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Effect of Additional CO_2 and N_2 Gas Blanket On Biodiesel Psychochemical Properties in Storage Tank

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Abstract: Ship movement and contaminants may be the main causes of accelerated biodiesel degradation during the ship storage process. One of the techniques to protect biodiesel storage on the ship is by applying a blanketing system. In this study, CO_2, N_2, and natural air blankets were added to the biodiesel stainless steel tanks (B100 and B50) that swing in the sinusoidal to simulate ship movement at sea and It was stored for six months. The Physicochemical properties of biodiesel gas blanket were tested according to ASTM and EN standards. The result in this study was found that storing biodiesel in a blanket with natural air, CO_2, and N_2 gases for 210 days has changed the biodiesel properties in proportional to the storage duration. The addition of CO2 gas blanket was influenced to reduce the oxidation times, and water content. On another side, it has increased the value of particle count, TAN, flash point, Kinematic Viscosity, and density. While additional N2 gas blanket does not have an extreme effect on the biodiesel properties.

Keywords: Biodiesel, storage, degradation, psychochemical, gas blanket, properties

1. Introduction

The Indonesian government has obliged that all industries, automobiles and the marine sector has been implemented palm oil biodiesel blend (B30) since 2019. Biodiesel or FAME (Fatty Acid Methyl Ester) is obtained from the esterification and transesterification process. It is an alternative fuel without aromatic, sulfur content, easy to degrade, and does not cause significant air pollution [1]. Generally, during the bunkering process, biodiesel must be stable for at least 3 months. Some research has found that biofuel degradation can be extended up to 6 months with the addition of antioxidants depending on biofuel quality and characteristics [2]. The biodiesel implementation on the shipping was experiencing several obstacles, especially the decrease in power, blocking filters, and damage to spare parts, especially in the fuel system which is faster caused by biodiesel degradation. Some of the causes of degradation in biodiesel are due to the Solvency Effect where ester compounds.

Accumulation of water at the bottom of the tank will encourage the growth of many microbes. The difference in affinity levels of biodiesel and diesel oil causes the formation of an emulsion which is characterized by the cloudiness of the fuel. Water content in the biodiesel is also caused by the growth of fungi and bacteria. Microbiology that grows in biodiesel causes blocking conditions on pipes and filters of the engine. The hydrolytic reaction begins with a high

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content of free fatty acids and water, as well as other hygroscopic impurities [3]. Biodiesel degradation during storage also can be caused by hydrolytic and oxidative reactions. In the early stages, the formation of free carboxylic acids is characterized by an increase in the acid number, then hydro-peroxides are formed, followed by the formation of polymer products and an increase in the viscosity of the fuel. The hydrolytic reaction begins with a high content of free fatty acids and water, as well as other hygroscopic impurities. The rate of oxidative degradation depends on the composition of free fatty acids, exposure to air, light/sun heat, and antioxidants [4].

The main cause of biodiesel degradation is due to the air contamination and condensation of water that enters the storage tank, Air contains several particles including 78.1% Nitrogen (N_2), 21% Oxygen (O_2), 0.9% containing Ar, Ne, He, H_2O, CO_2, and other gasses. Several articles mentioned that biodiesel degradation can be reduced with a nitrogen blanket in the storage tank, but it is still unknown with certainty the efficiency of nitrogen administration on the quality of biodiesel. Storage of the fuel system on ships still used natural air vents, where air can enter and leave freely [5]. The gas blanket process generally was carried out for fire protection, especially for tanker ships. Gases are used CO_2 for oil tankers and N_2 for chemical tankers. Most oil tankers use CO_2 because the process is more economical. It can be produced from the combustion system obtained by the generator and main engine.

The basic method of slowing down the oxidation changes of fats is to eliminate biodiesel contact with oxygen. This can be done by replacing oxygen with an inert gas blanket. Nitrogen and carbon dioxide are commonly used in the food industry to reduce the autoxidation process. Nitrogen is poorly soluble in both water and fat. For this reason, it is used as a fill gas, which reduces the concentration of other gases in the package and prevents it from collapsing. Carbon dioxide is highly soluble in both water and fat, and its solubility increases with decreasing temperature. Carbon dioxide is more permeable through the package than nitrogen [6]. The density of gas blanket that is generally used, CO_2 gas (44 g/mol) is heavier than Nitrogen (N_2) (28 g/mol) and O2 (32 g/mol). The objective of this study is to investigate the effect of additional CO_2 as gas blankets in the storage tank on the physicochemical properties of biodiesel.

