Effect of Bioinhibitor Additives on Biosolar Quality

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Abstract. Alternative fuel oil that is renewable and environmentally friendly because it is made from vegetable oil, one of which is biodiesel. Biodiesel has a biodiesel composition produced from unsaturated fatty acids that cause oxidative degradation of biodiesel. The hygroscopic nature of biodiesel is susceptible to oxidation which causes faster corrosion of the biodiesel storage area itself. The use of organic inhibitors or bioinhibitors is effective and not harmful to the environment. This study aims to determine the quality of biodiesel before and after adding a bioinhibitor. The bioinhibitors used were cocoa beans, guava leaves, and betel leaves as inhibitors obtained from the maceration method with ethanol solvent at room temperature for 48 hours, plus ascorbic acid as a bioinhibitor. The addition of bioinhibitors was carried out with various variations, namely as much as 2mg/100ml, 8mg/100ml, 12mg/100ml. After the addition of the bioinhibitor, tests were carried out including density, viscosity, flash point, pour point and microbial tests. After testing, it was found that the addition of the bioinhibitor did not affect the quality of the biodiesel. The addition of these materials does not affect the quality of biodiesel and still meets SNI standards for biodiesel. Furthermore, testing the quality of biodiesel to ensure the quality of biodiesel is maintained with the addition of a bioinhibitor.

Keywords: bioinhibitor, cocoa bean, guava leaf, betel leaf, ascorbic acid

1 Introduction

1.1 A Subsection Sample

Biodiesel (B30) is corrosive because of the degradation process due to oxidation of the unsaturated fatty acid composition of the biodiesel composition. This corrosive nature can be caused by the presence of impurities such as water, free fatty acids, glycerol and others during the product purification process. Biodiesel is more hygroscopic than diesel (Suherna, 2020) (Mohsen, 2020) because it easily absorbs

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water and moisture which leads to corrosion. Biodiesel is more corrosive due to the presence of water and free fatty acids.

Corrosion inhibitors are substances which when added in small concentrations to an environment can prevent or minimize corrosiveness. There are two types of corrosion inhibitors commonly used in industry, namely inorganic inhibitors and organic inhibitors. Inorganic inhibitors such as arsenate, chromate, silicate and phosphate are expensive, dangerous and environmentally unfriendly chemicals. Therefore, many natural inhibitors have been developed to be an alternative to corrosion inhibitors which are commonly called bioinhibitors. With the addition of this bioinhibitor, it is hoped that the corrosiveness of the material will be reduced and the quality of the biodiesel will not change.

One way to prevent corrosion in biodiesel storage is by adding biomass. The biomass used comes from natural ingredients including cocoa beans, guava leaves and betel leaves. where these materials were previously extracted to separate the material from the mixture using a solvent. Extraction using solvents is based on the solubility of the components in other components in the mixture. Polar solvents will dissolve polar solutes and non-polar solvents will also dissolve non-polar solutes which is then called "like dissolves like" (Shriner et al 1980).

From previous research (Maryanty et al, 2021) it is known that the best natural ingredients to be used as inhibitors are Arabica coffee extract, cocoa beans and tea. Utilization of coffee grounds, tea and cocoa beans is very effective for preventing corrosion of steel and its content in the form of environmentally friendly organic compounds. Caffeine is an alkaloid compound belonging to the type of methylxanthine (1,3,7-trimethylxanthyne) or C8H10N4O2. The use of cocoa beans as an ingredient for the manufacture of bioinhibitors is carried out by a maceration process. With a variable ratio of ethanol solvent and organic matter, namely 225 grams of organic matter: 450 grams of ethanol. With immersion time for 0, 1, 4, 7 and 10 days. The results of the greatest inhibition efficiency obtained were 98% after soaking for 10 days. In this study, bioinhibitors were made from guava leaves and betel leaves with the same treatment as cocoa beans.

The content contained in guava leaves and betel leaves is tannin, which can be a corrosion inhibitor. Tannins function as anti-corrosion agents because in tannin compounds there is a hydroxyl (-OH) functional group, so that tannins can form chelate complexes with iron and other metal cations. In addition, betel leaf also contains flavonoids, alkaloids, and polevenolad. The presence of these antioxidant compounds can support the further use of guava leaves and betel leaves as organic inhibitors. Peroxide formed at the initiation of oxidation in which hydrogen is taken from oleofin compounds generates free radicals. This antioxidant activity can reduce free radicals and antioxidants are inhibitors of the oxidation process, even in relatively small concentrations. Therefore, the addition of antioxidant compounds from guava leaves and betel leaves can reduce the oxidation reaction in biodiesel.

