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Study on corrosion behavior of storage tanks filled with biodiesel and the blends

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Abstract. Corrosion is one of rising problem in the use of biodiesel. Improper storage of biodiesel may cause corrosion to occur faster and give a worse damage effect. Biodiesel is commonly stored longer in B100 (neat biodiesel). In this work, the corrosion characteristics of three different material of tanks for B100 and the blends (B20) are examined. Those metallic materials used are Stainless Steel 304 (SS), Carbon Steel (CS), and Galvanic Steel (GS). The fuel has been monitored every 45 days in 135 days. The corrosion occurrence related to some changes in the physical properties of the fuel stored. It is also identified through the change in tanks' thickness, weight, and the morphology of metal tank surfaces. The result shows a great change in biodiesel physical properties occurred in GS tank, where the BXX acid value increased by 25.39% and the water content changed to 43.18%. While, biodiesel which stored in SS tank performed best with minor change in base and wall thickness with the change of under 1% and the weight change was only 0.02%. In a certain of time, the morphological examination shows CS as the recommended material for biodiesel storage due to uniform corrosion performance.

1. Introduction

1.1. Corrosion in Fuel Tank

Corrosion is a process of the degradation of construction material due to electrochemical reaction with its environment. It is considered a very serious problem as it causes damages to properties and environment, in addition to high costs of mitigation of engine failure. Corrosion could also be problem in the fuel oil storage. Corrosion in fuel oil storage tanks occurs due to the contact of stored oil with the tank during its use. Even if non-polar hydrocarbon in fuel oil has been known will not cause corrosion, yet corrosion may occur due to a number of initiators. Contributors for corrosion to occur may come from specific constituents in the fuel oil, e.g. sulfur compound, organic acid and in-organic acid soluble in water or oil. Among any others, are active sulfur (sulfur element, hydrogen sulfide) and water. Previous studies have observed the corrosion of biodiesel in in specified material of tanks, but it was not thoroughly studied the characteristics of corrosion and its relation to changes in physical properties of the fuel stored that may occurred.

Fuel oil for industrial use is generally stored in tanks made from metal. It had been convinced that the only metallic materials compatible and recommended being used with biodiesel. On the other hand, metals are thermodynamically unstable under normal conditions and it is natural for the system (comprising metals and their alloys) to achieve a form with a better thermodynamic stability [1]. The stainless steel and aluminum were strong recommended materials [2]. Storage tank made from metal intended to store fuel oil for long period (more than 10 years) should consider the chemical stability of the stored fuel. There are different corrosion zones in the storage tank depends on position and the adjacent area [1]. Almost all part of this zone is in contact with water, soluble salt, organic and/or inorganic precipitate. The organic precipitate consists of hydrocarbon and biofilm, and the inorganic deposit may consist of corrosion products, salt and sand [3]. The behaviour of potential corrosion occurred in each tank of biodiesel is important to be studied in order to find the best metals materials for storing the fuel and its blends.

1.2. Biodiesel and its stability during storage

Biodiesel can be used as fuel in mixture with petro-diesel. It may directly use in engine without modification, particularly in low blends (<20%). Due to the force for using biodiesel in mixture with petro-diesel as fuel oil, equipment related with this fuel oil should be prepared as to prevent failure or equipment components' damage whilst they are in operation, including potential corrosion in storage tanks. The change of biodiesel characteristics will give significant effect to the performance and lifetime of storage tanks. Air and atmospheric oxygen may dissolve in fuel during its storage. These substances may diffuse to storage tank during distribution. With the change of temperature which is fluctuate between day and night, water and its contaminants may be separated from fuel stored in the tank, forming thin film of electrolyte. Normally, this film is formed in tank wall and moving downward. This causes electrochemical reaction to occur.

Biodiesel is composed from molecules with double bond, causing it to have high reactivity against oxygen, especially when it is contacted with air. Consequently, biodiesel storage at certain period of time may cause degradation of fuel physical properties [4, 5]. Biodiesel can hold many times more dissolved water than conventional diesel fuel. The presence of water in biodiesel may induce the proliferation of microorganisms and increase corrosiveness of biodiesel [3]. Various process may occur during storage of biodiesel, including oxidation, condensation and polymerization.

Detected contaminants during long period of fuel storage include corrosion products, organic particle and deposit. Parts of the dirt like materials tend to adhere to tank's bottom and side wall, even though major parts were existed in the fuel and present in the machine room at operation. Components and certain impurities (iron oxide, sulphide) are also affect the burden given by the fuel properties, it may cause an increase in surface wear of the main machine. Biodiesel encounters degradation via vapour absorption, auto oxidation and microbial attack during storage.