2. Material and Method

2.1 Biodiesel Palm Oil

The main source of raw material for biodiesel in Indonesia is using palm oil. The biodiesel production process generally used a 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 glycerol as follow-up products [7]. In this study, Biodiesel (B100) samples were produced from palm oil Fatty Acid Methyl Ester (FAME) by PT. Wilmar. Furthermore, the biodiesel B50 was made with 50% FAME and 50% Pertamina DEX as fossil oil.

2.2 Gases

The Nitrogen (N_2) and Carbon dioxide (CO_2) gases were delivered by PT. Wonokoyo, where the purity of gasses is around 99.9% food-grade standard in the high-pressure tank. The gases were distributed to the stainless steel storage tank via a regulator valve to reduce the pressure from 200 bar gas to around 0.2 bar gas. The regulator valve to be used keeps gas pressure in the storage tank if any leakage in the system. The pressure of gas in the storage tank can be monitored by a pressure gauge.

2.3 Biodiesel Storage Condition

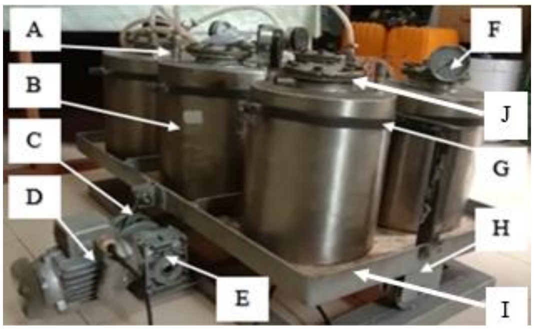
The sample of biodiesel B100 in this research has been used PT. Wilmar Biodiesel product. One of the biggest biodiesel refineries is located in Gresik City, East Java, Indonesia. The Biodiesel was stored in two types B100 and B50. Biodiesel B100 means 100% Fatty Acid Methyl Ester (FAME), and Biodiesel B50 means 50% FAME was blended with 50% fossil oil. It was stored in 6 units of stainless steel cylinder tank filled with eight liters for each sample of biodiesel, Furthermore, all the tanks were placed on the cradle. An electric motor with 500 rpm was installed to swing the cradle in sinusoidal movement at approximately 7.6 degrees as shown in figure 1. Biodiesel samples were placed in a dark room. The room temperature was maintained at approximately 28oC with an air conditioning system, the air humidity has been maintained not less than 70% with a humidity sensor, water spray nozzles, an electric pump, and two electric fans in the room that works automatically.

2.4 Biodiesel Sampling

The samples of biodiesel were stored for 210 days. At every 45-day interval, the samples were taken at about 400 ml. The preparation of sampling from the storage tank has been stirred using a magnetic bar with a length of 5 cm into the storage tank at the beginning of the biodiesel filling. It was done for 60 minutes to make sure the biodiesel was completely mixed. The samples were drained through a drain valve located at the bottom side of the tank. Then a total of 350 ml was filled into a bottle which has a capacity of 1 liter made of HDPE material. Furthermore, biodiesel samples in the bottles were filled with gases blanket and sent to Laboratory.

2.5 Biodiesel Properties Test

The Physicochemical properties of biodiesel in this study were tested according to ASTM and EN standards [2]. Several key properties were measured to determine the quality of biodiesel, Physical characteristics were the flash point, kinematic viscosity, density, and particle count 4, 6, and 16 microns [6] where The chemical characteristics were monitored Oxidation stability, Total Acid Numbers (TAN), and FAME content, water content.



