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Original article

Technical assessment of biodiesel storage tank; A corrosion case study

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A B S T R A C T

The compatibility problems become main concern in the utilization of biodiesel especially regarding to degradation and corrosion. The present study is conducted to describe the corrosion behaviour that occurs in steel tanks after contact with palm-based biodiesel for a period of 7 months. The storage tank used is respectively made of galvanised steel (GS), carbon steel (CS) and stainless steel (SS). It is performed in vertical cylinders with a floating-roof model. In every 30 days of storage time, the profile changes in the wall, roof and base surface of each tank were observed. The oil fuel properties were monitored in the parameter of viscosity, acid numbers, water content and oil colour. The topographic profiles on the surface of the walls and bottom of each tank wetted by biodiesel were examined over three zones inside the tanks using an endoscope imager. The main results of this study indicate that the tank steel with different protective layers exhibits different types of corrosion. The corrosion was localized in SS tanks but generalized in GS and CS tanks. The oil contamination in SS tanks was relatively lower than that in CS and GS tanks. The type of corrosion performed differently in different zones on the inside of the tank. The potential for leaks is greater at the base than on the walls and roof of the storage tank.

1. Introduction

Degradation, contamination and corrosion still become main issues in biodiesel utilization problem. As known, biodiesel having higher susceptibility to degradation and contamination (Cardeño et al., 2020; Nguyen and Vu, 2019; Fazal et al., 2018; Groysman, 2017; Sundus et al., 2017; Jin et al., 2015). Biodiesel exhibits lower storage stability due to biodiesel is sensitive to oxygen (Kovács et al., 2015; Komariah et al., 2019; Singh et al., 2019; Fernandes et al., 2019). When biodiesel oxidation took place some of derivatives are formed due to degradation. It may produce compounds which triggers contamination in oil fuel. As known, biodiesel is more corrosive compared with petrodiesel oil (Fazal et al., 2018; Adams et al., 2018; Tabish, 2018; Thangavelu et al., 2015).

Corrosion is one of the major problems found in fuel storage tanks. More than 80% of the diesel tank systems exhibited moderate-to-severe corrosion. Corrosion currently accounts for billions of dollars each year to fix or replace corroded items (Bennett, 2019). A lot of industrial users believe that one main reason for storage tank failure is corrosion. Most of the leakages of tanks for oil fuel storage and the pipelines are commonly initiated by lack of corrosion assessment and poor maintenance.

Steel becomes the most popular materials selected for handling and storing fuel in industrial application. Steel convincedly offers affordable building costs and good chemical resistance. The resistance of steel is obtained by providing a protective layer on the surface. Resistance to corrosion is enhanced by higher chromium (Cr) and molybdenum (Mo) content (Hussaini et al., 2014). A test by (Kugelmeier, et al (2021), they concluded that carbon steel and stainless steel presented surface morphology with slightly changes compared to aluminium and copper. However, practically biodiesel is rarely stored in aluminium and cobalt tanks. The corrosion is still very possible to occur with different profiles and rates. So far, there has not been an adequate study to highlight corrosion type and behavior in the different zones inside the fuel tank made from different coating elements. This behavior is also related to a change in the physical properties of the fuel stored particularly in higher blend of biodiesel. This interaction complexity is important to be formulated and explained further. The present research is conducted to analyse the characteristics of biodiesel corrosion on different protective layers of steels. In order to increase the life span of biodiesel storage and prevent its contamination and corrosion,

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the update technology in storing and handling biodiesel must be provided. The results can be used to improve the design in storage tank, selection of steel protection materials and afterward the service life of the biodiesel storage tank can be planned longer.

2. Material and methods

The storage of neat biodiesel (B100) is carried out in three tanks with relatively similar designs but made from three different types of material, namely carbon steel (CS), galvanised steel (GS) and stainless steel (SS). The grade and major elemental of protective layers on the steel materials is presented in Table 1.

The period of observation was 210 days (5040 h). Visual observations were made on three surface zones of the inner tank material exposed to biodiesel, and one zone on the outside of the tank, as shown in Fig. 1. The zones observed were roof, wall and base/bottom of the storage tanks.