Corrosion is higher with biodiesel than petro-diesel fuel. The rate of corrosion is influenced by temperature, water content, microbial growth, and type of feedstock used for synthesis of biodiesel [6]. Wu et al., [7] were tested biodiesel storage for 52 weeks at temperature 4 ^{o}C and 20 ^{o}C. Degradation of 40% of the properties was occurred at storage temperature of 40^{o}C. The chemical with high triglyceride content, if stored at room temperature will be hydrolysed and its FFA content may increase to 76% within 6 months storage.

Biodiesel oxidation is caused by unsaturated fatty acid chain and the presence of double bond in its molecule, which may cause increase in its reactivity to oxygen, especially when placed in container which allow contact with air or water [4]. In some case, biodiesel oxidation was known may cause formation of deposit and corrosive materials [8].

Generally, fuel oil is stored using common method by preventing it from moisture, sunlight, the change in temperature and pollutants. With the same storage style, Terry (2005) has taken note that storage of B100 and B20 shows the occurrence of oil quality change shown by the change of acid number, cetane number and viscosity in the period of 6 months. Contamination of water in BXX may cause biodiesel more aggressive in increasing electric conductivity, accelerate oxidation process, so that corrosion process also occurs quicker [9]. Corrosion attacks for metal surfaces are comparatively more in biodiesel than that in diesel fuel [10].

There are many types of metals used as materials for fuel tank, such as stainless steel, mild or galvanic steel, carbon steel, etc. Stainless steel (SS) is a highly alloyed, low-carbon steel with a high chromium content (about 11%). In more aggressive condition, the basic type of SS may corrode. There are most common forms of corrosion in metals, such as general corrosion, crevice corrosion, pitting corrosion, stress corrosion cracking, intergranular cracking and galvanic corrosion [11]. Pitting is one of the most destructive types of corrosion.

2. Methods

The equipment and materials used in this research are storage tanks made from Stainless Steel SS 304, Carbon Steel and Galvanic Steel. The focus of this research is to observe the effect of variation of construction material for the tanks to corrosion occurrence in the side wall of the of the tank and the bottom of the tank. The fuel used in this test is biodiesel (FAME). The samples of biodiesel are stored for 90 days at room temperature, in two storage conditions, that are inside and outside door. The samples are stored and prevented from direct contact with air (closed), and the properties of biodiesel was analysed. Test parameters for biodiesel properties are viscosity, density, acid value and water content. Biodiesel (B100) was taken from PT Sumiasih Oleochemicals, Bekasi, East Java, which is compatible with the standard of EN 14214. Biodiesel used is based on CPO, especially from RBD Stearin.

Table 1. Parameters and analysis method of the fuel sample

Parameters	**Density, at 15 C**	**Viscosity, at 40 C**	**Acid value**	**Water content**
Unit	kg/m^2	mm2/sec	mg KOH/g	ppm
Analysis Method	ISO 3675/ASTM D5453	ASTM D445	ASTM D664	ASTM D6751

It was assumed that the fuel has been stored for more than 3 months before it is used for this work. Analysis to sample of B100 carried out for this work involved parameters of viscosity, density, acid value, and water content. The detection of corrosion characteristics on the metal tanks was conducted using approximation of dimension changes and the weight loss. For visual examination of metal surface (tank), equipment of Celestron Digital Microscope Imager with magnification to 500x has been employed.

3. Result and Discussion

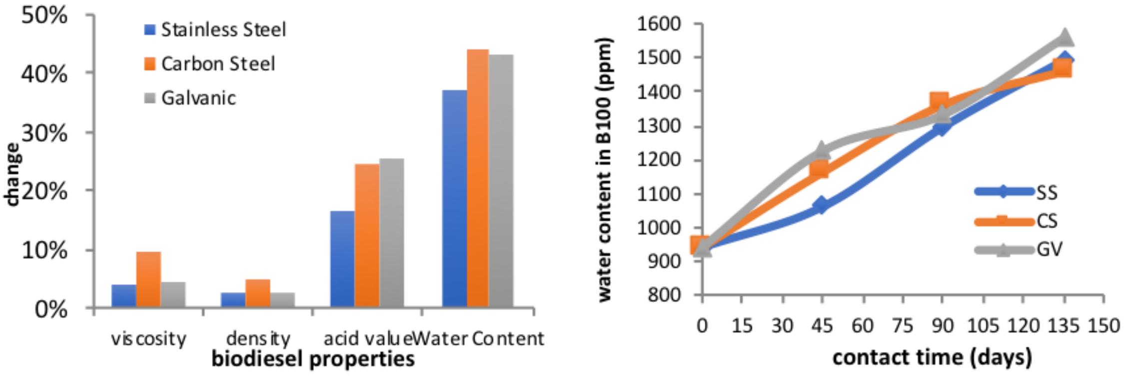
As has been reported by previous researchers in metal tank, biodiesel properties have also encountered change significantly during storage time [12]. In this work, the properties of stored biodiesel has changed in any type of metal fuel tanks. From the measurement of biodiesel properties, its changes may correlate to the corrosion of tanks' materials as presented in Table 2

