesel, which enhanced its performance [26]

Pure biodiesel B100 showed as much as around 54.2% drop from the initial induction period of 1441 minutes on the second week to 660 minutes on the fourth week. However, pure biodiesel with the addition of TBHQ and GMS showed only an 8.5% drop from the initial induction period of 1837 minutes on the second week to 1680 minutes on the fourth week. The data revealed that the use of TBHQ and GMS as additives in biodiesel was beneficial in preventing oxidation, as indicated by a minor decline in the induction period during a two-week storage period.

Fig. 6. Final kinematic viscosity comparison between biodiesel samples
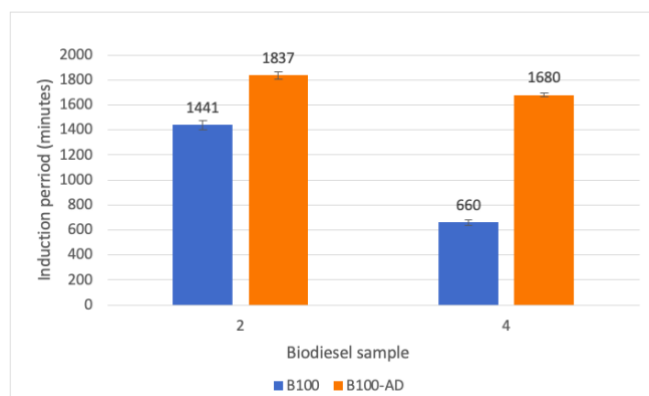
Fig. 7. Induction period analysis for pure biodiesel (B100)

Fig. 7 shows clearly the change in induction period of pure biodiesel B100 and biodiesel B100 within the span of two weeks. Furthermore, during the fourth week, another sample of B100 with only the addition of TBHQ was tested for further comparison in the significances of GMS in this parameter.

The further analysis to assess the effect of surfactant GMS addition to pure biodiesel was carried out by comparing the induction period of the sample with TBHQ only and the previous sample. The results for pure biodiesel B100 with only the addition of TBHQ shows an induction period of 1685 minutes as can be seen in Fig. 8. Comparing this to pure biodiesel B100 with the addition of TBHQ and GMS (B-AD), shows a five minutes difference. Due to the small difference, it can be concluded that there is not a significant difference between the two and that the addition of GMS doesn't have any significant effect in this parameter. However, the addition of antioxidant into biodiesel in the B100-AD and B-TBHQ samples was effective in preventing oxidation, as evidenced by their significantly longer induction periods compared to pure biodiesel. Just like previous measurements all three B100 samples we able to comply with SNI 7182 standards at more 360 minutes.

In a comparison to other antioxidant additives such as Propyl Gallate and natural plant extracts from mango, the performance of TBHQ and GMS was found to be relatively similar, with an 8.5% decrease in the induction period. Propyl gallate was able to maintain the stability of palm-oil based biodiesel with only a 1.96% reduction in induction period during a 2-week storage period, while the natural antioxidant from mango extract showed a lower performance with an 18.76% decrease [24]. It is important to acknowledge that these results may be impacted by multiple factors, including the raw materials used to produce the biodiesel and its overall quality.
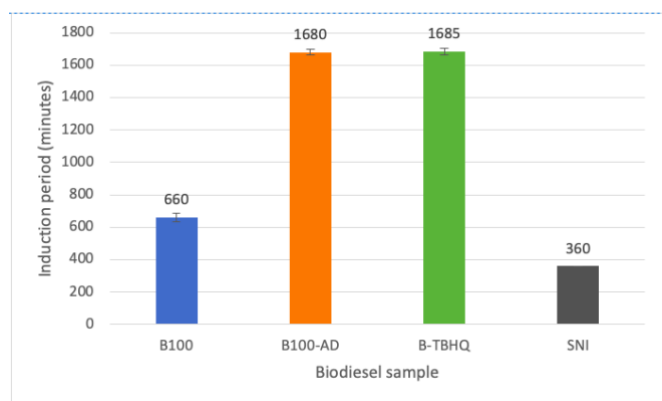

Fig. 8. Induction period comparison between different biodiesel samples

3.2. Antioxidant Additive Performance in Commercial Blended Biodiesel (B30)

The performance of antioxidant TBHQ and surfactant GMS in improving oxidative stability was evaluated for commercial blended biodiesel B30. Referencing this evaluation, a comparison can be made between the performance of TBHQ and GMS in both commercial biodiesel B30 and biodiesel B100.

The parameters that were tested were similar to the parameters tested for this research, which are the acid number, iodine value, kinematic viscosity, and the induction period. Similarly, the test was also conducted within the span of four weeks beginning from week zero. The comparison can be seen in Table 1.

In regards to the acid value, it can also be seen that in biodiesel B30 the acid formation rate is much higher in pure B30 from 0.14 to 0.22 mg KOH/g sample, which is about 53.47% increase. And when compared to B30-AD the increase in acid number is around 31.5% from 0.143 to 0.188 mg KOH/g sample, therefore it can be concluded from the results of this comparison that the addition of additives TBHQ and GMS is able to retard the formation of acids during oxidation and therefore increase the fuels oxidative stability both in commercial biodiesel B30 just like in B100.