The thickness and diameter measurements are made using a digital thickness gauge with an accuracy of 0.01 mm/0.0005 in., meanwhile the weight of the material was weighed using an analytical balance with an accuracy of 0.01 gr. An endoscope imager with a 500x magnification was used to obtain a visual surface of the tank after the specified storage time. The topography of the metal surface after exposure is known to substantially affect the bulk properties of a material. This surface topography is primarily investigated and observed by microscopic measurements using Scanning Electron Microscope (SEM).

The biodiesel used for this research is based on palm oil which has met the requirements of ASTM D6751. In this work, the fuel quality was monitored and analysed in every 30 days. The properties of biodiesel used, its standard and method of analysis are presented in Table 2.

The uncertainties in this study are possibly coming from several measurements and analysis. However, each measure stages were carried out using equipment that is in proper condition, trustworthy, and showing high measurement accuracy. The measurement instruments used are thickness gauge and analytical balance. While, for fuel properties analysis, the equipment deemed to perform a low level of uncertainty in accordance with the standards set by ASTM for each of the analysis procedures as listed in Table 2. All the instruments used were calibrated regularly with accredited procedures. So, it can be stated that the values obtained in this study are reliable and properly judged. The calculation of the uncertainty is generated based on guide to the expression of uncertainty in measurement (GUM). It is the approach applied to express the result of a measurement along with an associated measurement uncertainty. It will better be reported in details separately.

3. Results and discussion

The relationship between the storage stability of biodiesel and its corrosiveness with selected steels will be shown through the results of storage tests and corrosion analysis carried out in this study.

3.1. The changes in biodiesel physical properties

In the present study, the physical properties of biodiesel are dramatically changed with prolonged storage duration. The instability of biodiesel over oxidation contributed to the parameters such as total acid number, viscosity and water content, which found significantly increased with the increase of storage time as shown in Fig. 2.

The increase in viscosity can be attributed to the formation of products of higher molecular weight and double bond isomerization as explained by Tabish (2018). Biodiesel also contains a higher amount of unsaturated fatty acids than saturated ones which make it lower oxidation stability (Gülüm et al., 2020). The formation of oxidized products is occurred after a long period of storage time (more than 4 months). Those molecules formed are polar and contained more oxygen. Further oxidation process led to increased level of free fatty acids, formation of double bond isomerization and increased saturation and production of molecules with higher molecular weight.

Furthermore, biodiesel can absorb water because of the persistence of mono- and di-glycerides generated from an incomplete reaction in the syntheses of methyl esters. The molecules can act as an emulsifier and promote water to be mixed with biodiesel. The presence of water is a crucial trigger of reactions that leads to corrosion.

In Fig. 2(b) it is shown that the water content of biodiesel was initially high, and after 7 months of storage, it is significantly increased at an average of 59%. This phenomenon is possibly attributed to the tank design with a roof seal, which is not fixed and completely sealed.

The total acid number is used to indicates the change in acidity of fuel upon exposure. As seen on Fig. 2(c), biodiesel acidity increased with prolonged storage duration in each storage tank. Therefore, the increase in acid value may not have resulted from exposure with steel tank materials but rather from the oxygen content of biodiesel and molecule interactions during storage duration. A larger quantity of free fatty acid present in fuel will not only lead to greater acid value but can also be the reason of rusting in the fuel pipeline (Dugala et al., 2020). Some researchers suspect that the presence of biodiesel as a fuel causes an increase in the acidity of the fuel and contributes to an increase of corrosion rate (Thangavelu et al., 2015; Dharma et al., 2018).

3.2. The clarity and color of biodiesel

The clarity and colour of the biodiesel at initial condition and after 7 months of storage time are compared among three different storage tanks. As seen on the Fig. 3, they were performed in a very contrasting ratio. The differences in the level of clarity and colour

Table 1
Grade and major metal element composition of steel tank.

