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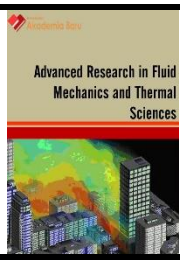

Influences of Marine Environment to the Characteristics of Palm Oil Biodiesel during Storage

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ABSTRACT

Biodiesel from palm oil is one of the alternative energies developed in Indonesia and has been implemented since 2018 for marine transportation, especially for ships. However, there are pertinent cases that experienced many obstacles related to the occurrence of gels, engine power reduction, blocking filters, and injection in the engine. The occurrence of those cases is due to the prolonged storage of biodiesel onboard of ships. During a significant storage process, periodic biodiesel monitoring is required which is difficult to do onboard. In this paper, a study on the physical/chemical characteristics of biodiesel and microbiological growth had been carried out in a controlled effect of the marine environment. Samples of biodiesel blends B20 were placed in locations near the sea and land base areas. It was found that there were significant changes in some chemical parameters of the biodiesel, such as flash point, viscosity, and acid number after 30 days. Microbiological growth, specifically bacteria, appeared on the 45th day of the outdoor-land sample. On the other hand, fungus growth on the out-door-sea was also detected on the same day. It suggested that the growth of microorganisms, growth of fungus and change in characteristics of the marine environment causes the degradation of biodiesel.

1. Introduction

Since 2016, the Indonesian government has been implemented biodiesel (B20) for automotive and land used transportation. The Biodiesel application for land use has been made successfully without any obstacles. In September 2018, the Indonesian government has announced for implementation of biodiesel into trains, ships, and power plants. Unfortunately, the use of biodiesel in ship was found to cause several problems such as the gelling at the bottom side of fuel tanks, blocking filters, some problems at fuel piping system and needed more fuel consumption for every

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trip while ship sailing [1]. These problems are caused by the degradation of biodiesel during storage. In addition to these problems, the maintenance period of biodiesel system equipment must be conducted in a shorter duration than the fossil-fuel system, so to eliminate this problem the ship crews were required to carry out regular monitoring.

The effect degradable of biodiesel storage can be divided into two factors. First are the physical/chemical factors related to fuel characteristics, and the second is the biological influence in the form of bacterial or fungus growth. Leung *et al.,* [2] have investigated the degradation of biodiesel under different storage conditions. Biodiesel showed degradable properties, absorbs water and solvents, and the presence of microbiology is known to have changed physical/chemical characteristics during the process of storing biodiesel for a long time. The air exposure and high temperature have increased in the biodiesel degradation rate. Besides the two factors as above, the water content in biodiesel also affects biodiesel degradation [2]. Gelling is the leading cause of problems in the fuel system such as blocking filters and injector nozzle on diesel engines on board.

In the Zhang *et al.,* [3] studied, that showed an increase in bacterial growth and microscopic activity compared to pure diesel. The research conducted by Gitte found that microorganisms are very diverse involved in fuel degradation [4]. Microorganism population consists of *Pseudomonas aeruginosa, Bacillus sp.,* and *Micrococcus* proved to be especially effective in degrading hydrocarbons. Some bacteria can also form capsules and mucus, as well as flagella and pili, which microbial activity in fuel systems on ship use is one of the leading causes of excessive formation of solids, which causes filter clogging [5].

Besides the gelling problem at the fuel system, the location of the fuel tanks at the bottom side of the ship also makes it very difficult for the crew to monitor fuel quality regularly. The purpose of this study was to determine the dominant factors on the characteristics of B20 biodiesel palm oil under different environmental influences

2. Material and Method

2.1 Crude Palm Oil

The primary source of raw material for biodiesel in Indonesia is from palm oil [5]. The biodiesel technical specifications are regulated in the Decree of the Director-General of EBTKE No. 100.K / 10 / DJE / 2016, which refers to SNI 7182: 2015 second revision. The biodiesel production process generally uses methanolysis (transesterification with methanol) reaction, which is a reaction between vegetable oil and methanol assisted by a base catalyst (NaOH, KOH, or sodium methylate) to produce a mixture of fatty acid methyl esters with follow-up products, glycerol [1]. The transesterification reaction with alcohol represented by the general equation as shown on Figure 1. Biodiesel samples are obtained from markets that are distributed locally in Indonesia. Each biodiesel mixture (B20) is mixed from 20% fatty acid methyl ester (FAME) and 80% diesel oil.