In this study, biomass production was carried out using natural ingredients of cocoa beans, guava leaves and betel leaves by maceration extraction. The natural ingredients used are macerated for 2x24 hours and then filtered to obtain the filtrate and distillation is carried out to obtain the extract. After that, the results of the extraction of biomass were studied for their effect on biodiesel when applied as a bioinhibitor.

2 Literature Review

Bioinhibitor Extract:

Content of Cocoa Beans. The polyphenol content in cocoa beans is dominated by catechins and epilogalokateki. Cocoa beans contain polyphenolic compounds as much as 120-180g/kg (in fat-free powder). Polyphenols can be used as antibacterial compounds to kill unwanted microorganisms or to prevent and inhibit their growth. The antimicrobial properties of cocoa bean extract are due to the presence of several antimicrobial compounds such as catechins, flavonoids, tannins and anthocyanins (Felita, 2000).

These compounds are phytochemical components resulting from plant secondary metabolites. These phytochemical components can be extracted from plants by extraction with the method used is maceration using organic solvents such as ethanol. One of the phytochemical components in plants that can inhibit the corrosion rate is caffeine (Kayaputri et al., 2014).

Guava Leaf Content. The tannin content in guava leaves can be a corrosion bioinhibitor. Tannins are easily hydrolyzed because they are gallic or ellagic acid polymers with ester bonds with a sugar molecule, while condensed tannins are tanpolymers of flavonoid compounds with carbon-carbon bonds (Waghorn et.al. 2003). These tannins function as anti-corrosion agents because in tannin compounds there is a hydroxyl functional group (-OH) attached to the aromatic ring, so that tannins can form chelate complexes with iron and other metal cations. In addition, guava leaves also contain flavonoid compounds, especially quercetin (Ali, et al. 2014).

Tannins are polyphenolic compounds that have large molecular weights consisting of hydroxy and carboxyl groups that can be dissolved in polar solvents such as aquadest, ethanol, methanol, and acetone (A. Kristianto, 2013) (Ismarani, 2012). Tannin compounds consist of two types, namely condensed tannins and hydrolyzed tannins (Hovart, 1981). Tannin compounds have a bitter and chelating taste, can react by agglomerating proteins or various other organic compounds such as amino acids and alkaloids. Bioactive components such as flavonoids, tannins, and phenols are damaged at temperatures above 50°C, because they can change their structure (Handayani and Sriherfyna, 2016).

Betel Leaf Content. Betel leaf also contains tannins which can be used as inhibitors. Red betel leaf contains phytochemical compounds, namely alkaloids, saponins, tannins and flavonoids. Flavonoids are natural phenolic compounds that have antioxidant properties (Rosi et al., 2015), in which these antioxidant compounds can support the further use of betel leaf as an organic inhibitor. This antioxidant activity can reduce free radicals.

Ascorbic Acid. Ascorbic acid or better known as Vitamin C was first isolated as a pure substance in 1928 and the determination of its structure in 1933. The name ascorbic acid comes from the Italian Scrobtus (bloody gums). Ascorbic acid is an organic compound that has the chemical formula C6H¬8O6, is in the form of white crystals, odorless, has a molar mass of 176.12 g/mol, has a boiling point of 190-192°C, and a density of 1.65 g/cm3. Ascorbic acid is soluble in water, 95% ethanol, glycerol and propylene glycol, and this acid is insoluble in diethyl ether, chloroform, benzene and fatty oils. Ascorbic acid is an environmentally friendly organic inhibitor (Tjiro et al. 1999).

Biosolar Quality Assay:

Density. Density or density is a measurement of the mass of each unit volume of an object. The higher the density of an object, the greater the mass per volume. The SI unit of density is kg/m3. Density functions to determine substances (Setiawati and Edward, 2012). The formula for density is $\acute{\rho}$=m/V

Viscosity. Viscosity is a number that states the amount of resistance of a liquid material to flow. The higher the viscosity, the thicker it is and the more difficult it is for the material to flow (Demirbas, 2008). If the viscosity value is too high, the friction in the pipe will be greater, making filtering difficult and allowing dirt to be absorbed. Conversely, if the viscosity is too low, it will result in thin lubrication, if left unchecked it will result in wear and tear (Setiawati and Edward, 2012).

