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Stability of B50 biodiesel added with glycerol ester additive based on palm oil oleic acid

Stabilitas biodiesel B50 yang ditambahkan aditif gliserol ester berbasis asam oleat sawit

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Abstrak

Biodiesel di Indonesia merupakan campuran Fatty Acid Methyl Ester (FAME) *dan minyak diesel. Pencampuran* FAME *dan minyak diesel merupakan tantangan karena* FAME *terpisah dengan minyak diesel pada suhu rendah. Perubahan sifat fisika kimia biodiesel selama penyimpanan menurunkan kualitas biodiesel akibat adanya oksigen terlarut yang berpotensi merusak mesin. Penggunaan gliserol ester (GE) sebagai aditif dapat menjadi solusi alternatif dalam mengatasi permasalahan tersebut. Penelitian ini mengkaji stabilitas biodiesel yang ditambahkan GE. Sebagai pembanding, digunakan aditif komersial dietil eter (DEE). Konsentrasi aditif yang ditambahkan ke biodiesel divariasikan dari 1000, 2000, dan 3000 ppm sedangkan suhu penyimpanan divariasikan pada 12, 25, dan 42°C. Stabilitas biodiesel dievaluasi selama tiga bulan dengan mengukur angka asam, viskositas, laju korosi, dan kadar air. Nilai angka asam dari variasi jenis dan konsentrasi aditif masih memenuhi standar SNI 7182-2015 (0,5 mg KOH g^{-1}sampel) dengan rentang nilai 0,148-0,392 mg KOH g^{-1} sampel. Viskositas kinematis memiliki rentang nilai 3,12-3,58 cst yang juga memenuhi standar SNI 7182-2015 (2,3-6 cst). Laju korosi tertinggi untuk GE dan DEE ada pada minggu ke-1, dengan nilai masing-masing 0,447 dan 0,261 mpy. Biodiesel B50 kontrol maupun biodiesel B50 dengan penambahan 1000 ppm GE memiliki nilai kadar air yang sama pada hari ke-18 yaitu sebesar 0,046%, dan nilai tersebut merupakan kadar air tertinggi. Secara keseluruhan, aditif GE pada biodiesel B50 dengan variasi konsentrasi memenuhi standar SNI biodiesel 7182-2015.*

[Kata kunci: angka asam, laju korosi, sifat fisiko-kimia, viskositas, kandungan air]

Abstract

Biodiesel in Indonesia is a mixture of Fatty Acid Methyl Ester (FAME) and diesel oil. Mixing FAME and diesel oil is challenging since FAME is separated from diesel oil at low temperatures. Changes in the physico-chemical properties of biodiesel during storage decrease biodiesel quality due to dissolved oxygen, potentially damaging the engine. Using glycerol ester (GE) as an additive can be an alternative solution to tackle that problem. This research examined the stability of GE-added biodiesel. As a comparison, commercial diethyl ether (DEE) additive was used. The concentration of additive added to biodiesel varied at 1000, 2000, and 3000 ppm while the storage temperature varied at 12, 25, and 42°C. The stability of biodiesel was evaluated for three months by measuring the acid value, viscosity, corrosion rate, and water content. The acid values of the various types and concentrations of additives still meet the SNI 7182-2015 standard (0.5 mg KOH g^{-1} sample) with a value range of 0.148-0.392 mg KOH g^{-1} sample. Kinematic viscosity had a value range of 3.12-3.58 cst, which also meets the SNI 7182-2015 standard (2.3-6 cst). The highest corrosion rate for GE and DEE was in the first week, with values of 0.447 and 0.261 mpy, respectively. Both B50 biodiesel control and the addition of 1000 ppm GE had the same water content value on the 18th day, which was 0.046%, and this value was considered the highest water content. This means adding an additive can maintain the water content in B50 biodiesel. Overall, GE additives in B50 biodiesel with various concentrations comply with SNI 7182-2015 standard.