CS (Mild Steel)		GS		SS (304L)	
Fe	Bal	Fe	Bal	Fe	bal
C	0.16–0.18%	Al	8.5–9.0%	Cr	18.3%
Mn	0.70–0.90%	Zn	0.45–0.50%	Ni	9.97%
Si	< 0.40%	Si	0.17–0.30%	Si	0.48%
		C	0.42–0.50%	Mn	1.78
		Ni	0.01–0.25%	Mo	0.30%
		Cu	0.02–0.25%	Cu	0,20%
P	< 0.04%	P	< 0.035%	P	< 0.027%
S	< 0.04%	S	< 0.035%	S	< 0.006%

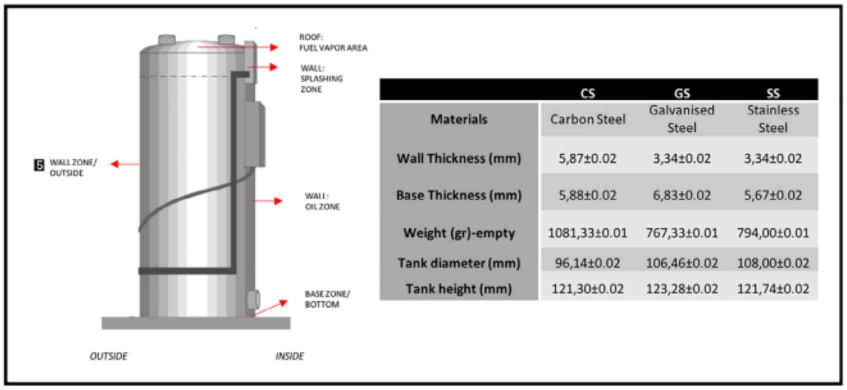

Fig. 1. Biodiesel storage tank for corrosion analysis.

Table 2
Biodiesel properties and the method of analysis.

Properties	units	Standard	Value (initial)	Method
Viscosity	mm^2/s (cSt)	2,3–6,0	3,7	ASTM D445
Density	kg/m3	860–890	868	ASTM D941
Total Acid Number	mg KOH/g	0.80 (max.)	0.485	ASTM D664
Water content	% vol.	0.050 (max)	0.0945	ASTM D2709

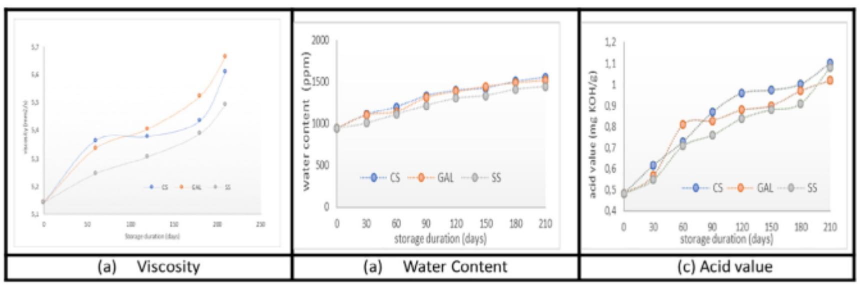

Fig. 2. The profile of biodiesel physical properties changes in CS, GS and SS tanks.

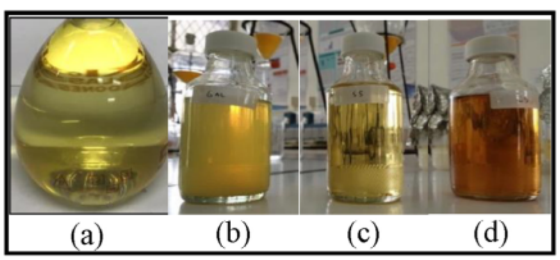

Fig. 3. Biodiesel (a) before storage, after storage (b) in GS, (c), in SS, (d) in CS Tank..

of the biodiesel indicated deterioration or contamination that may occurred during storage in each tank.