Flash Point. Flash point or flash point is the lowest temperature of the fuel that can burn if brought close to a flame. The high or low flash point depends on the hydrocarbon components in the fuel. The usefulness of this flash point can be used to determine the ease of evaporation or burning of a fuel fuel and is an indication of contamination with other products or materials (Suminta, 2006).

Pour Point. The pour point is the lowest temperature point where the fuel oil begins to freeze and paraffin crystals form which can clog the fuel line. This pour point test is intended to determine or estimate at which point the fuel oil freezes, to avoid the freezing during the storage stage of the fuel oil. So it can be concluded that the fuel pour point test can run well and in accordance with the reference range. The maximum biodiesel pour point is 18°C. (Luh Jingga Sasmita, 2014)

Microbial assay. The microbes that cause microbial corrosion are aerobic bacteria that play an active role in the corrosion process, namely Thiobacillus. These bacteria are capable of producing corrosive acidic environmental conditions resulting from the oxidation of sulfur to sulfuric acid. The species Thiobacillus ferroxidans is a Gram-negative bacterium that is bacilli-shaped and has a polar flagellum (Ruiz et.al., 2014).

3 Research Methodology

3.1 Research methods

This study aims to make biomass from natural materials that can be used for various things, one of which is as a bioinhibitor in biodiesel. Beginning with the manufacture of biomass from cocoa beans, guava leaves and betel leaves by maceration with organic solvents and distillation to evaporate the organic solvents to obtain the extract. Followed by the application of biomass made into biodiesel to determine the quality of biodiesel. Where the bioinhibitor formulation used is based on the best composition that has been carried out by Dwi I & Najla (2021), namely 225 g of organic matter: 450 g of ethanol which is macerated and the filtrate is concentrated by distillation, then mixed with biodiesel with variations of 2mg/100ml, 8mg/100ml dam 12mg/100ml.

3.2 Tools and materials

3.2.1 Tool

The tools used in this research are pycnometer, Ostwald viscometer, a set of flash point testers, oven, electric bath, pH meter, condenser, thermometer, analytical balance, blender, measuring vessel, Erlenmeyer flask, container, pipette, stirrer, cork cover, container. cooler, and water bath.

3.2.2 Ingredient

The materials used in this study include bioinhibitors, biodiesel, aquadest, 96% ethanol. The procedure details are described below:

a. Inhibitor Manufacturing
The manufacture of bioinhibitors uses three natural ingredients, namely cocoa beans, guava leaves and betel leaves. Each ingredient is dried in the oven for 20 minutes. After drying, the cocoa beans, guava leaves and betel leaves are pureed with a blender. Then the three ingredients were macerated each using 96% ethanol solvent for 2 x 24 hours with a material ratio of 225 grams of material: 450 grams of ethanol. Furthermore, the material is filtered to get the extract. To remove the solvent in the extract, distillation was carried out to evaporate the solvent.
b. Addition of Bioinhibitors and Biosolar Quality Testing
After obtaining the extract of the bioinhibitor, the bioinhibitor was mixed with biodiesel and the quality of the biodiesel was tested to determine the effect of the bioinhibitor on biodiesel. The tests carried out include testing for density, viscosity, flame test, pouring test and anti-microbial assay.

4 Results And Discussion

Raw Material Preparation

The raw materials used to make crude bioinhibitors consist of cocoa beans, guava leaves and betel leaves. The three ingredients are dried in a stove oven for 20 minutes. Then grind it using a blender. During the drying process, the color of the material changes. Cocoa beans that are initially light brown to blackish brown, have a smooth texture on the skin and are easier to crush, and emit a cocoa powder aroma. In guava leaves and betel leaves, which were originally green and reddish when dried, they changed color to brown and dry.

4.1 Raw Material Extraction

The prepared material was then extracted by maceration method using 96% ethanol solvent with a ratio of 225 grams of raw material: 450 grams of ethanol for 2 x 24 hours. The material is soaked with 96% ethanol in a jar and tightly closed for 2 x 24 hours. After that, it was seen that the ethanol became cloudy brown in color, smelled slightly pungent, and the submerged material became like a paste, there was no noticeable color change in the material after maceration. The material is filtered with filter paper to get the filtrate.

