

The effect of pyrogallol antioxidant addition and storage temperature to the change of biodiesel quality during storage period

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Abstract. Biodiesel is an alkyl ester compound of fatty acids prepared from a source of naturally renewable triglycerides and used as diesel engine fuel, commonly made through the process of esterification or transesterification. In its application and storage, biodiesel is potentially damaged by oxidation reaction due to internal factors (high unsaturated fatty acid content) and external factors (air, heat or light) resulting in changes of the characteristics and quality of biodiesel. In order to maintain the characteristics and quality of biodiesel to conform to established standards, it is necessary to add antioxidants that can inhibit oxidation reaction in biodiesel. In this study, pyrogallol antioxidant is added to the biodiesel of palm oil with various concentrations and storage temperatures. The observed biodiesel parameters during the storage period are those that can represent oxidation such as changes in kinematic viscosity, density, acid value, and iodine value. The results showed that the addition of pyrogallol antioxidant can inhibit the oxidation reaction in biodiesel. The use of antioxidant with a concentration of 0.1% at storage temperatures of 30°C and 60°C is known to retain the characteristics and quality of biodiesel during storage from damage caused by oxidation reaction.

1. Introduction

Some developments of alternative energy from renewable resources (bioenergy) namely biodiesel, bioethanol, and biogas. Biodiesel is known to be used as one of the renewable alternative energy sources because it does not produce excess sulfur emissions, biodegradable and has better combustion efficiency than diesel [1].

Although the production of biodiesel has met the established standards, biodiesel can be degraded to other compounds during the storage that results in the change of the biodiesel component so that the product no longer meets the standard. The change occurs due to storage conditions and its use. Biodiesel is easily degraded into compounds such as acids, aldehydes, ketones, esters, peroxides and alcohols [2]. Changes in biodiesel characteristics due to the oxidation process include increased viscosity value, peroxide value, acid value and decreased induction period [3]. Therefore, it is necessary to ensure that biodiesel does not degrade or damage due to oxidation reaction during storage period. One way is to do the addition of antioxidants. Antioxidants are compounds that can resist the rancidity and inhibit oxidation reaction in materials containing fat or oil, even at small concentrations [4].



In this research, the addition of antioxidant is by using antioxidant pyrogallol (PY). Study of antioxidant effect to biodiesel is done by using antioxidant PY with two storage conditions by setting two different temperatures for each sample; temperature 30°C or room temperature and at temperature of 60°C which is kept constant. Biodiesel is synthesized from palm oil. The observed parameters during the storage period that indicate the oxidation of biodiesel are kinematic viscosity, density, acid value, and iodine value. Observations will be carried out once a week for 4 weeks of storage.

2. Material and methods

2.1. Addition of pyrogallol antioxidant to biodiesel

Biodiesel was added with pyrogallol antioxidant. Characteristics and specifications test of biodiesel were conducted which include acid value, iodine value, kinematic viscosity, and 40°C density. This was done to know the initial condition of biodiesel that has been obtained used as a reference.

After the biodiesel characteristics was obtained, the next step is the addition of pyrogallol antioxidant into biodiesel by varying different concentrations of 0.05%, 0.07% and 0.1% of the total volume of the biodiesel sample to be used as the test samples. Pyrogallol solution is made from 4.5 ml methanol mixture, 2 ml ethyl acetate, and 0.03 g of pyrogallol antioxidant. Afterwards, the antioxidant was mixed into all test samples.

2.2. Storage of biodiesel test sample

Biodiesel sample will be stored after antioxidant PY was mixed into biodiesel sample. There were two different storage conditions: at room temperature 30°C and 60°C.

2.3. Oxidation Resistance Test on Each Biodiesel Sample

After PY antioxidant was mixed into the biodiesel then oxidation resistance test would be conducted. The oxidation resistance carried out in this study include acid value test, iodine value test, kinematic viscosity test and density test. Each test was done in every week of storage period. In this study, the storage was evaluated for 4 weeks.

3. Result and discussion

3.1. Palm oil biodiesel product test

Following is the results of initial test of biodiesel used in this research:



Figure 1. Palm oil biodiesel.