Description:
- A- Pipe & valve connection for gas blanket
- B- Stainless Steel Biodiesel Storage Tank
- C- Connecting rod
- D- Electric Motor
- E- Gearbox
- F- Pressure gauge
- G- Holder
- H- Steel Cradle
- I – Drain valve
- J – Filling Cap

Fig. 1 - Biodiesel gas blanket storage condition

3. Result and Discussion

3.1 Physical Characteristic

Flashpoint is the temperature at which the fraction will evaporate and cause fire when exposed to sparks or high temperatures and pressures. This characteristic was determined by ASTM D93 method. The flash point number for minimum marine fuel according to IMO regulation was mentioned as not less than 60℃ [8]. The result of measuring the flash point value of the B100 blanket overall is above the ASTM standard also Marine fuel standard as shown in fig.2. The results of testing the flash point value of the overall B50 gas blanket are above ASTM D93 standard also marine fuel standard. The flash point value has increased with the duration of biodiesel storage. The effect of the blanketing system shows that the biodiesel CO_2 Blanket was found to have a higher value than the others. The biodiesel with natural air blanket sample has a lower value than the N_2 blanket.

Fluid viscosity is a unit that states the measure of friction in a fluid. In fuel properties, viscosity affects fuel injection capabilities. The viscosity of samples was measured according to ASTM D445 method with a limit of viscosity values on diesel fuel 2.0 - 4.0 cSt. Biodiesel B100 gasses blanket kinematic viscosity as shown in figure 3, It has still in the standard values. It has slightly increased along with biodiesel storage duration. The kinematic viscosity of biodiesel B50 was found still inside the standard values. It was shown to increase along with the biodiesel storage duration. The effect of the Blanketing system shows that the Biodiesel B100 and B50 CO_2 Blanket was found to have a lower value than the others, while the Natural Air (NA) blanket sample has a higher value than the N_2 Blanket.

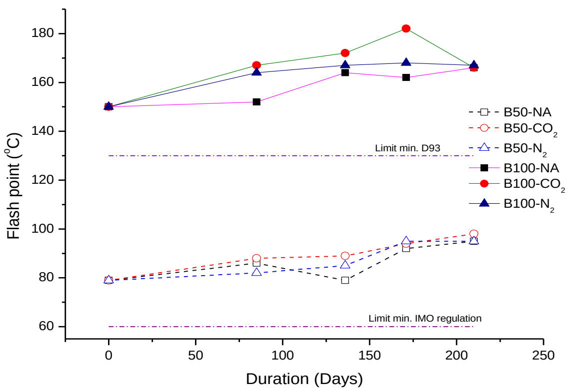


Fig. 2 - Flash point biodiesel gas blanket

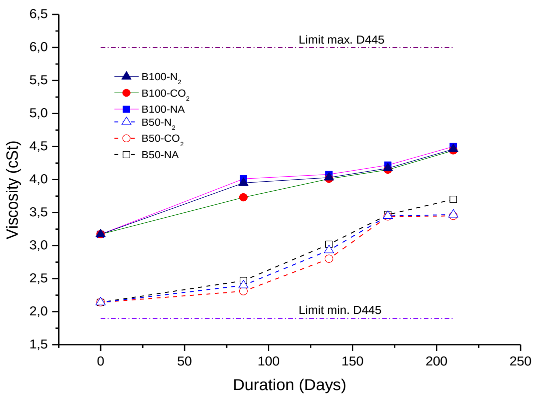


Fig. 3 - Kinematic viscosity of biodiesel gas blanket

The density of biodiesel diesel was measured using the ASTM D1480 method at a temperature of 15℃. Biodiesel density from day to day obtained a fluctuating value as shown in figure 4. The whole sample has increased but it was still in the standard values. The density value of the B100 blanket has slightly increased along with the storage time of biodiesel. The effect of the Blanketing system shows that the Biodiesel B100 CO_2 Blanket was found to have a higher value than the others. The biodiesel with natural air (NA) blanket sample has a lower value than the N_2 Blanket, but after 135 days the N_2 Blanket has a lower density value than the NA blanket. The density value of the B50 blanket has increased along with the storage time of biodiesel. The effect of the blanketing system shows that the Biodiesel B50 with CO_2 gas blanket was found to have a higher value than the others, while the N_2 blanket has a lower density value than the NA blanket. Particle count is a comparison between two principal quantities, namely mass, and volume. Due to the variety of shapes and sizes of contaminants, In this study was conducted the fuel cleanliness measurement by Laser Net Fines Q200 according to ASTM D7596 [9], It has been measured the number of particles larger than 4 µm, 6 µm, and 14 µm in a 100 ml of liquid sample. Based on the test results in Figures 5 to 7, it was found that most of the particles in the biodiesel blanket value exceed the standard. In biodiesel B100 CO_2 Blanket has a value greater than N_2 and NA, while in Biodiesel B50 N_2 blanket has a higher particle number than the others. In general, both biodiesel B100 and B50 values of particle content have increased along with the storage duration.