One of the phytochemical components in cocoa beans that can inhibit the corrosion rate is caffeine. The caffeine content in cocoa beans is 23.51%, these results were obtained by testing using the GC-MS method (Kayaputri et al, 2014). Caffeine is an alkaloid compound that has the same properties as amines. The amine groups in caffeine are expected to stick to metal and form a layer to prevent corrosion of metal walls. Caffeine is a polar compound that is soluble in water (1:50), alcohol (1:75), or chloroform (1:6) but less soluble in ether. The results of the greatest inhibition efficiency obtained by previous researchers (Dwi I & Najla, 2021) were 98% after soaking for 10 days.

Compounds taken from guava leaves and betel leaves are tannin compounds. The tannin content in guava leaves is 12-18% (Jimenez et al, 2001), and the tannin content in betel leaves is around 0.1-1.3% (Pradhan et al, 2013). The tannin compounds in guava leaves and betel leaves can form complex compounds with Fe(III) on the metal surface, then the complex compounds will block corrosive ions on the metal surface so that the corrosion reaction rate will decrease (Budi, 2019). This addition is intended to prevent corrosion of biodiesel as was done by (Mohsen, 2019) with the addition of guava leaf extract with a concentration of 80 mg/l which has the highest inhibitory effect of 98.9%

The choice of solvent for ethanol is because ethanol is a universal solvent used which can attract most chemical compounds. Ethanol solvent was more effective in extracting phytochemical components than using acetone-water solvent. Based on phytochemical screening, cocoa bean extract contains alkalis, flavonoids, tannins, saponins and triterpenoids (Kayaputri et al. 2014). After maceration with ethanol solvent, then filtered to get a thick extract from the raw material. 4.3. Reduction of Ethanol Solvent Level

The viscous extract obtained from the filtering still contains ethanol as solvent. To evaporate the ethanol solvent which is still contained in the extract, simple distillation is carried out. The material is evaporated until the solvent runs out, so that it can produce a dry extract. The extract obtained with the yield of 13.33% for cocoa beans, 11.35% for guava leaves and 11.73% for betel leaf.

From the materials used which include cocoa beans, guava leaves and betel leaves, extraction with ethanol solvent was carried out to extract caffeine compounds contained in cocoa beans and tannins in guava leaves and betel leaves. Based on previous research (Adinda, Shafara 2021) which has tested using HPLC to determine the caffeine content in cocoa beans, it is known that the caffeine content in cocoa beans by maceration extraction with a ratio of solvent and ingredients 2:1 is 1240.213 ppm. Caffeine is an alkaloid compound that has the same properties as amines. The amine groups in caffeine are expected to stick to metal and form a layer that prevents corrosion of metal walls.

One of the active compounds contained in guava leaves is tannin. Tannins are organic compounds that are non-toxic, environmentally friendly, soluble in water and are classified as polyphenols found in nature. Tannins are found in the leaves, fruit, bark and wood of plants. The applications of tannins in industry include the manufacture of inks, antioxidants, food additives, drugs and corrosion inhibitors (Naji, 2013). Testing the tannin content using UV-VIS spectrophotometry, the tannin content was 2.79%. Tannins contain OH groups in the ortho position on the aromatic ring, so that they are able to form chelates with iron and other metal cations. Iron tanates can be formed well because the tannins are hydrolyzed. When $Fe3+$ ions react with $OH-$ in the ortho position, a blue-black iron tanate complex solution will be formed. Tanat will be attached to the iron surface which will prevent the corrosion process (Peres, 2012).

4.2 Addition of Bioinhibitor Extract Into Biosolar

Furthermore, the obtained material filtrate is used as a biodiesel inhibitor by mixing it into biodiesel with a ratio of 2mg/100mL, 8mg/100mL and 12mg/100mL (Mohsen, 2019). Then tested the quality of pure biodiesel and biodiesel that has been mixed with inhibitors. The data obtained in the form of density test, viscosity test, flash point test, and microbial test. In this study, a test was conducted to determine the quality of pure biodiesel and the quality of biodiesel after added with a bioinhibitor

4.3 Analysis of the Effect of Bioinhibitors on Biosolar

4.3.1 Density assay

Density is one of the test parameters to determine the quality of biodiesel. Density is a measurement of the mass per unit volume of an object. The higher the density of an object, the greater the mass per volume. The standard density of biodiesel according to SNI is around 815-880 kg/m3 at a temperature of 15°C. To measure the density of this biodiesel using a pycnometer.