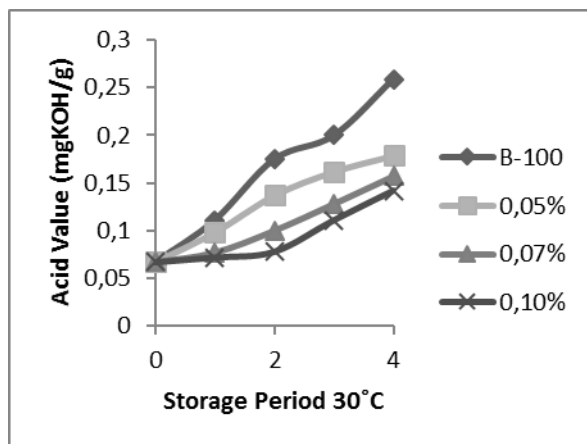
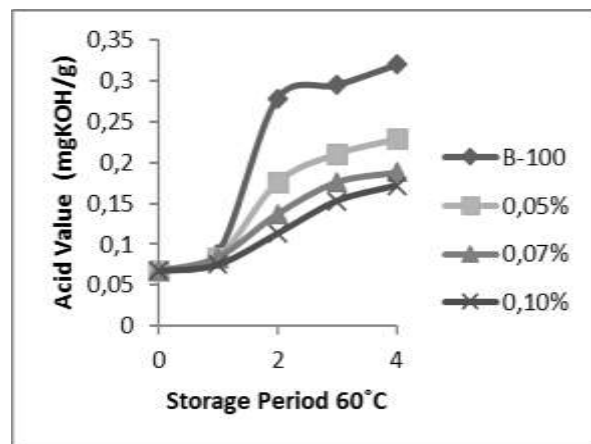
Table 1. Results of biodiesel product test.

Parameter	Unit	SNI 04-7182-2012	Value
Acid Value	mg KOH/g	0,6	0,067
Iodine Value	%mass (g-I ₂ /100 g))	Max 115	72,7
Kinematic Viscosity 40°C	mm ² /s (cSt)	2,3 – 6,0	4,46
Density 40°C	kg/m ³	850 – 890	0,8521
Ester Content	% wt	>96,5	98,7
Free Glycerol	% wt	<0,02	0,006
Total Glycerol	% wt	<0,24	0,198

Based on the test results, the biodiesel used is still in an acceptable condition and still in accordance with the specified standard. It is seen that the value of several parameters tested is still in the range of Indonesian standard SNI 04-7182-2012.

3.2. Effect of antioxidant addition to acid value during storage

One indication of oxidation damage to biodiesel is the increase of acid value, which is caused by the decomposition of peroxide compounds from the oxidation reaction. High acidity level in biodiesel is unfavorable because it can cause damage to the vehicle's machine. The higher the acid value then the lower the quality of biodiesel [5]. High acid value is associated with the corrosion of the media [5]. Additionally, it will shorten the life of pumps and filters on machines [6].

**Figure 2.** Acid value at 30°C.**Figure 3.** Acid value at 60°C.

According to the graphs, the type of the added antioxidant concentration has an effect on the change of the acid value. The higher the added concentration then the lower the acid value [7]. In this study, the addition of antioxidant at the concentration of 0.1% was able to suppress the lowest acid value, whereas the addition of antioxidant at 0.05% and 0.07% showed no significantly different results in inhibiting the increase of acid values. On the other hand, biodiesel samples without the addition of antioxidant underwent the highest increase of acid values compared to biodiesel samples with the addition of antioxidant. This is caused by peroxide compounds from the oxidation of oxidized unsaturated fatty acids that form aldehyde compounds. Aldehydes will be oxidized further to form carboxylic acids which lead to an increase in the acid values [8].

3.3. Effect of antioxidant addition to iodine value during storage

The effect of antioxidant addition to iodine value can be seen in figure 4 and 5.