[Keywords: acid value, corrosion rate, physico-chemical properties, viscosity, water content]

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Introduction

The need for energy continues to increase, while fossil fuel-based energy availability is decreasing daily. Through the 2015 Minister of Energy and Mineral Resources Regulation No.2 and the No.16 2020 update (Ministry of Energy and Mineral Resources, 2020), the government has determined that Indonesia will gradually implement biodiesel as a substitute for fossil fuels. The government is gradually replacing diesel fuel with biodiesel with the B35, B40, and B50 programs, which means 35%, 40%, and 50% are biodiesel, diesel biohydrocarbon, and the rest is diesel. The use of fossil-based fuels causes increasing scarcity and impacts the bad environment, including increasing the earth's surface temperature (global warming) and climate change (Ramakrishnan et al., 2019; Reham et al., 2015).

Currently, the most predominant fuel in the world is biodiesel (Melo-Espinosa et al., 2015; Radhakrishnan et al., 2018), green gasoline (Joensen et al., 2011), and natural gas (Reham et al., 2015). Renewable energy development and research is currently a trend and continues to be carried out because bioenergy has advantages over fossil fuels. Emissions from burning biodiesel are cleaner than burning fossil fuels. Burning biodiesel can reduce emissions of carbon monoxide (CO), total hydrocarbons (THC), particulate matter (PM), and polyachromatic hydrocarbons (PAHs), however, emissions from nitrogen oxides (NOx) are still high (Basha, 2018; Basha & Anand, 2014; Vellaiyan, 2020; Vellaiyan et al., 2018; Vellaiyan et al., 2019). Thus, the use of biodiesel is an environmentally friendly solution. Biodiesel can be synthesized from oils of various plants in Indonesia, such as oil palm, coconut, *Calophyllum inophyllum*, *Jatropha curcas*, soybean, and sunflower (Mahmudul et al., 2017). However, biodiesel applied in Indonesia is synthesized mostly from palm oil into fatty acid methyl ester (FAME).

A high yield of FAME up to 95% can be synthesized from palm oil (El-Araby et al., 2018). However, mixing FAME and diesel fuel is difficult as FAME will be separated from diesel fuel and form a gel at low temperatures. This is due to the hygroscopic nature of FAME (Melo-Espinosa et al., 2015); the combustion process is incomplete because the presence of water causes dregs or scale to form in the pipes of motor vehicles (Sheriff et al., 2020). The decline in biodiesel quality can also due to changes in some physical and chemical characteristics during storage. The main reason is the presence of dissolved oxygen which leads to a reaction between the methyl esters and the remaining glycerol, both mono and di-glycerides remaining in FAME to form alcohols, aldehydes, ketones, carboxylic acids, and residues. This can also occur due to the hydrolysis of the methyl ester with dissolved water, causing an increase in the acid value. Such circumstances make motorized vehicles require extra care (Lau et al., 2022; Paryanto et al., 2019). Thus, the problems in biodiesel require additives that can be stable for a certain period of time so that biodiesel does not separate from diesel.

Additives in biodiesel function as emulsifiers and can reduce emissions of hydrocarbon gases, CO, CO_2, and NOx compared to without additives (Basha, 2018; Basha & Anand, 2014). The use of nano additives (Annamalai et al., 2016; Khalife et al., 2017; Basha, 2018) also showed that there were differences in the stability of biodiesel with and without additives. The addition of nano additives in the form of nanocarbon and nanocerium increases the stability and homogeneity of biodiesel. However, nano additives application for biodiesel is costly. An alternative additive that can be used in biodiesel is glycerol ester. Glycerol esters can be synthesized from glycerol and oleic acid. Sari et al. (2017) stated that glycerol ester could improve the quality of oil-based mud (OBM) for drilling. Glycerol ester is an emulsifier with emulsion and lubricant properties (Sari et al., 2017). The potential use of glycerol esters to improve fuel quality should be explored further. Therefore, this study aimed to examine the application of glycerol ester as an additive in B50 biodiesel on the storage stability, including visual appearance, acid value, kinematic viscosity, corrosion rate, and moisture content.

Materials and Methods

Materials

The additives used in this study were glycerol ester (GE) and diethyl ether (DEE) pure analysis obtained from Smartlab. Fatty acid methyl ester (FAME) was obtained from PT Golden Surfaktan Indonesia, while diesel fuel was purchased from PT Pertamina.