With respect to iodine value analysis in both samples, B30 and B30-AD, there was no significant difference found in the decrease of iodine value within 4 weeks of storage. Since the composition of biodiesel in this sample was only 30%, it means that the number of double bonds was much lower compared to pure biodiesel. As a result, the probability of oxidation in the biodiesel sample is significantly decreased.

In terms of kinematic viscosity, all four samples B30, B30-AD, B100, and B100-AD remained relatively stable over the weeks. The difference can be seen only during the initial week between the B30 samples and the B100 samples. The induction period for both B30 samples is quite stable as well, around more than 48 hours. The smaller amount of FAME in blended biodiesel B30 contributes to a better stability in term of induction period.

Overall, the use of antioxidant additives derived from TBHQ and GMS surfactant has been effective in enhancing the oxidative stability of biodiesel, particularly for pure biodiesel. These additives can prevent the increase in acid number and decrease in iodine number, and prolong the induction time of biodiesel, which enables it to comply with the standards established in Indonesia. The combination of TBHQ with various surfactants, including Sorbitan Monooleate (SMO), has been studied for its potential to act as an antioxidant in biodiesel made from used cooking oil. This combination has been shown to reduce the formation of acid and decline in iodine value during a four-week storage period. Despite this, its performance remains lower than that of TBHQ and GMS. In another study, the effectiveness of Pyrogallol, a phenolic antioxidant, was evaluated for palm oil-based biodiesel with the addition of three surfactants: GMS, PG4IS, and SMO. The surfactants were found to enhance the dispersion of Pyrogallol in the biodiesel, thus improving its antioxidant activity [21].

Table 1. Comparison of antioxidant performance between B30 and B30-AD

	B30		% difference	B30-AD		% difference
	Initial (week 0)	Final (week 4)		Initial (week 0)	Final (week 4)	
Acid Value (mg KOH/g sample)	0.14	0.22	53.47% increase	0.14	0.19	31.5% increase
Iodine Value (mg I2/100 g sample)	15.39	13.00	15.49% decrease	15.00	12.42	17.17% decrease
Kinematic viscosity (cSt)	3.17	3.13	1.17% decrease	3.17	3.00	5.42% decrease
Induction period (minutes)	>48 hrs	>48 hrs	-	>48 hrs	> 48 hrs	-

4. Conclusion

Addition of additives TBHQ and GMS has proven to significantly enhance oxidative stability of pure biodiesel in term of acid number, iodine value, and induction period. In terms of kinematic viscosity, surfactant GMS was able to control the rise in viscosity that was found to naturally occur when TBHQ is added into biodiesel. Nevertheless, all B100 samples across the four oxidative parameters were able to comply under Indonesian standards.

In comparison to commercial blended biodiesel B30, the addition of additives TBHQ and GMS has the ability to inhibit the formation of acids. However, it showed no significant improvement in terms of iodine value and kinematic viscosity. Moreover, commercial B30 was shown to be very stable according to induction period.

Acknowledgements

References

[1] International Energy Agency, "Global Energy Review 2019," France, 2020.

[2] S. Paraschiv, L.S. Paraschiv, "Trends of carbon dioxide (CO$_2$) emissions from fossil fuels combustion (coal, gas and oil) in the EU member states from 1960 to 2018", Energy Reports, 6, pp.237-242, 2020.

[3] T. Martins, A.C. Barreto, F.M. Souza, A.M. Souza, "Fossil fuels consumption and carbon dioxide emissions in G7 countries: Empirical evidence from ARDL bounds testing approach", Environmental Pollution, 291, p.118093, 2021.

[4] A. Rehman, A. Rauf, M. Ahmad, A.A. Chandio, Z. Deyuan, "The effect of carbon dioxide emission and the consumption of electrical energy, fossil fuel energy, and renewable energy, on economic performance: evidence from Pakistan", Environmental Science and Pollution Research, 26, pp.21760-21773, 2019.

[5] A. Robbins, "How to understand the results of the climate change summit: Conference of Parties21 (COP21) Paris 2015", Journal of public health policy, 37(2), pp.129-132, 2016.

[6] H. Lund," Renewable energy strategies for sustainable development", Energy, 32(6), pp.912-919, 2007.

[7] O. Ellabban, H. Abu-Rub, F. Blaabjerg, "Renewable energy resources: Current status, future prospects and their enabling technology", Renewable and sustainable energy reviews, 39, pp.748-764, 2014.

[8] G. Knothe, "Biodiesel and renewable diesel: a comparison", Progress in energy and combustion science, 36(3), pp.364-373, 2010.

[9] H. Huo, M. Wang, C. Bloyd, V. Putsche, "Life-cycle assessment of energy use and greenhouse gas emissions of soybean-derived biodiesel and renewable fuels", Environmental science & technology, 43(3), pp.750-756, 2009.

[10] T. Issariyakul, A.K. Dalai,"Biodiesel from vegetable oils", Renewable and Sustainable Energy Reviews, 31, pp.446-471, 2014.