Table 2. Physical properties of biodiesel B100 after observation for 135 days

Physical properties of B100		Storage Tank1 (Stainless Steel 304)		Storage Tank 2 (Carbon Steel)		Storage Tank 3 (Galvanic Steel)	
		T_0	T_{90}	T_0	T_{90}	T_0	T_{90}
Viscosity	mm2/s	3.700	3.850	3.800	4.060	3.700	3.870
Density	kg/m3	0.852	0.876	0.852	0.894	0.852	0.876
Acid value	mgIOD/g	0.575	0.672	0.575	0.716	0.575	0.721
Water Content	ppm	945.600	1298.900	945.600	1363.400	945.600	1353.900

High change in viscosity and density occurs in biodiesel stored in tank of Carbon Steel as compared with the ones stored in Stainless Steel and Galvanised Steel tanks, as seen in Figure 1a.

The increase in viscosity and mass density of the oil stored in tank of CS indicates that tank material of CS is more prone to molecular interaction with oil. In this case, the viscosity and mass density were connected with the formation of corrosion products, including dissolved sediment. As known, oxidation process occurred during fuel storage may cause the formation of free fatty acid, isomerization of double bond (change of cis- into trans-isomers), saturation and production of higher molecular weight substances. In Figure 2a., the same pattern of changes in acid value and water content in those three materials.



(a) *(b)*

Figure 1. (a) Percent change of biodiesel properties during storage in metal tanks, 1(b) The change in water content of B100 after storage time

High acid value in biodiesel reflects high free fatty acid comes from oil or fat hydrolysis, or from bad treatment process. Acid value of biodiesel tends to increase with storage time, which is connected to the increase of hydroperoxide formed which subsequently oxidized further to form acid. Acid may form if there is water to cause ester hydrolysis into alcohol and acid. A study made by [13] reported that metals (mild steel) is oxidised at a higher rate at high temperature which causes oil to desorb from the surface of mild steel. It has proven that there are strong relation and interactive effects between acid condition with metals corrosion. As seen on Figure 1b., the water content of each sample in three tanks were increased by the increase of contact time. The samples taken from galvanic tank was performed the highest content in water content compared to stainless steel and carbon steel tank. However, high water content in oil fuel samples stored in three different types of tank material is not identical to the corrosion profiles that occurs on each tank. As stated by [3] the effect of water content on corrosion rate is not significant but It does give effect on corrosion process. The corrosion products and some impure precipitates are easily to gather and stick to the wall and/or bottom of fuel tank under the static condition. It performed as protective film and hindered the diffusion of corrosive medium or water molecules to the metal surface and dissolved diffusion of metal ions, and meanwhile caused anodic polarization and cathodic polarization [14].

3.1 The Change of Dimension of Metal Tanks

The change of tank dimension analysed are thickness of tanks' side wall (mm) and the tanks' bottom wall (mm) or base which made from SS, CS and GS. The test is carried out after 135 days exposure with using digital depth gauge for thickness measurement. In Figure 2, it showed the change in dimension considering the base thickness, wall thickness and weight of each tank materials in 135 days of observation.

In general, each metal tank showed a reduction in the thickness of the base and the tank wall. It is detected after the oil has been removed from the tank and some corrosion products have been eroded (the outer most layer of the metal tank). After 135 days of storage, the changes that occurred on the tank wall are a thickness reduction. Galvanic Steel seemed performing the highest base thickness decrease, while the acceptable degree of decrease in industrial application is 0.07%. Carbon Steel shows a little decrease in wall thickness same as indicated by the GS. The position of measurement is crucial to indicate the changes in thickness, it is due to some corrosion products is adhered to the wall or collected at the base or bottom of the tank. The layers of metal tanks eroded in oil and dissolved, then it discharged during tank observations.