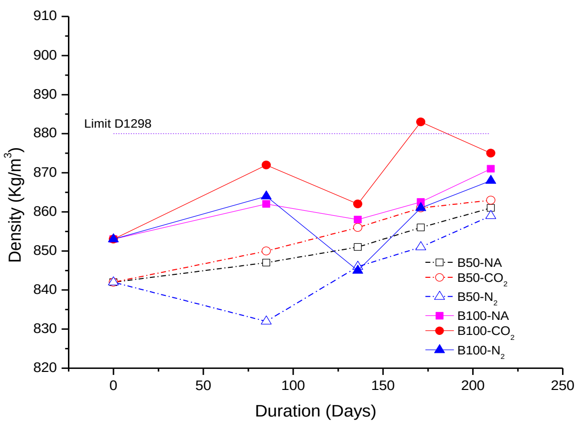


Fig. 4 - Density of biodiesel gas blanket

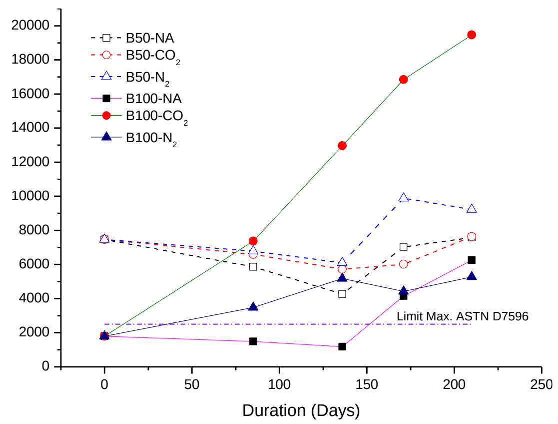


Fig. 5 - Particle count 4 µm of biodiesel gas blanket

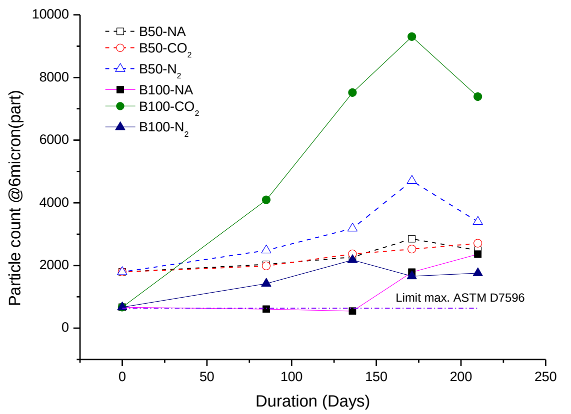


Fig. 6 - Particle count 6 µm of biodiesel gas blanket

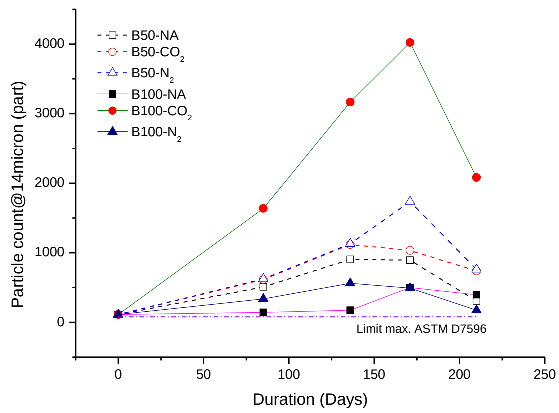


Fig. 7 - Particle count 14 µm of biodiesel gas blanket

3.2 Chemical Characteristic

FAME content testing in this study is expected to determine the effect of blanket gas on biodiesel quality by measuring the percentage of FAME in biodiesel. Testing was carried out with Eralytic FTIR. The results of the FAME content test on biodiesel B100 during storage there found a decrease of about 3% in a few days of sampling. As shown in fig. 9. The average value of FAME content of biodiesel B100 CO_2, N_2, and NA blanket was not a significant decrease. FAME content in biodiesel blending B50 was known to increase along with the duration stored. Biodiesel bland B50 samples with CO_2 blanket had a lower value, while the Biodiesel N_2 blankets had a higher value than NA blankets.

The water content in biodiesel can be classified as free, emulsion, and soluble water. It has been tested by Karl Fischer ASTM D1744 with a maximum limit on the diesel oil water content is 500 ppm or 0.05% by volume. The results of measurements of water content in biodiesel B100 since the beginning of sample storage have exceeded the maximum value limit standard. As shown in figure 10. The water content in the biodiesel B100 has increased with a longer storage duration. The effect of the Blanketing system shows that the Biodiesel B100 NA blanket was known to have a higher value than the others, while the N_2 blanket sample has a lower value than the CO_2 blanket. Water content in biodiesel B50 since the beginning of sample storage was below