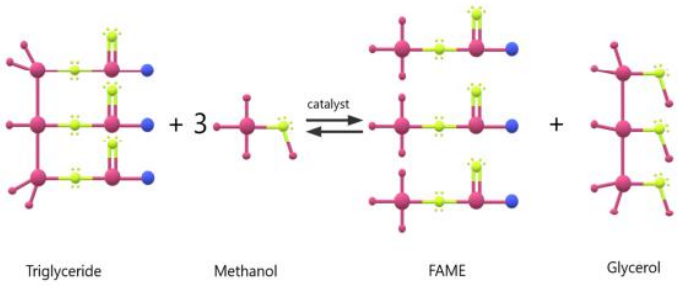

Fig. 1. Transesterification process [6]

2.2 Biodiesel Storage Condition

The samples of biodiesel B20 in this study were purchased commercially from the Surabaya-Indonesia market. A statement letter from the refinery factory claimed that the biodiesel B20 has been blended with 20% FAME and 80% fossil fuel using the inline blending method, and it was received after 14 days before the conditioning process. This experiment has been conducted in February – May 2019 near of Surabaya port, which located at 7°11'44.3" South 112°44'13.3" East coordinate. The B20 ware stored in 4 units of glass bottles of 1 liter for each sample to avoid the storage tank material influences and it was placed in four different locations; a. Outdoor sea, b. Outdoor Marine, c. Outdoor Land, d. Indoor Dark as shown in Table 1.

Table 1
Sample biodiesel under different condition

Sample	Condition
Outdoor Sea (OS)	The sample was placed on the edge of the sea, which may be exposed to the sun's heat and rain. Besides that, it will also be affected by the conditions of humidity on the shore as shown Figure 2(a)
Outdoor Marine (OM)	The sample was placed on a pipe that is allowed to float on the sea so that it is possible to move up and down as shown Figure 2(b)
Outdoor Land (OL)	The sample was placed in a field that is likely to be exposed to sunlight and rain as shown Figure 2(c)
Indoor – Dark Room (IDRM)	The sample was placed in a confined space free of sun exposure and from outside weather as shown Figure 2(d)

The biodiesel samples were conditioned for 90 days. Every 15 days intervals, a quantity of 70 ml has been taken to monitor chemical/physical characteristics and microbiological growth.

(a) Outdoor sea (b) Outdoor marine (c) Outdoor land (d) Outdoor–Dark Room

Fig. 2. Storage condition under various conditions

2.3 Properties Test

The properties test of biodiesel (B20) in this research has been done according to the ASTM standard. Several key properties should be measured to determine the quality of biodiesel: kinematic viscosity, density, flash point and pour point [7]. In order to know the stability oxidation, the other characters need to be monitored, such as total acid numbers and water content.

Humidity and temperature in each environmental condition are recorded every 15 days. Besides, several factors were kept constant during the experiment. For storage conditions, all samples must be placed in the same location before and after the test to reduce the side effects resulting from different environments.

2.4 Microbiological Test

This study focuses on observing bacteria and fungus growth that occurs in biodiesel samples. The small samples taken from different environmental conditions were homogenized using a magnetic stirrer at a constant speed of 800 rpm at tropical room temperature around 27℃ - 33℃ for an hour. The homogenization process is expected to ensure the bacterial and fungus population were thoroughly mixed in biodiesel for every layer in the bottle.