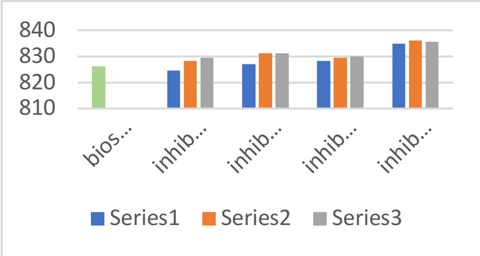

Fig 4. 1. Biosolar Density After addition of inhibitor (SNI 815-850)

In the bar graph above, it can be seen that the increase in density was very good according to the addition of 2mg, 8mg, and 12mg bioinhibitors of each bioinhibitor of cocoa beans, guava leaves, betel leaf and ascorbic acid. The density is very high seen in experiment 4 which is a mixture of biodiesel with 12 mg ascorbic acid bioinhibitor which is about 835,664. The lowest graph is biodiesel with a mixture of 2 mg cocoa bean bioinhibitor, which is 824,511. This density is still included in the standard biodiesel density ratio of 815-880 kg/m3. So it can be explained that there is no major influence on the quality of biodiesel. With the addition of bioinhibitors with different materials, there is a change in density for each addition of the material. But the changes that occur are not too significant so that the density of biodiesel is still within the limits based on SNI.

4.3.2 Viscosity assay

The second test is the biodiesel viscosity test. Viscosity or viscosity is a measurement of the resistance of a fluid (fluid) which is changed by pressure or stress. Where the function of the viscosity measurement itself is to measure the speed of a liquid flowing through a glass pipe (capillary glass). The measuring instrument for measuring this viscosity is the Ostwald Viscometer and a stopwatch. For biodiesel viscosity standards based on pertamina standards, namely 2.0-5.0 mm2/s.

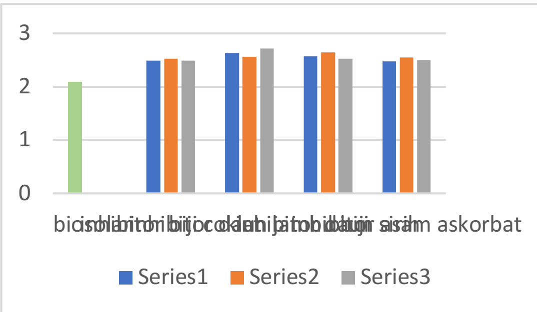

Fig 4. 2. Biosolar Viscosity

From the results of the viscosity test above, it is known that the changes are different for each addition of a bioinhibitor. Viscosity is the viscosity of a fluid, the test observed is kinematic viscosity, which is the ratio between dynamic viscosity and density. In the biodiesel mixture with 12 mg guava leaf bioinhibitor, the viscosity number is high, which is around 2.7186 and in the biodiesel mixture with 2 mg cocoa beans, the viscosity is low, around 2.4918. Guava bioinhibitors have a high viscosity number because guava has a density heavier than the density of cocoa beans, therefore when testing the viscosity of guava leaves it takes a slower time than cocoa beans to arrive at the second point determined on the viscometer. In addition, the concentration in the solution also affects the high number of viscosity. The results of the viscosity in this experiment can be said to be still in the standard ratio of biodiesel, which is the quality standard of biodiesel viscosity, which is 2.0-5 cSt.

4.3.3 Flash point test

Furthermore, the flash point test or flash point of biodiesel is carried out. This flash point indicates the lowest temperature of a material to give off a vapor that can ignite / ignite instantly when exposed to a sufficient heat source. For this test, it is done by heating the material with a test tube in a heater, then observing the moment where the first steam appears and measuring the temperature when the steam appears for the first time.