Mixing additive with B50 biodiesel

The addition of GE and DEE additives was carried out by mixing GE or DEE with concentrations of 1000, 2000, and 3000 ppm in B50 biodiesel using a *homogenizer* at 6000 rpm for 1 hour. Concentration selection was based on a rough calculation of the economic value of the fuel if additives were added.

Product stability test

The product stability test was carried out according to Mulyana (2014), by storing emulsified biodiesel at 12, 25, and 42°C for 12 weeks to observe product stability at cold, room, and heat temperatures. Then, the product stability was evaluated based on the acid value (SNI 7182-2015), viscosity (SNI 7182-2015) by using a Brookfield DV-III ultra viscometer, density using an Anton Paar DMA 4500M density meter, water content with the Karl Fisher method (Dean et al., 2010), and corrosion rate (ASTM G-31). The separation possibility of emulsified biodiesel was observed for 12 weeks.

Experimental design

The experimental design in this study was a Completely Randomized Factorial Design. The treatments were the type of additive, additive concentration, and storage temperature. Additive-type treatment consisted of two levels: GE and DEE. The additive concentration treatment consisted of three levels: 1000, 2000, and 3000 ppm. The storage temperature treatment consisted of three levels: 12, 25, and 42°C. The experiment was carried out with three replications. Duncan's further test would be carried out if there was a significant treatment effect.

Results and Discussion

Storage stability test of B50 biodiesel with GE and DEE addition

Storage of biodiesel with additional additives should be considered because an effective and efficient storage system could affect the quality of biodiesel so that it remains within the quality limits set by the SNI 7182-2015 standard. The decrease in biodiesel quality is due to changes in the physical and chemical characteristics during storage. The main cause of the stability problem in biodiesel quality is the presence of dissolved oxygen which causes a reaction between the methyl esters and the remaining glycerol, both mono and di-glycerides remaining in the FAME product to form aldehydes, alcohols, ketones, carboxylic acids, and residues (Yaakob et al., 2014). This quality decrease can also occur due to the hydrolysis of the methyl ester with dissolved water, causing an increase in the acid value.

A biodiesel stability test was carried out at 12, 25, and 42°C to determine the effect of environmental conditions and the time period for biodiesel storage as a mixture according to regulations set by the government. The constraints of storing biodiesel at low temperatures are the decrease of solubility and the formation of microbes. Meanwhile, storage at high temperatures and relatively long storage time will increase acid value and viscosity. The visual appearance of B50 biodiesel storage with GE additive is depicted in Figure 1.

Visually, the appearance of biodiesel that had been added with additives (both GE and DEE) was slightly different; storaged at 25°C had a bright yellow color and no precipitate (B50 biodiesel remained homogeneous), whereas, at 12°C, there was a colloidal phase at the bottom of the container which was the saturated fatty acid fraction of FAME in solid form in B50 biodiesel. FAME tends to be hygroscopic and forms a gel at low temperatures (Melo-Espinosa et al., 2015). Meanwhile, B50 biodiesel was homogeneous with no sediment at 42°C storage temperature.

Acid value analysis

The acid value test of the fuel was done to determine the remaining free fatty acids in B50 biodiesel. The higher the acid value value makes biodiesel easily oxidized, which generates corrosion in vehicle engines and storage tanks. The acid values of B50 biodiesel that had been added with additives are summarized in Table 1. Table 1 shows that type of additive, concentration of additive, and storage temperature affected significantly the acid value of the B50 biodiesel, and there was also an interaction between the three factors ($\alpha = 0.05$).

(a) (b) (c)

Figure 1. B50 biodiesel with GE additive at storage temperature a) 12°C, b) 25°C, and c) 42°C
Gambar 1.Biodiesel B50 dengan aditif GE pada suhu penyimpanan a) 12°C, b) 25°C dan c) 42°C