[11] A.S.A.A. Elgharbawy, "Cost analysis for biodiesel production from waste cooking oil plant in Egypt." International Journal of Smart Grid-ijSmartGrid 1, no. 1, pp. 16-25, 2017.

[12] B. Nyoni, S.P. Hlangothi, "Evaluating the Potential of Algal Pyrolysis Bio-Oil as a Low-Cost Biodiesel for use in Standby Generators for home Power Generation." International Journal of Smart Grid-ijSmartGrid 6, no. 4, pp. 128-131, 2022.

[13] S. Dewang, S. Hadriani, E.S. Lestari. "Viscosity and calorie measurements of biodiesel production from Callophyllum Inophyllum L using catalyst and time variations for stirring in tansesterfication process." In 2017 IEEE 6th International Conference on Renewable Energy Research and Applications (ICRERA), pp. 734-738. IEEE, 2017.

[14] E.K. Çoban, C. Gençoğlu, D. Kirman, O. Pinar, D. Kazan, A.A. Sayar. "Assessment of the effects of medium composition on growth, lipid accumulation and lipid profile of Chlorella vulgaris as a biodiesel feedstock." In 2015 International Conference on Renewable Energy

Research and Applications (ICRERA), pp. 793-796. IEEE, 2015.

[15]   R. Arslan, Y. Ulusoy. "Utilization of waste cooking oil as an alternative fuel for Turkey." In 2016 IEEE International Conference on Renewable Energy Research and Applications (ICRERA), pp. 149-152. IEEE, 2016.

[16]   V.K. Mishra, R. Goswami, "A review of production, properties and advantages of biodiesel", Biofuels 9: 273–289, 2018.

[17]   J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, "Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels", pp.11206-11210, 2006.

[18]   N. Kumar, "Oxidative stability of biodiesel: Causes, effects and prevention", Fuel, 190, pp.328-350, 2017.

[19]   Z. Yaakob, B.N. Narayanan, S. Padikkaparambil, "A review on the oxidation stability of biodiesel", Renewable and Sustainable Energy Reviews, 35, pp.136-153, 2014.

[20]   H. Sutanto, B.H. Susanto, M. Nasikin, "Solubility and antioxidant potential of a pyrogallol derivative for biodiesel additive", Molecules, 24(13), p.2439, 2019.

[21]   S. Yusri, M. Nasikin, H. Sutanto, "Effect of surfactant addition on the dispersion and antioxidant performance of pyrogallol in biodiesel", Makara Journal of Science, 24(4), p.6, 2019.

[22]   M.M. Rashed, M.A. Kalam, H.H. Masjuki, H.K. Rashedul, A.M. Ashraful, I. Shancita, A.M. Ruhul, "Stability of biodiesel, its improvement and the effect of antioxidant treated blends on engine performance and emission", RSC advances, 5(46), pp.36240-36261, 2015.

[23]   G. Dwivedi, M.P. Sharma, "Impact of cold flow properties of biodiesel on engine performance", Renewable and Sustainable Energy Reviews 31, pp.650-656, 2014.

[24]   E. Yuliarita, N.A. Fathurrahman, L. Aisyah, N. Hermawan, R. Anggarani. "Comparison of synthetic and plant extract antioxidant additives on biodiesel stability", In IOP Conference Series: Materials Science and Engineering, vol. 494, no. 1, p. 012030. IOP Publishing, 2019.

[25]   T.T. Kivevele, Z. Huan, "Effects of antioxidants on the cetane number, viscosity, oxidation stability, and thermal properties of biodiesel produced from nonedible oils", Energy Technology 1, no. 9, pp.537-543, 2013.

[26]   H. Sutanto, B.H. Susanto, M. Nasikin, "The effect of surfactant addition towards dispersion and antioxidant activity of tert-butylhydroquinone in biodiesel", Int. J. Renew. Energy Res, 8(4), pp.1974-1979, 2018.

[27]   K. Amri, A. Kismanto, M.D. Solikhah, F.T. Pratiwi, A.G. Arisanti, "Study of biodiesel specifications for heavy-duty gas turbine application", In Journal of Physics: Conference Series (Vol. 1858, No. 1, p. 012040). IOP Publishing, 2021.

[28]   R.A. Yupitasary, I. Maulana, D.U. Mardiani, H. Budiastuti, S. Widarti, "Characterization and Production of Environmentally Friendly Biodiesel from Patin Fish". In International Seminar of Science and Applied Technology (ISSAT 2020) (pp. 27-33). Atlantis Press, 2020.

[29]   J. Pullen, K. Saeed, "An overview of biodiesel oxidation stability", Renewable and Sustainable Energy Reviews, 16(8), pp.5924-5950, 2012.

[30]   E.C. Zuleta, L. Baena, L.A. Rios, J.A. Calderón, "The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: a review", Journal of the Brazilian Chemical Society, 23, pp.2159-2175, 2012.

[31]   S. Nogales-Delgado, J.M. Encinar, J.F. González, "Safflower Biodiesel: Improvement of its Oxidative Stability by using BHA and TBHQ", Energies, 12(10), p.1940, 2019.