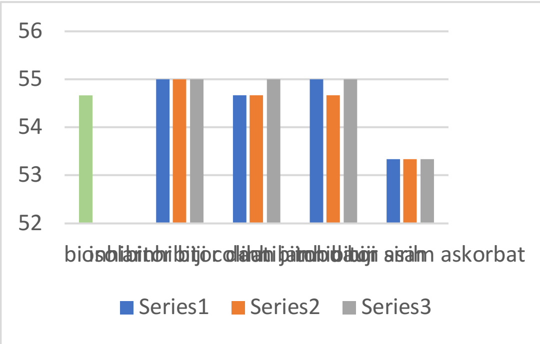

Fig 4. 3. Flash Point Biosolar

The flash point is the lowest temperature the oil will ignite when exposed to a spark. The data above shows many similarities in each sample, the average flash point results obtained from a mixture of biodiesel and cocoa bean bioinhibitors 2 mg, 8 mg, and 12 mg at a temperature of 55°C. Likewise, the mixture of biodiesel with 12 mg guava leaves, a mixture of biodiesel with betel leaf 2 mg and 12 mg. The results of the low flash point test are a mixture of biodiesel with ascorbic acid which the flash point is at a temperature of 53.33°C. The higher the temperature, the less water content in the oil so that the fire grabs faster and the flash point obtained is getting smaller (Nasrun, et al. 2016). The cause of the high flash point value is related to the viscosity value, because a high viscosity value can mean that the water content contained in the biodiesel oil is small. The flash point obtained from this study includes the flash point of biodiesel according to SNI, which is 55°C

4.3.4 Pour point Assay

Finally, testing is carried out for the pour point or pour point of biodiesel. The pour point is the lowest temperature at which a liquid can still flow. The pour point is useful in preventing freezing of the fuel. The pour point test was carried out by pouring biodiesel material and a mixture of biodiesel with inhibitors into a reaction tube and then frozen in an inclined position. Then the frozen material is lifted and tilted until there is the first drop of material after freezing, the temperature of the first drop shows the pour point of the biodiesel.

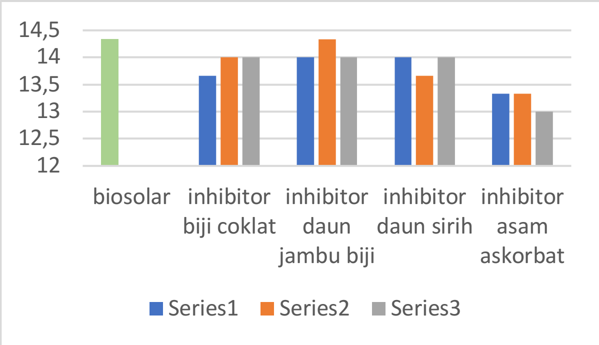

Fig 4. 4. Pour Point Biosolar

In the result data above, the pour point value occurs when the temperature ranges from 13-14.3°C. The lowest pour point value is known in the mixture of biodiesel with ascorbic acid bioinhibitor, which is 13°C. Pour point, which is the lowest temperature the oil can still flow, is used to prevent freezing of liquid fuel in storage.

4.3.5 Anti Microbial Assay

All parameters tested starting from density, viscosity, flash point to pour point of biodiesel showed that all of these parameters did not experience significant changes to the quality of biodiesel tested and were still within the limits set by SNI (SNI 7182:20157). To ensure that the quality of the biodiesel does not change even though the inhibitor is added, microbial tests are also carried out for biodiesel and a mixture of biodiesel with its inhibitor material. Microbial test was carried out by pouring cup method with TCA media. Then the sample was incubated for 24 hours to see the microbial growth.

The results of the microbial test with an incubation time of 24 hours showed microbial growth in pure biodiesel. With the addition of inhibitors from cocoa beans, fewer microbes grow than pure biodiesel. Likewise with the addition of guava leaf inhibitor, betel leaf and ascorbic acid. Even with the addition of inhibitors from betel leaf, very few microbes were seen. Inhibitors from cocoa beans contain caffeine which is an organic inhibitor so that the inhibition process is caused by the adsorption of molecules on the metal surface. Inhibitors adsorbed on the metal surface form a passive layer that protects the metal against further corrosion, so that the inhibitor does not damage the content of the biodiesel itself but coats the metal surface to prevent corrosion.

5 Conclusion

Based on research and discussion, it can be concluded that:
1. The biomass extraction process to obtain extracts that can be used as bioinhibitors in biodiesel is by maceration which is carried out by immersion for 2x24 hours and distillation to remove organic solvents and obtain the desired filtrate.
2. The yield of the biomass used is 13.33% for cocoa beans, 11.35% for guava leaves and 11.73% for betel leaves.
3. Overall, the bioinhibitors made from the biomass of cocoa beans, guava leaves and betel leaves did not affect the quality of the biodiesel used. All the parameters of the biodiesel testing carried out are still within the specified SNI range.

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