Prior to the microbiological test, the autoclave sterilization medium was treated with water vapor pressure with a temperature that can reach 121°C and a load of 1 atm for 15 minutes. Using the streak plate method, the sample spread on the surface of the media according to a pattern. The bacteria monitoring medium used was Natural Agar, while the fungus medium used was Sabouraud Dextrose Agar (SDA). Both two biodiesel samples above were planted with Duplo scratch method. After that, the samples were incubated for seven days and monitored every 24 hours.

3. Results and Discussion

3.1 Environment Condition

The biodiesel samples were stored in the four different environmental conditions in this research. Variability of air humidity and temperature have been measured for each environment every 15 days for 90 days. The maximum and minimum humidity each variable is averaged has been recorded the humidity and temperature characteristics in each of the different environments.

Figure 3 and 4 have shown data record temperature and humidity at maximum and minimum conditions from *timeanddate.com* in Surabaya and surrounding areas that were used to validate the temperature conditions that are around the sample. The temperature as shown Figure 5 has been monitored at the maximum and minimum temperature conditions in the biodiesel samples placed, including the Outdoor Sea (OS), Outdoor Marine (OM), Outdoor Land (OL) and Indoor Dark Room (IDRM), while for humidity shown in Figure 6. The data of temperature and humidity were taken every 15 days.