Duncan's further test results for acid value with three factors and a total of 24 treatments showed that each level of treatment gave significantly different results. The acid value, measured from week 0 to week 12, tended to increase. The lowest acid value, 0.148 mg KOH g^{-1} sample, was from the addition of the DEE additive at a concentration of 3000 ppm in week 0 (at the start of storage). In comparison, the highest acid value was 0.392 mg KOH g^{-1} sample from biodiesel without additive addition in week 12 (at the end of storage). Storage temperature also affected the increase of acid values from week 0 to week 12. Storage at higher temperature, 42°C, resulted in higher acid values compared to 25°C and 12°C due to the faster oxidation rate of methyl ester at high storage temperatures. Methyl esters are very susceptible to degradation reactions such as hydrolysis and oxidative degradation (Aricetti & Tubino, 2012). Biodiesel quality will decrease if stored at high temperatures compared to low temperatures (Aricetti & Tubino, 2012; Leung et al., 2006). Biodiesel that is degraded has an increased acidity value because the fatty acid methyl ester molecules break down during degradation, and the fatty acid chains increase the acid value in biodiesel. Oxidation reactions are characterized by a decrease in the number of unsaturated bonds in the carbon chain with the formation of compounds such as alcohols, aldehydes, and ketones (de Lira et al., 2010). Research by Leung et al. (2006) showed that biodiesel storage at different temperatures affected biodiesel acid value and purity. The longer storage at high temperatures causes an increase in acid value.

In this study, the addition of acid value during the storage period was below the standard maximum value of acid value based on SNI 7182-2015 of 0.5 mg KOH g^{-1} sample. According to Sari et al. (2017), GE is non-corrosive and environmentally friendly. The GE additive added to B50 biodiesel can be used as a renewable bio-additive alternative compared to petroleum-based DEE additive. The acid values produced by these two additives were still below the SNI 7182-2015 standard. The addition of GE and DEE additives with various concentrations of 1000 ppm, 2000 ppm, and 3000 ppm is still acceptable as seen in the addition of acid values which are below the SNI biodiesel standard 7182-2015. So, using the lowest additive addition, 1000 ppm, is recommended as it is cost-effective.

Table 1. Acid value analysis on B50 biodiesel that has been added with additives

Tabel 1. Analisis angka asam pada biodiesel B50 yang telah ditambah aditif

Additive type *Jenis aditif*	Concentration (ppm) *Konsentrasi (ppm)*	Temperature (°C) *Suhu (°C)*	Acid value in the 2nd week of storage (mg KOH g^{-1}) *Angka asam pada minggu kedua penyimpanan (mg KOH g^{-1})*			
			0	4	8	12
DEE	0	12	0.182 $^{eg*)}$	0.201 ^{ch}	0.215 ^{bc}	0.262 ^{ab}
		25	0.207 ^{h}	0.199 ^{bg}	0.209 ^{ab}	0.256 ^{a}
		42	0.177 ^{df}	0.259 ^{l}	0.310 ^{n}	0.375 ^{h}
	1000	12	0.174 ^{ce}	0.183 ^{ac}	0.201 ^{a}	0.257 ^{a}
		25	0.191 ^{fg}	0.179 ^{a}	0.221 ^{cd}	0.282 ^{d}
		42	0.172 ^{ce}	0.216 ^{gj}	0.247 ^{hi}	0.285 ^{de}
	2000	12	0.159 ^{ac}	0.209 ^{fi}	0.215 ^{bc}	0.268 ^{bc}
		25	0.178 ^{df}	0.205 ^{ei}	0.198 ^{a}	0.260 ^{a}
		42	0.161 ^{ac}	0.237 ^{k}	0.234 ^{eg}	0.293 ^{f}
	3000	12	0.148 ^{a}	0.220 ^{hk}	0.223 ^{ce}	0.279 ^{d}
		25	0.152 ^{ab}	0.191 ^{af}	0.215 ^{bc}	0.271 ^{c}
		42	0.169 ^{ce}	0.210 ^{fi}	0.229 ^{df}	0.309 ^{g}
GE	0	12	0.166 ^{bd}	0.185 ^{ad}	0.237 ^{fh}	0.271 ^{c}
		25	0.164 ^{bd}	0.180 ^{ab}	0.231 ^{df}	0.262 ^{ab}
		42	0.183 ^{eg}	0.269 ^{l}	0.310 ^{n}	0.392 ^{k}
	1000	12	0.172 ^{ce}	0.204 ^{in}	0.247 ^{hi}	0.295 ^{f}
		25	0.179 ^{df}	0.196 ^{af}	0.245 ^{gi}	0.290 ^{ef}
		42	0.182 ^{eg}	0.223 ^{ik}	0.264 ^{kl}	0.309 ^{g}
	2000	12	0.191 ^{fg}	0.196 ^{af}	0.251 ^{ij}	0.312 ^{g}
		25	0.193 ^{g}	0.187 ^{ae}	0.231 ^{df}	0.262 ^{ab}
		42	0.182 ^{eg}	0.232 ^{jk}	0.283 ^{m}	0.345 ^{i}
	3000	12	0.168 ^{ce}	0.206 ^{ei}	0.259 ^{jk}	0.322 ^{h}
		25	0.182 ^{eg}	0.204 ^{in}	0.247 ^{hi}	0.295 ^{f}
		42	0.183 ^{eg}	0.229 ^{jk}	0.272 ^{l}	0.323 ^{h}