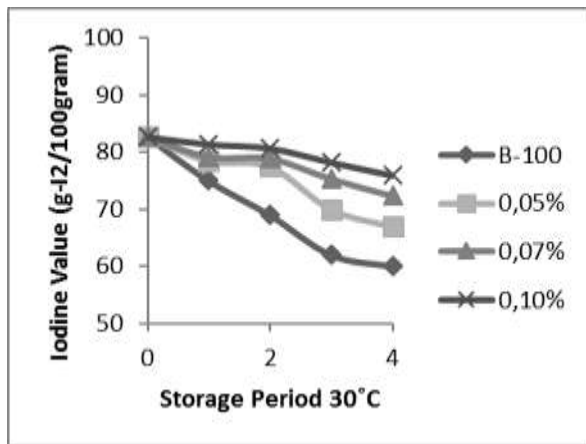


Figure 4. Iodine value at 30°C.

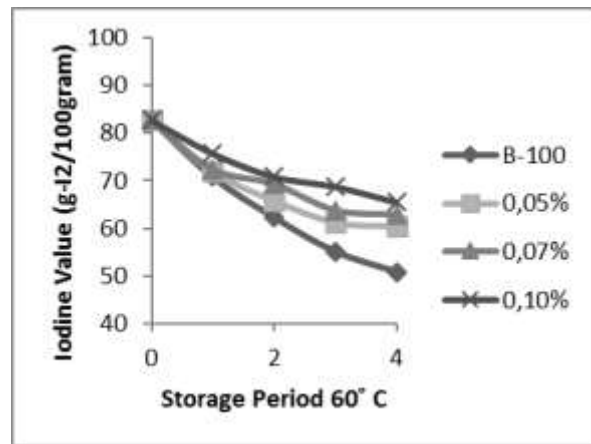


Figure 5. Iodine value at 60°C.

The iodine value is determined by the degree of oil unsaturation. If the level of oil unsaturation is high then the oil will bind the iodine in larger quantities so that the iodine value is higher. High level of oil unsaturation makes oil become more easily to be oxidized. If the oil is easily oxidized, the degree of unsaturation decreases as the double bond is broken and the result is the smaller iodine value.

In this study, it can be seen that the iodine value of each sample decreased. Figure 4 and 5 above shows the effect of addition of pyrogallol antioxidant to the decrease of iodine number from each sample. According to the result, the higher the concentration of antioxidant used then the iodine value is still high. However in the sample that does not use antioxidant, the iodine value shows a significant decrease.

3.4. Effect of antioxidant addition to kinematic viscosity of biodiesel

The effect of pyrogallol antioxidant addition to the value of kinematic viscosity of biodiesel is shown in figure 6 and 7.

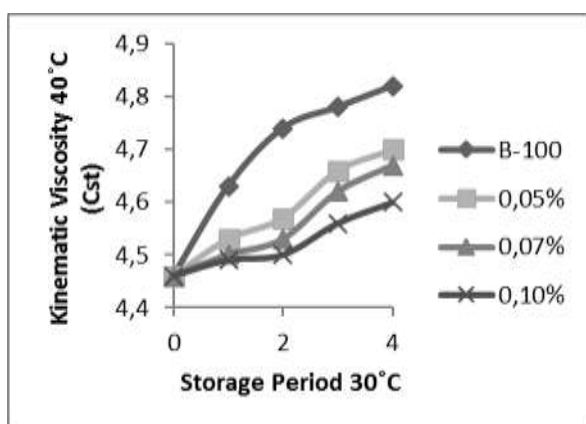


Figure 6. Kinematic viscosity 30°C.

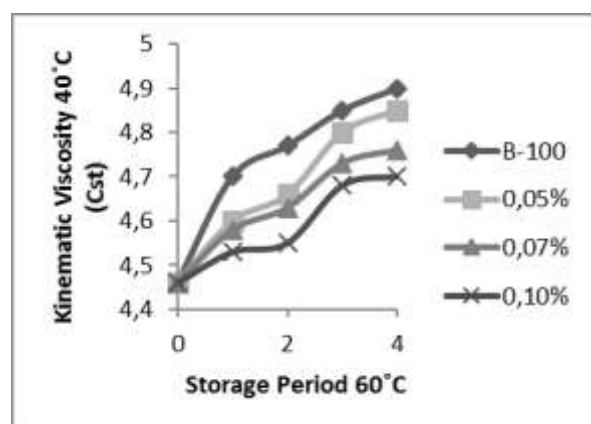


Figure 7. Kinematic viscosity 60°C.