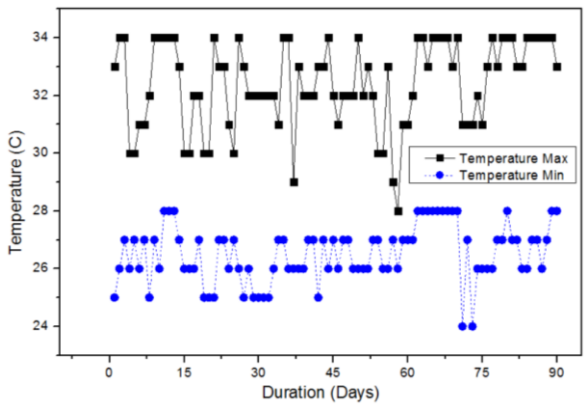

Fig. 3. Ambient temperature in Surabaya based on *timeanddate.com*

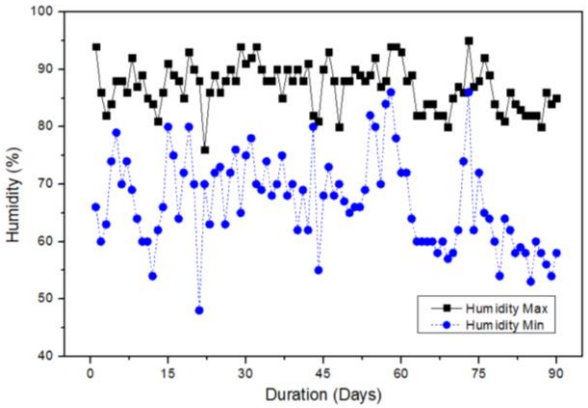

Fig. 4. Ambient humidity in Surabaya based on *timeanddate.com*

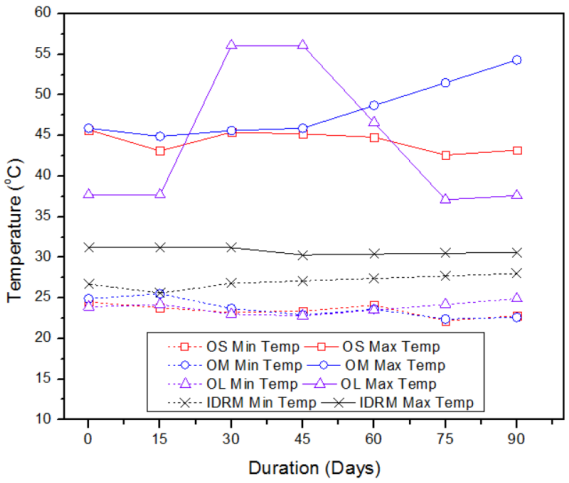

Fig. 5. Temperature in several environmental conditions

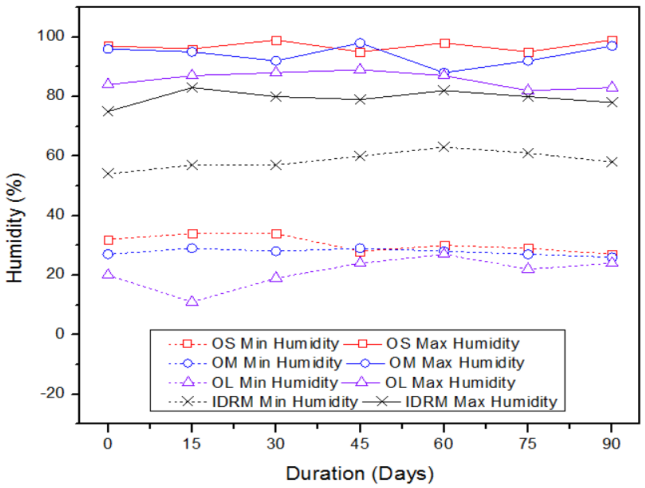

Fig. 6. Humidity in several environmental conditions

3.2 Palm Oil Biodiesel Characteristic

Physical and chemical characteristics such as flash point, density, pour point, the viscosity, and the water content of the palm oil biodiesel fuel (B20) were tested out according to specific ASTM standards.

3.2.1 Flashpoint

Flashpoint is the temperature at which the fraction will evaporate and cause a fire when exposed to sparks or high temperatures and pressures. This characteristic was determined using the ASTM D92 method with a minimum value of 52℃ [9]. Flashpoint number for minimum marine use according to IMO regulation is 60℃.

As shown Figure 7, The results of the flashpoint test have found that the four biodiesel samples have a significant decrease in flashpoint to day 45, but after that, the flashpoint number of points tends to be stable at 60℃, where this value is slightly above the standard used but right at the marine minimum value.

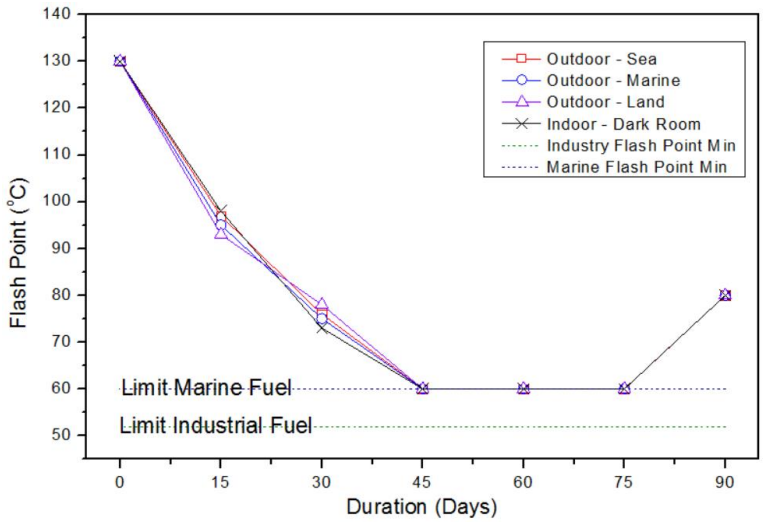

Fig. 7. Flash point of biodiesel based on days

3.2.2 Pourpoint

Pourpoint is the lowest temperature at which some fractions can flow. This pouring point was influenced by the degree of unsaturation; the higher the unsaturation will have lower the pouring point. This characteristic also influenced by the length of the carbon chain. The longer the carbon chain will have higher the pourpoint. The pour point characteristic has been determined using the ASTM D97 method, with a maximum limit of diesel fuel pourpoint is 18℃ [10].

As shown Figure 8, two pourpoint tests were carried out and found that each sample experienced a fraction of each day, but overall, the pourpoint is decreased slightly, but it was still within the standard value.