*) Note: the same letter in the same column is not significantly different in the DMRT (Duncan's Multiple Range Test) test with a significance level of 5%

*) *Catatan: huruf yang sama pada kolom yang sama menunjukkan tidak berbeda nyata pada uji DMR (Duncan's Multilple Range Test) dengan taraf nyata 5 %*

Kinematic viscosity analysis

One of the standard parameters of SNI 7182-2015 regarding biodiesel is kinematic viscosity. If the viscosity value does not meet the SNI standard, biodiesel can reduce engine performance or damage the vehicle engine. The kinematic viscosity value of biodiesel based on SNI 7182-2015 is 2.3-6 mm^2/s (cst). High viscosity values can cause incomplete fuel, air atomization, and minimum evaporation, resulting in incomplete combustion (Jain & Sharma, 2010).

A kinematic viscosity test was carried out to determine how much resistance B50 biodiesel fuel has to flow. The higher the kinematic viscosity value, the more difficult it will be to flow, so this is a concern and must comply with the established SNI standards. The results of the analysis of variance in the influence of the type of additive factor, the concentration of the additive, and the storage temperature are presented in Table 2. In general, Table 2 shows an interaction of these three factors and significantly affected the viscosity of the biodiesel produced ($\alpha = 0.05$).

Based on Table 2, in general, the viscosity value of B50 biodiesel increased with increasing storage time. Additive type, additive concentration, and storage temperature significantly affected the viscosity of B50 biodiesel. The molecular structure, such as the length of the molecular chain, influences the increase in kinematic viscosity. Along with the length of storage and differences in storage temperature, storage with high temperatures at 42°C had a higher kinematic viscosity value than storage at 25°C and 12°C. This is related to carbon chain length, degree of saturation, and the number of double bonds of the methyl ester. The longer the carbon chain, the higher the kinematic viscosity value. The higher the storage temperature, the faster biodiesel is oxidized, and this affects physical and chemical properties of biodiesel, such as increasing the acid value, peroxide number, and viscosity (Das et al., 2009).

Table 2. Results of viscosity analysis on B50 biodiesel which has been added with additives
Tabel 2. Hasil analisis viskositas pada biodiesel B50 yang telah ditambah aditif