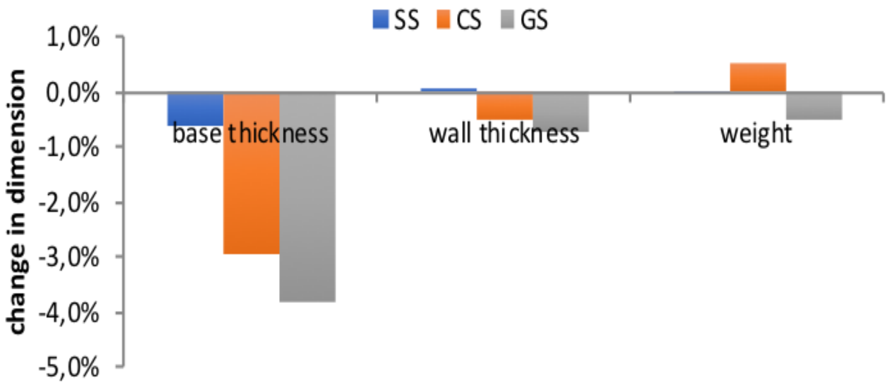


Figure 2. Change in tank dimension

Oxygen content in biodiesel exposed to metal surface of storage tank may be increased with time. It can be indicated with the extreme increases on the fuel' water content after 135 days of storage. Oxygen presents in the form of compounds namely iron carbide or iron oxides. Subsequent formation of oxide compounds and their dissolution seems to degrade the metal surfaces [10].

In some other condition it may presents as corrosion product so the metal thickness will be changed. In the tank wall section, CS and GS tank thickness decreases while SS tank tends to increase. The corrosion products formed on GS and CS tanks tend to erode or crush the surface of the tank wall. Furthermore, carbon steel is susceptible to stress corrosion cracking (SCC) in fuel under particular conditions [3].

3.2 Weight Loss Analysis of the Metal Tanks

Weight analysis is used to measure when there is any change in tanks' weight using analytical balance. After examined for 135 days, the over-all weight of the tanks has decreased by 0.5-0.8%, except for GS tank as seen in Figure 2. The increase in weight of GS tank is caused by adhered material to the bottom of the tank which comes from tank's wall corrosion products when the tank is contacted with B100. Moreover, the material found at the bottom of the tank may also come from the degradation of B100 entrapped in corrosion products, since the oil has been stored for long and it has encountered instability of its physical properties. Best materials for the storage tank from weight loss examination come from SS or CS, excluding GS due to its inconsistent sequence. The corrosion processes were accelerated by bubbling with air, leading to a slight weight loss in the tested metals, particularly in galvanic tank.

3.3. Visual Analysis at Metal Tanks' Surface

Three sample tanks of the same materials, SS, CS and GS are also observed for more than one year exposed to the environment. Various morphological changes of the tanks' surface were detected as corrosion to take place. Morphological view of tanks' surface made from CS, GS and SS were shown in Figure 3-5.

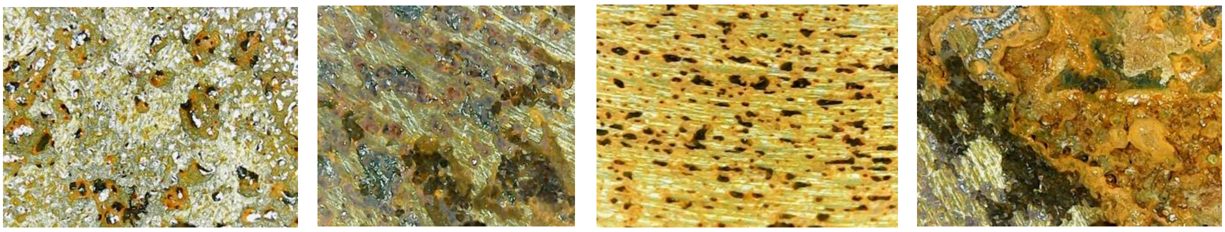


Figure 3. Morphological looks of carbon steel (CS) tanks' surface

From Figure 3, it is obvious seen that CS shows uniform corroded metal surface. The black deposit is also found in the surface. It caused by the reaction between metal oxides and fatty acids to form salts, which strongly stick to the metal surfaces [1]. These appearances lead to conclusion that CS is the better material for biodiesel storing, since it has the most uniform morphological surface, which preventing it of having localized corrosion during its usage, hence give predictable corrosion rate and thus the lifetime of the tank. As reported by Ortega, carbon steel showed passive behaviour in B100 and biodiesel-diesel blends, but active uniform corrosion in diesel. Stainless steel remained passive in all exposures while other metals was susceptible to pitting corrosion [2].