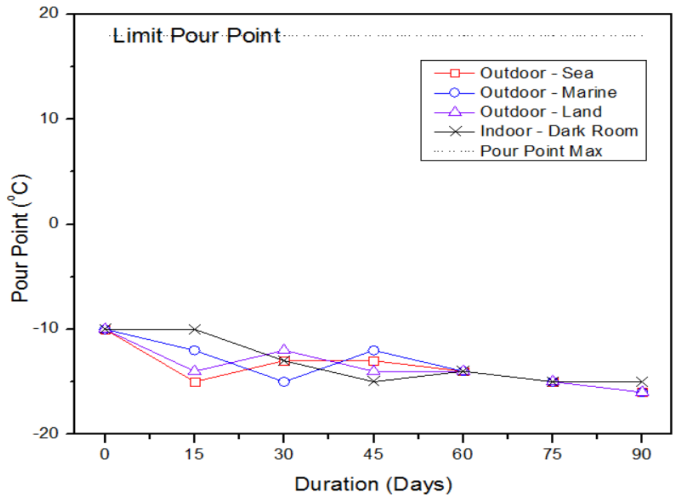

Fig. 8. Pour point of biodiesel based on days

3.2.3 Density

Density is a comparison between two principal quantities, namely mass and volume. Its density depends on the amount of material. Because the volume changes according to temperature, the density of a substance with a fixed mass will depend on the temperature (see Figure 9). The higher the temperature, the lower the density of the liquid, and vice versa. The specific gravity of diesel fuel was measured using the ASTM D4052 or ASTM D1298 method at a temperature of 15℃ with a limit of 815 - 860 (kg/m^3) [11].

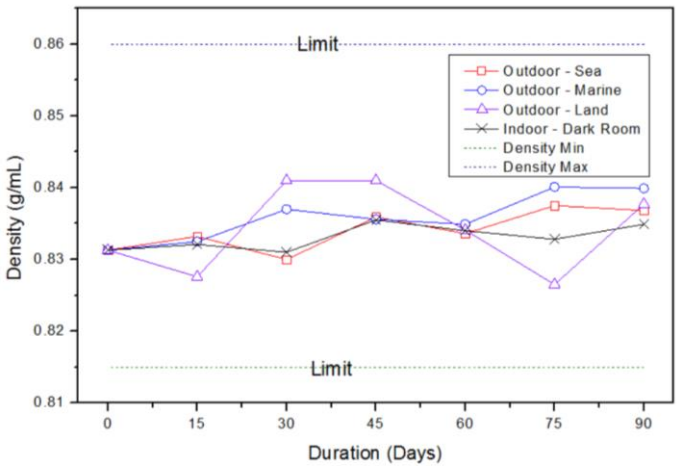

Fig. 9. Density of biodiesel based on days

3.2.4 Acid number

The acid number is the mass of *potassium hydroxide* (KOH) in milligrams, needed to neutralize one gram of a chemical. Acid numbers are a measure of the number of *carboxylic acid* groups in a chemical compound. Acid numbers are used to determine the amount of acid present, for example, in a biodiesel sample. Acid numbers are alkaline levels, expressed in milligrams of *potassium hydroxide* (KOH), which are needed to neutralize acidic constituents in 1 gram of the test sample. Standard methods for the determination of acid numbers have been conducted according to ASTM D974 [12].

As shown in Figure 10, the total acid number of biodiesels placed in the room initially increased on the 15th day. Furthermore, there was a decline and tended to be stable below the 0.6 limits of the ASTM standard, while the outdoor increases with times.