the maximum limit value of the standard. This overall value of the water content in biodiesel B50 was increased along with the duration stored. On days 125 to 175 the water content value had passed the standard. The effect of the blanketing system has been found that the Biodiesel B50 with N_2 blanket is known to have a higher value than the others, while the water content of biodiesel with CO_2 blanket has a lower value than the NA blanket but on days 171 and 210 the water content value of the B50-CO_2 blanket was above the B50-NA blanket.

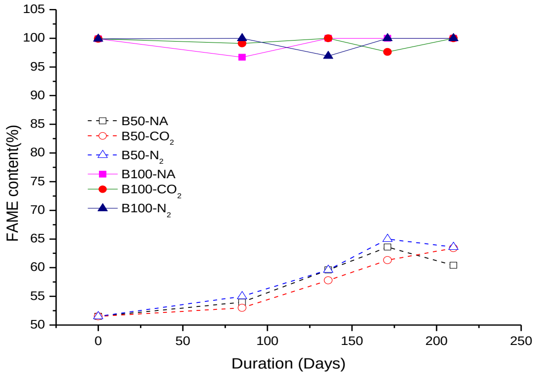


Fig. 8 - Fame content of biodiesel gas blanket

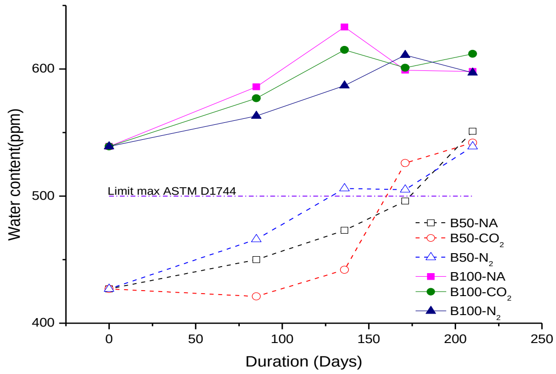


Fig. 9 - Water content of biodiesel gas blanket

Total acid number (TAN) is the mass of potassium hydroxide (KOH) in milligrams, needed to neutralize one gram of a chemical. Standard methods for the determination of acid numbers were conducted according to ASTM D664 by Titrator 848 Titrino Plus. Total acid numbers were measured by the Titration Method. The test results of the TAN value of biodiesel B100 gasses blanket are all still below the ASTM D664 standard. From figure 11. The TAN B100 blanket has an increasing trend with the length of storage time. The effect of the blanketing system shows that Biodiesel B100 Natural Air Blanket has a higher value than the others, while the N_2 blanket sample has a lower value than the CO_2 blanket. The measurement results of the TAN value of biodiesel B50 gas blanket were all still below the standard except for CO_2 blanket on day 171 which was higher. The TAN values of B50 gas blanket have increased along with the storage time. The effect of the blanketing system was found biodiesel B50 with CO_2 blanket has a higher value than the others, while the N_2 blanket sample has a lower value than the NA blanket.