Additive type *Jenis aditif*	Concentration (ppm) *Konsentrasi (ppm)*	Temperature (°C) *Suhu (°C)*	Acid value in the 2nd week of storage (mg KOH g^{-1}) *Angka asam pada minggu kedua penyimpanan (mg KOH g^{-1})*			
			0	4	8	12
DEE	0	12	3.180 $^{g*)}$	3.220 ^{h}	3.277 ^{i}	3.220 ^{b}
		25	3.240 ^{l}	3.170 ^{c}	3.180 ^{a}	3.310 ^{h}
		42	3.130 ^{b}	3.270 ^{l}	3.230 ^{f}	3.450 ^{n}
	1000	12	3.150 ^{d}	3.240 ^{h}	3.280 ^{i}	3.270 ^{f}
		25	3.257 ^{n}	3.230 ^{i}	3.177 ^{a}	3.357 ^{j}
		42	3.177 ^{g}	3.290 ^{m}	3.450 ^{n}	3.527 ^{q}
	2000	12	3.160 ^{e}	3.203 ^{f}	3.240 ^{g}	3.253 ^{e}
		25	3.250 ^{m}	3.210 ^{g}	3.190 ^{b}	3.337 ^{i}
		42	3.140 ^{c}	3.360 ^{p}	3.530 ^{o}	3.570 ^{r}
	3000	12	3.163 ^{e}	3.170 ^{c}	3.207 ^{cd}	3.230 ^{c}
		25	3.240 ^{l}	3.223 ^{h}	3.210 ^{d}	3.380 ^{l}
		42	3.170 ^{f}	3.307 ^{o}	3.397 ^{l}	3.490 ^{p}
GE	0	12	3.213 ^{j}	3.210 ^{h}	3.260 ^{h}	3.207 ^{a}
		25	3.120 ^{a}	3.163 ^{b}	3.190 ^{b}	3.233 ^{cd}
		42	3.210 ^{h}	3.260 ^{k}	3.410 ^{m}	3.427 ^{m}
	1000	12	3.193 ^{h}	3.200 ^{f}	3.287 ^{j}	3.230 ^{c}
		25	3.160 ^{e}	3.150 ^{a}	3.227 ^{f}	3.283 ^{g}
		42	3.210 ^{h}	3.300 ^{n}	3.290 ^{h}	3.370 ^{k}
	2000	12	3.200 ^{i}	3.190 ^{e}	3.220 ^{e}	3.240 ^{d}
		25	3.190 ^{h}	3.200 ^{f}	3.203 ^{c}	3.270 ^{f}
		42	3.220 ^{k}	3.260 ^{k}	3.330 ^{k}	3.463 ^{o}
	3000	12	3.223 ^{k}	3.170 ^{c}	3.287 ^{j}	3.250 ^{e}
		25	3.190 ^{h}	3.180 ^{d}	3.290 ^{h}	3.287 ^{g}
		42	3.270 ^{o}	3.393 ^{q}	3.563 ^{p}	3.580 ^{s}

$^{*)}$ Note : the same letter in the same column is not significantly different in the DMRT (Duncan's Multiple Range Test) test with a significance level of 5%

$^{*)}$ *Catatan: huruf yang sama pada kolom yang sama menunjukkan tidak berbeda nyata pada uji DMRT (Duncan's Multilple Range Test) dengan taraf nyata 5 %*

The kinematic viscosity values in this study ranged from 3.120-3.580 cst at a variation of the addition of 0 ppm GE additive at 25°C and the addition of 3000 ppm GE additive at temperature 42 °C. The analysis of variance showed that the type of additive treatment, additive concentration, and storage temperature significantly affected the kinematic viscosity of B50 biodiesel, and there was an interaction between these factors at $\alpha = 0.05$. Duncan's further test showed that those treatments significantly affected the resulting viscosity value. The types of additives (DEE and GE) provide a significant difference compared to without adding additives, the concentration of additives that mutually influence the viscosity produced, and the storage temperature. The relatively high temperature made the viscosity value higher than the low storage temperature (25°C and 12°C). A decrease in biodiesel quality in several vegetable oils and cooking oils under different storage conditions increase the acid value, peroxide value, and viscosity with the length of storage time (Bouaid et al., 2007). Thus, the addition of additives with variations of 1000, 2000, and 3000 ppm and storage temperatures of 12, 25, and 42°C still meet SNI standards.

Corrosion rate analysis

The corrosion of the fuel is one of the important parameters because it is related to damage to the vehicle engine. Corrosion is a chemical process of a metal reacting with chemicals in the environment. The fuel corrosion test will closely relate to B50 biodiesel fuel storage and vehicle engine tanks. The plate used was copper according to the immersion test method based on ASTM G-31. This study's results indicate that there is no significant interaction between the additive type and the additive concentration at $\alpha = 0.05$. A significant effect is shown by the type of additive on the corrosion rate. Meanwhile, additive concentration did not significantly affect the corrosion rate. The effect of the type of additive on the corrosion rate can be seen in Figure 2.

The corrosion rate in the first week was the highest compared to the week after, which was 0.447 mils per year (mpy) for GE and 0.261 mpy for DEE. The corrosion rate decreased until the 4th week, then remained constant until the 12th week. The high corrosion rate in the early weeks occurred because the surface of the copper plate material was corroded (indicated by a decrease in the mass of the copper plate) by biodiesel and additives. However, there was no decrease in mass on the copper plate, so in Figure 2, from week 7 to week 12, there was no significant difference between the types of DEE and GE additives. The corrosion rate of GE was higher when compared to DEE because GE has a high acid value, around 11.35 mg KOH g^{-1} compared to DEE (Ali et al., 2016). High acid values will trigger oxidation and corrosion of fuels and metals.