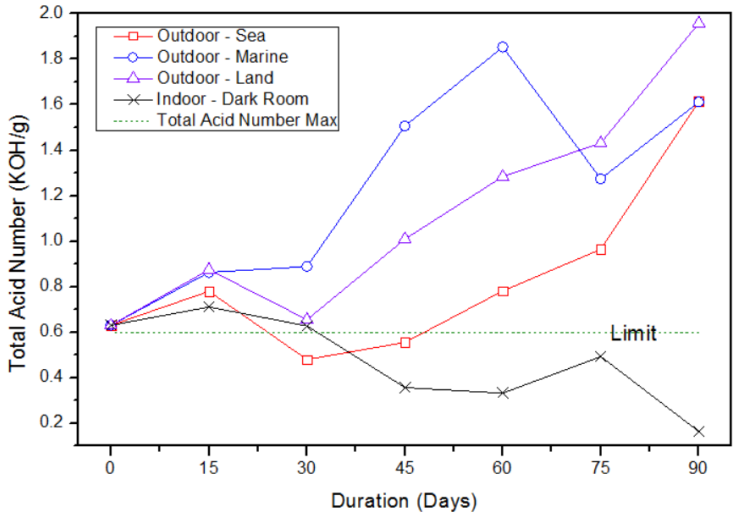

Fig. 10. Acid number of biodiesels based on days

3.2.5 Kinematic viscosity

Fluid viscosity is a unit that states the measure of friction in a fluid. In fuel properties, viscosity affects fuel injection capabilities. The higher the kinematic viscosity of fuel, the lower the atomization occurs, so the engine is difficult to start. If the viscosity is higher, the resistance to flow will be higher. It has affected the performance of the injector on the diesel engine. The higher temperature has a lower viscosity, which means it is easier to flow and experience atomization. The viscosity of diesel fuel was measured using the ASTM D445 or D1298 method with a limit of viscosity values on diesel fuel is 2.0 - 4.0 cST [13].

The viscosity of biodiesel has decreased past the lower limit of existing standards. It has been seen at the time of storage on the 45th day until the 60th day. Furthermore, it began to increase on the 90th day, as shown in Figure 11.

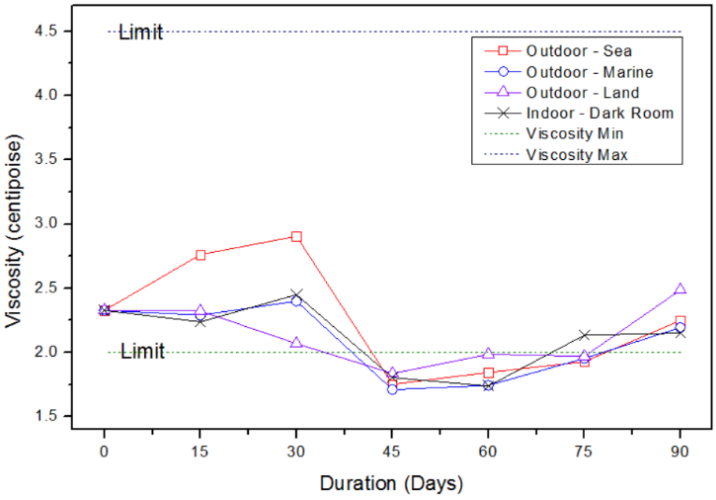

Fig. 11. Kinematic viscosity of biodiesel based on days

3.2.6 Water content

The water content in diesel fuel will influence the burning properties. The presence of water can cause corrosion and the growth of micro-organisms that can impede the flow of fuel. The nature of the diesel fuel itself is a problem of moisture, which significantly affects the diesel equipment. Water condensation in storage tanks of diesel fuel is a routine problem that must be solved by all users of diesel fuel. The longer the stored fuel is increasingly becoming a significant problem. The test of water content using ASTM method D1796 or D95 with a maximum limit on the diesel oil water content is 0.05% by volume.

The water-content of the biodiesel for outdoor marine, outdoor sea, also outdoor land has increased during the storage process. As shown in Figure 12, the value of the water content in the indoor-darkroom sample decreased based on time.