Oxidation Stability is the tendency of fuels to react with oxygen at ambient temperatures and describes the relative susceptibility of the fuel to degradation by oxidation. In this study, the measurement of oxidation stability was carried out by a rancimat EN15751 standard. The results of the oxidation value of the biodiesel B100 gas blanket were initially above EN15751 standard 3 hours. As Figure 12 shows that the oxidation stability value decreased along with the longer storage time. The effect of the blanketing system shows that the Biodiesel B100 CO_2 blanket was found to have a higher oxidation times value compared with the other gasses blanket, while the NA blanket sample has a lower value than the N_2 blanket. The biodiesel B50 gasses blanket were shown in figure 12. Starting of the storage process until day 85 there was a significant decrease, but after that, the oxidation stability values doesn't seem to decrease significantly. The biodiesel, B50 with CO_2 blanket was known to have a higher value than the others, while the biodiesel with NA Blanket has a lower value than the N_2 Blanket. Based on the properties of biodiesel B100 and B50 with gas blanket, it can be summaries in three grades high, medium, and low as shown in Table 1. Furthermore, the effect of gas blanket on biodiesel degradation can be categorized into good, moderate, and poor as shown in Table 2.

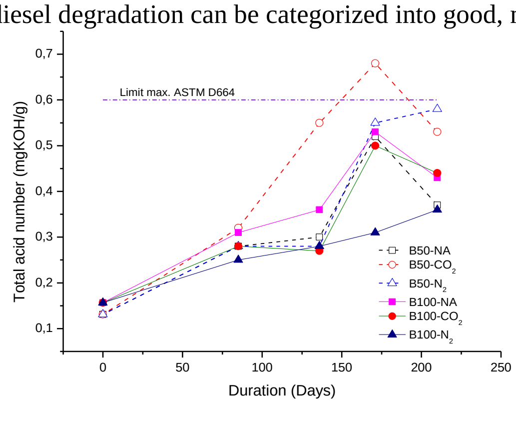


Fig. 10 - Total acid number of biodiesel blanket

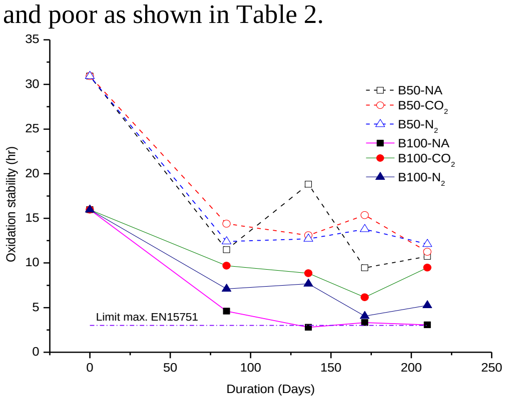


Fig. 11 - Oxidation stability of biodiesel blanket

Table 1 - Biodiesel gas blanket summaries

Physicochemical properties	B100 gas blankets			B50 gas blankets		
	High	Med	Low	High	Med	Low
Flash point	CO_2	N_2	NA	CO_2	N_2	NA
Viscosity	NA	N_2	CO_2	NA	N_2	CO_2
Density	CO_2	NA	N_2	CO_2	NA	N_2
Particle count 4,6 and 16 µ	CO_2	N_2	NA	N_2	CO_2	NA
Oxidation stability	CO_2	N_2	NA	CO_2	N_2	NA
Total acid number	NA	CO_2	N_2	CO_2	N_2	NA
Fame content	CO_2	N_2	NA	N_2	NA	CO_2
Water content	NA	CO_2	N_2	N_2	NA	CO_2

4. Conclusion

The results of storing biodiesel B100 and B50 in a blanket with Natural Air, CO_2, and N_2 gas for 210 days were found to change the properties of biodiesel along with the length of storage duration. The addition of CO_2 gas blanket was influenced to reduce the oxidation times, and water content. On another side, it has increased the value of particle count, TAN, flash point, Kinematic Viscosity, and density. While additional N_2 gas blanket does not have an extreme effect on the biodiesel properties.

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