Corrosion on copper plates is characterized by the formation of dark circles due to corrosion. This is Cu oxidized to CuO and Cu_2O. Cu metal is very reactive with organic acids formed due to the degradation process of B50 biodiesel. Images of copper plates before and after immersion for 12 weeks are shown in Figure 3.

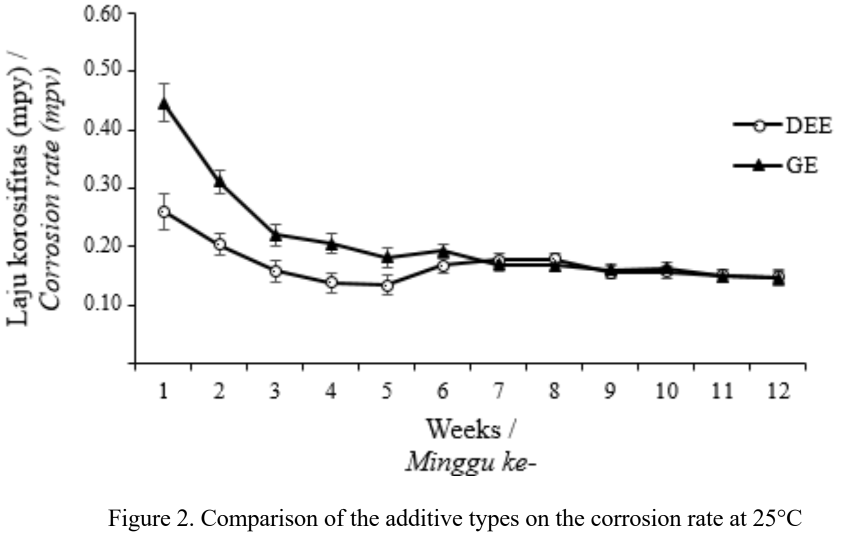

Figure 2. Comparison of the additive types on the corrosion rate at 25°C
Gambar 2. Perbandingan jenis aditif terhadap laju korosi pada 25°C

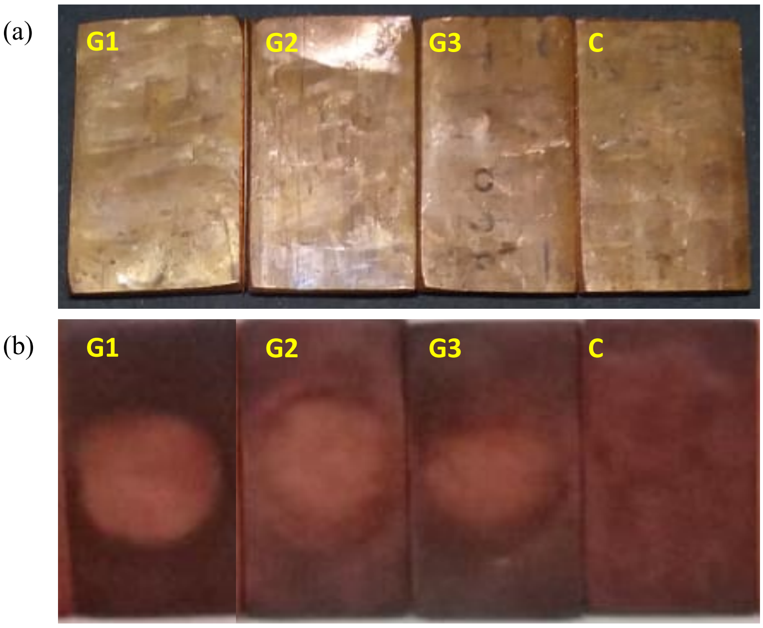

Figure 3. The copper plate before (a) and after (b) immersion in B50 biodiesel and GE additive for 3 months. G1 = GE 1000 ppm, G2 = GE 2000 ppm, G3 = GE 3000 ppm, and C = control