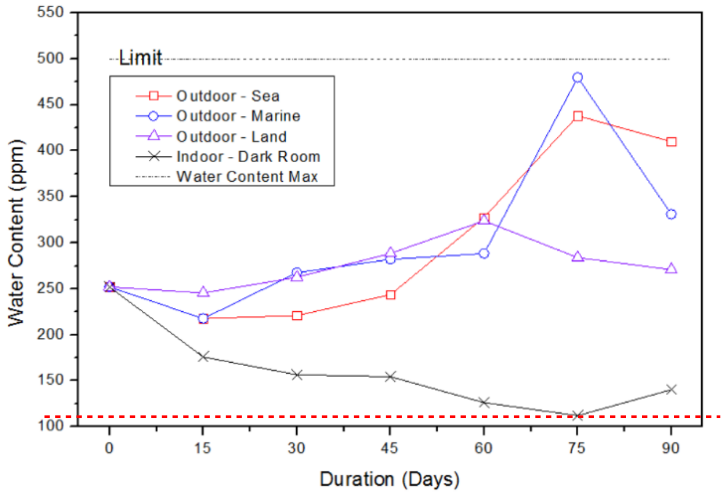

Fig. 12. Water content of biodiesel based on days

3.2.7 Microbiological growth

3.2.7.1 Bacteria growth

Standard limits on the number of bacteria and fungi that are permitted contained in biodiesel still do not exist. From observations, as shown in Figure 13 that on the 15th and 30th day, there was no bacterial growth. However, on 45th days, there found bacterial growth around 49 cfu/ml in outdoor land. Whereas in outdoor-marine and indoor-dark, there is a bacterial growth of about 19 cfu/ ml. while for outdoor sea found two cfu/ml during the 60th day incubation period. From the figure, the growth of biodiesel bacteria will be dominant in outdoor land, while in the outdoor sea and outdoor marine bacteria has no growth significantly.

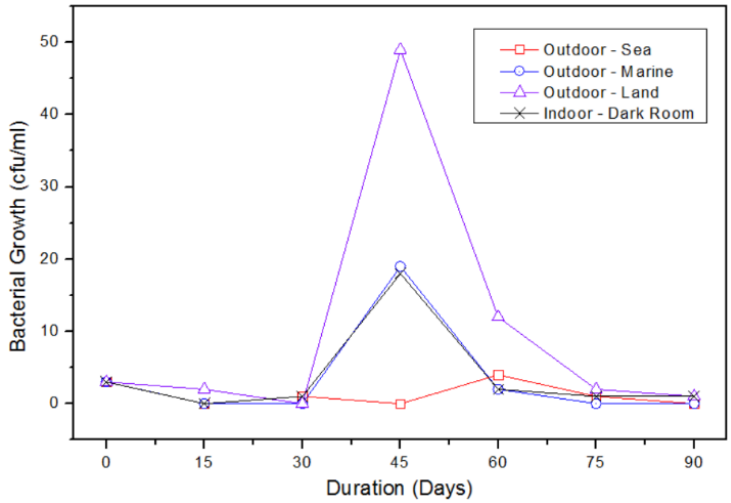

Fig. 13. Kinematic viscosity of biodiesel based on days

3.2.7.2 Fungus growth

As shown Figure 14, The biodiesel in the outdoor sea has found fungi growth about 17 cfu/ml on the 45th days of biodiesel storage. In the outdoor marine, two cfu/ml fungi had grown on the 60th day. While on the incubation period for indoor-dark and outdoor-land samples growth of only one cfu/ml.