The bottom surface of GS tank performed many various of metal degradation rather than the other tank' surface as seen in Figure 4. In one side of the GS surface, it presented the uniform corrosion but in other place it may detected a shallow but wide through pits which encompassed as local corrosion.

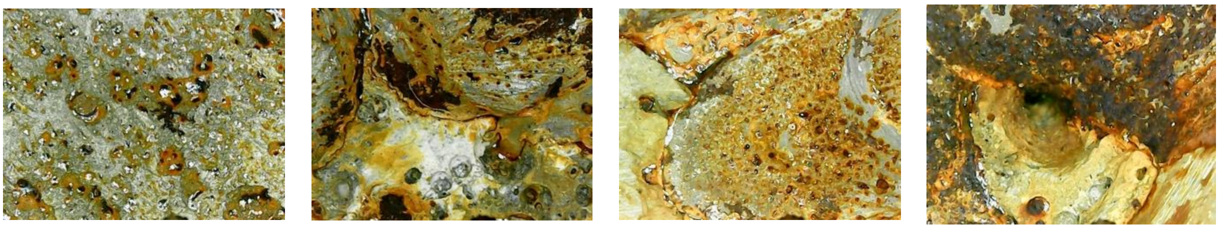


Figure 4. Morphological looks of galvanic steel tanks' surface

While the corrosion of each tank materials in the coupon exposures may possibly occurred due to the extreme environment conditions, such as high humidity and uncontrolled oxidation. Corrosion of metals in biodiesel may not fundamentally different from corrosion of metals in any aqueous solutions. Similar variables (dissolved water and oxygen, acids, bases, ions, microorganisms, temperature, fluid regime and velocity) can affect corrosion in biofuels [3]. The most problems with biodiesel occur due to its low stability on oxidation and its high solvency, tendency to absorb water which accelerate the corrosion process.

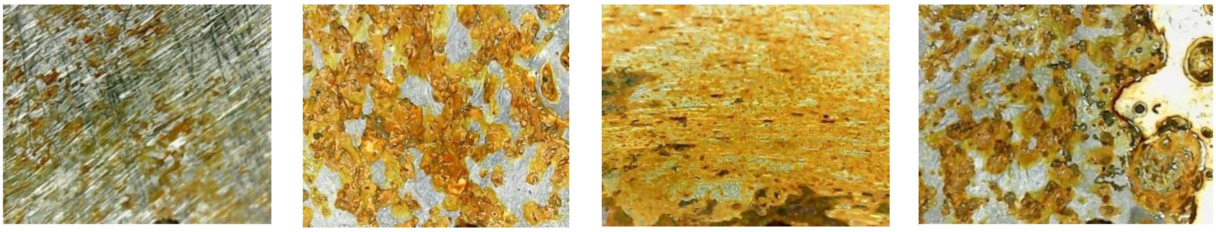


Figure 5. Morphological looks of stainless steel tanks' surface

The corrosion profile on SS tank is shown in Figure 5. It seems that SS has the least corroded surface than the other two metals. However, at high magnification of morphology imaged, the surface of SS was less attacked but still corroded in different pattern. After a certain of time, it is found that a pitting corrosion may be occurred. It can be seen from the narrow and deep pits found in the surface.

Corrosion in SS is more potential to occur in extreme environmental conditions such as low pH, moderate temperature, and high chloride concentration. The electrochemical reaction and oxidation that triggered by biodiesel properties may aggravate the degradation of metals. In term of the type of corrosion detected on the metal surface, from this work it suggests that tank made of SS is no longer recommended for storing biodiesel due to its prone to localized (pitt) corrosion. It may cause a leakage quicker than other type of metals.

4. Conclusion

During storage in the metal tanks, biodiesel encountered some changes in several parameters of its physical properties. Moisture content at each tanks' type has change at the highest with the increase of storage time. The limit of corrosion resistance of any metals depends on its constituent elements when exposed to corrosive environment and corrosive fluid. Biodiesel is recognized as more corrosive than traditional petro-diesel. The fatty acid methyl esters are readily hydrolyzed by microbes, which transform it into organic acids and highly corrosive hydrogen sulfide. Corrosion at biodiesel storage tank with various metal tanks' material show that the damage due to corrosion is the most at material of SS due to localized corrosion. The CS tank was performed more uniform corrosion. The mechanism of corrosion on tank beds and walls seems to be not the same in each type of metal. It may be caused by resistance of each materials to environmental factors. The properties of fuel oil and its aggressiveness may contribute to the corrosion behaviour depends on the presence of water, acid, and other constituents, particularly in relation to cause degradation and oxidation in biodiesel.

Acknowledgments

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