Gambar 3. Plat tembaga sebelum (a) dan sesudah (b) perendaman dalam biodiesel B50 dan aditif GE selama tiga bulan. G1 = GE 1000 ppm, G2 = GE 2000 ppm, G3 = GE 3000 ppm, dan C = kontrol

The corrosion process on the copper plate also causes the weight of the copper plate before and after immersion to be different. The mechanism reaction of corrosion on copper plates is described as follows (Rocha et al., 2019):

$2Cu + O_2 \rightarrow CuO + Cu_2O$ …………………..…. (1)

$2R'COOH + Cu_2O \rightarrow 2Cu(R'COO) + H_2O$ …. ..(2)

Cu metal in biodiesel can accelerate the catalytic reaction process, reducing the physico-chemical properties of biodiesel. Metals will react directly with fatty acids to produce alkyl fatty acids. Biodiesel in contact with oxygen will undergo an oxidation process. The methyl esters in biodiesel will form free radicals, giving rise to new products such as aldehydes, ketones, formic acid, and propionic acid.

Water content analysis

FAME has hygroscopic properties, so it is necessary to assess the parameter of water content in biodiesel. The presence of water in the fuel increases the value of the acid value, causing corrosiveness and scale on the engine (Vellaiyan et al., 2018). The analysis of the variance results of the additive type and the additive concentration on the water content at $\alpha = 0.05$ indicates that these factors influenced the water content. In contrast, the interaction of the two factors began to be seen on day 24. The effect of the type and concentration of the additive on the water content can be seen in Figure 4.

The highest water content was found on the 18th day at 0.046% with the addition of 1000 ppm GE additive compared to the control. The water content in control was also the highest on the 18th day at 0.046%. This means that additives can maintain the water content of B50 biodiesel. The water content of the fuel is expected to be as minimal as possible or with the addition of additives. The water content in this study meets the SNI Biodiesel standard 7182-2015 (maximum 0.05%). Thus, variations in the concentration of additives (1000, 2000, and 3000 ppm) in both GE and DEE are still acceptable.

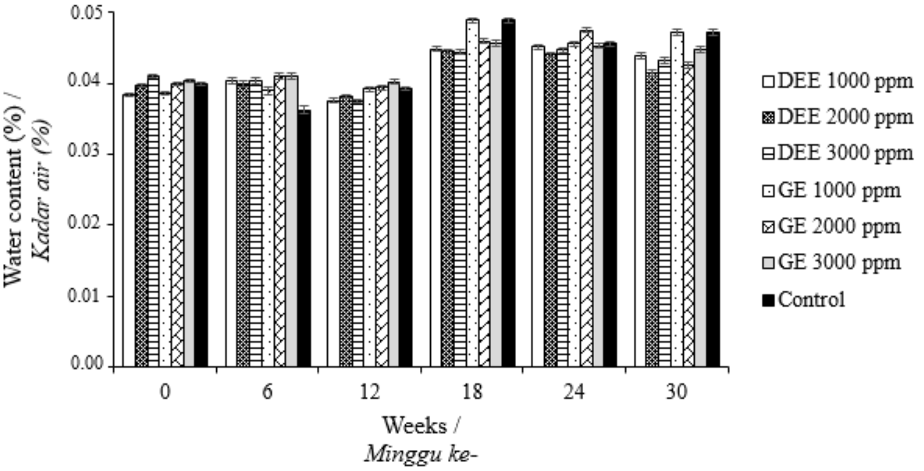

Figure 4. The effect of the type and the concentration of additives on the water content of B50 biodiesel during storage
Gambar 4. Pengaruh jenis dan konsentrasi aditif terhadap kadar air biodiesel B50 selama masa penyimpanan

Conclusion

Storage stability test results of B50 biodiesel with the addition of additives at temperatures of 12, 25, and 42°C showed that the addition of GE and DEE additives with concentrations of 1000, 2000, and 3000 ppm were stable for three months and met SNI biodiesel standards 7182-2015. The acid value values of the various types and concentrations of additives were range of 0.148-0.392 mg KOH g^{-1} sample. Kinematic viscosity had a value range of 3.12-3.58 cst. The highest corrosion rate for GE and DEE was in the first week, with values of 0.447 and 0.261 mpy, respectively. Both control and the addition of 1000 ppm GE had the same water content value on the 18th day, which was 0.046%, the highest water content.

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