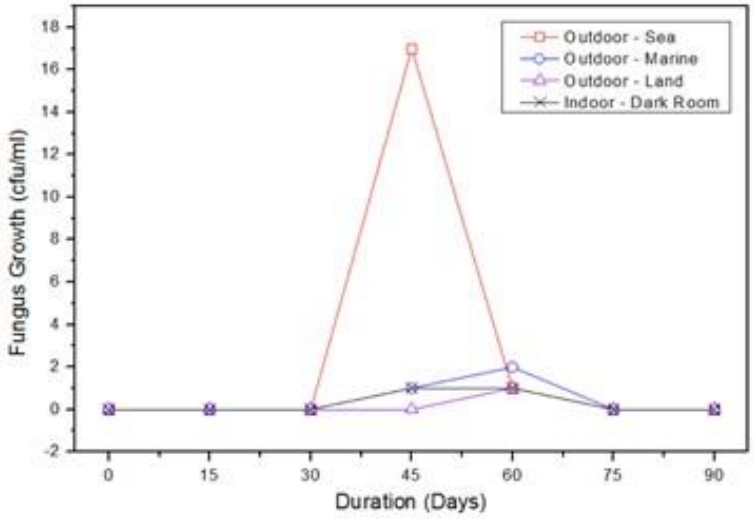

Fig. 14. Fungus growth of biodiesel based on days

4. Conclusions

Based on the data described in the previous section, the marine environment has a significant influence on the characteristics of biodiesel, such as the change in acid number and viscosity that exceeds the existing standards. As for the water content, there was an increase in outdoor, but in the indoor area, there was a reduction although it was still within the existing standard limits. It was found that there were significant changes in some chemical parameters, such as flash point, viscosity, and acid number after 30 days. For microbiological growth, it was found that there were bacteria that appeared on the 45th day of the outdoor-land sample while and fungus growth on the outdoor-sea was detected on the same day.

References

[1] R. Mulyana. *Pedoman Umum Penanganan dan Penyimpanan Bahan Bakar Biodiesel (B100) dan Campuran Biodiesel (BXX)*. Jakarta: Direktorat Bioenergi Direktorat Jenderal Energi Baru, Terbarukan Dan Konversi Energi Kementerian Energi Dan Sumber Daya Mineral, 2018.

[2] Leung, D. Y. C., B. C. P. Koo, and Y. Guo. "Degradation of biodiesel under different storage conditions." *Bioresource technology* 97, no. 2 (2006): 250-256. https://doi.org/10.1016/j.biortech.2005.02.006

[3] Zhang, Tianxi, Yapeng Chao, Nan Liu, Joe Thompson, Manuel Garcia, Brian B. He, Jon Van Gerpen, and Shulin Chen. "Case Study of Biodiesel-Diesel Blends as a Fuel in Marine Environment." *Advances in Chemical Engineering and Science* 1, no. 02 (2011): 65. https://doi.org/10.4236/aces.2011.12011

[4] Sørensen, Gitte, Dennis V. Pedersen, Anna K. Nørgaard, Ketil B. Sørensen, and Sune D. Nygaard. "Microbial growth studies in biodiesel blends." *Bioresource technology* 102, no. 8 (2011): 5259-5264. https://doi.org/10.1016/j.biortech.2011.02.017

[5] Chao, Yapeng, Nan Liu, Tianxi Zhang, and Shulin Chen. "Isolation and characterization of bacteria from engine sludge generated from biodiesel-diesel blends." *Fuel* 89, no. 11 (2010): 3358-3364. https://doi.org/10.1016/j.fuel.2010.05.041

[6] Zik, Nor Azyan Farrah Adila, Sarina Sulaiman, and Parveen Jamal. "Thermally Produced Nano Catalyst for Biodiesel Production: A Review." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 52, no.2 (2018): 139-147.

[7] Alptekin, Ertan, and Mustafa Canakci. "Characterization of the key fuel properties of methyl ester–diesel fuel blends." *Fuel* 88, no. 1 (2009): 75-80. https://doi.org/10.1016/j.fuel.2008.05.023

[8] Wu, Yo-Ping, Ya-Fen Lin, and Jhen-Yu Ye. "The Effect of Storage Condition on Biodiesel." *BIODIESEL–QUALITY, EMISSIONS AND BY-PRODUCTS* (2011): 71. https://doi.org/10.5772/27025

[9] P. Products. "Astm D93 Flash Point." 05, no. (November) (2004): 80112.

[10] ASTM. "ASTM D97: Pour Point." 2 (2016): 1–9.

[11] ASTM. "ASTM D 1298-12b Standard test method for density, relative density, or API gravity of crude petroleum and liquid petroleum products by Hydrometer method." Pennsylvania: American Society for Testing Materials, 2012.

[12] ASTM. "Standard Test Method for Acid Number of Petroleum Products by Potentiometric." *Current*. 2004.

[13] ASTM. "D445-18 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)." *Annu. B. ASTM Stand.*, 2010.