From figures 6 and 7, it can be seen that the kinematic viscosity of all samples during the storage period tends to increase in viscosity. This happens because biodiesel underwent oxidation reactions that trigger the formation of new compounds or polymers with high molecular weight. Khothe [9]

stated that the increase in the viscosity of biodiesel during the storage occurs due to the process of oxidation of biodiesel which produces free fatty acid compounds, double bond isomerization, saturation and formation of higher molecular weight compounds.

Kinematic viscosity is a measurement of fluid flow influenced by gravity. The viscosity of oils is expressed by the number of seconds in which the price or number represents a certain volume of oil to flow through a hole of a certain small diameter. A smaller number of seconds means lower viscosity [10].

3.5. Effect of antioxidant addition to the density of biodiesel

The effect of pyrogallol antioxidant addition to the density of biodiesel from palm oil is shown in figure 8.

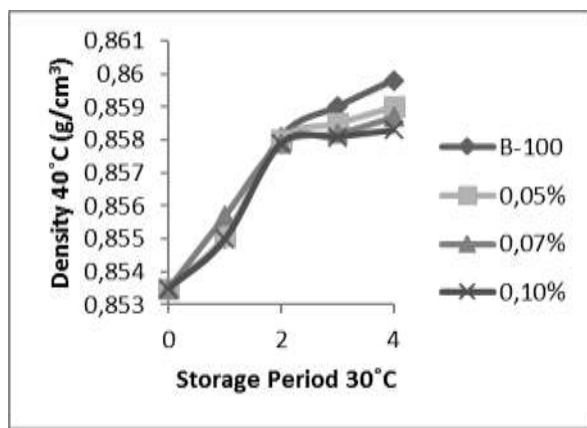


Figure 8. Density of biodiesel 30°C.

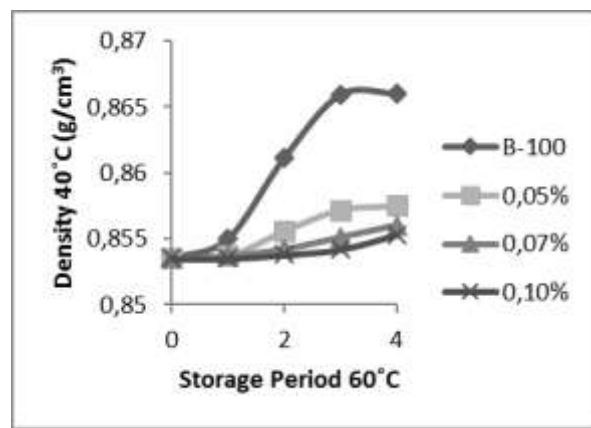


Figure 9. Density of biodiesel 60°C.

According to figure 8, the increase in the density value of each sample at a storage temperature of 30°C is not quite significant. This small change in density value is due to the fact that biodiesel is still relatively stable and there is no oxidation that results in the formation of short chain compounds, so the density values are still likely to remain the same.

On the other hand, in figure 9 with a storage temperature of 60°C primarily in the B-100 sample without the addition of antioxidant, it can be shown that there is an increase in the biodiesel density value. It happens due to the oxidation reactions has begun to occur in the sample during storage at high temperatures. Increased density values occur because of the degradation of the sample resulting in products such as gums and deposits which have high density values or the formation of high molecular weight compounds with a deposit nature [9]. It is also due to the oxidation reaction of biodiesel that produces short chain compounds and other compounds that potentially increase the density of biodiesel. Oxidation of biodiesel will yield short chain compounds that tend to crystallize so that it will decrease the volume and increase the density of biodiesel.

4. Conclusion

The addition of pyrogallol antioxidant in low concentration is able to maintain the quality of biodiesel from the damage of oxidation reaction. During 4 weeks of storage, all test samples underwent the change of several biodiesel quality test parameters. The acid value, kinematic viscosity and density increase while the iodine value decrease.

The quality of biodiesel which was made from palm oil could be maintained by the addition of pyrogallol antioxidant with concentration ranges from 0.05% to 0.1% during 4 weeks of storage. The best quality was achieved by the addition of 0.1% pyrogallol antioxidant.

5. References

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