Although the tracking of the metal content or carbon residue a in biodiesel samples has not been carried out yet, the sediment formation was detected visually in the samples stored especially in GS and CS tanks. This result indicated that the presence of carbons, such as organic deposits and amorphous carbon, is complex, as also revealed by (Jin et al. 2015). Moreover, a change in biodiesel colour indicates a change in fuel physical properties, and its compositions with a presence of metal species in the fuel. As stated by Tabish, 2018, biodiesel can oxidize itself and metal species can react as a catalyst in that reaction. The presence of red colour was strongly due to metal oxide in the diesel.

3.3. The images of the steel surface after exposed to biodiesel

The inside wall of the tanks was exposed to biodiesel during the storage period, and the outside was contacted to environment conditions. The optical microscope images of the tanks are shown in Fig. 4. The little changes were clearly visible in the tank' colour and texture but evenly distributed on the entire surface of the inner tank walls. Only cracks and rough strokes were found on CS carbon steel tank walls. Instead, the outer tank walls showed differently. It seems that contact with the environment became more dangerous compared to exposure to biodiesel.

Extreme surface texture or scratch was detected on the GS and SS outer tank walls. Numerous black dots on the metal surface were also found, majorly in CS tank. From the observations on the surface of the inner and outer tank walls, it was found that the damage caused by exposure to biodiesel and physical damage due to environmental influences gave different profiles but equally

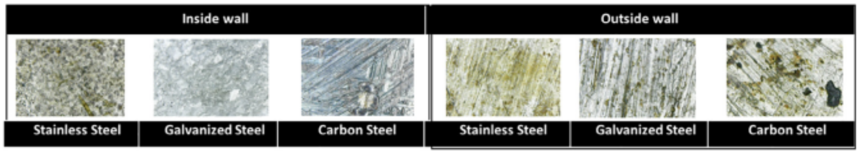

Fig. 4. Optical microscope images of steel surface after exposure to biodiesel.

destructive corrosion characteristics. As seen in Fig. 5 sticky hardened materials, considered as an effect of microbial growth, were found more at the outer side of CS tank.

3.4. Corrosion profile in the different zones of the steel tanks

Corrosion is detected in every type of storage tank, including to which constructed by stainless steel. Corrosion was found in different tank zones with various patterns. The roof of the tank is considered a biodiesel vapour interaction zone or called the splash zone. Contact with air is very likely to occur here. As seen in Fig. 5, on the roof of the tank, general corrosion tendencies occurred on the surface of CS and GS materials, but the SS tank showed a different pattern. Very visible colour changes on the metal surface occurred in CS tanks because of microbial growth. However, several more holes were found in several locations on the surface of the SS located at the top of the tank. The tank base in all tank materials contained more scratches and damaged surfaces than the walls and top of the tank. Overall corrosion occurred at the bottom of the GS and CS tanks. Conversely, several local spots were found in the SS tank, showing the formation of several shallow holes. A small cavity was detected on the SS base. The same profile is found in the SS wall, so the potential for localized corrosion is more likely to occur in SS tank. Meanwhile, many crusts, which are metal oxides, formed in the GS tank well due to entire metal coating. The distribution of the crust formed was relatively uniform. Therefore, general corrosion can be stated to occur in the GS tank walls. This uniform corrosion over the entire surface of the GS and CS tanks is rare and may lead to overall thinning, which has little effect outside of fatigue and stress condition. The irregular shape of the corroded carbon steel surface was also detected. Otherwise, after exposure more than 7 months, most of the steel surfaces emerged blackened and pitted. This is slightly different from what was concluded by (Grainawi et al. 2008), in which the surface of the steel coupons was exposed to the aggressive fuel blend.

SS tank seemed visually less susceptible due to the good resistance as shown in Fig. 5. It is previously believed because the thin, passive film of chromium oxide covering stainless steel prevents not only corrosion but also leaching of metal ions from its surface (Torsner, 2010).

However, it is not necessarily applied to the case of long biodiesel storage (up to 7 months). The corrosion in the present study only affected the surface and appeared to be uniform. No deep localized corrosion sites (pits) were observed. A pit may form on base metal because of the corrosive attack as well as the breaking down of oxygenated compounds. According to (Tang and Ballarini, 2011), pitting is a result of surface migration and focuses on the time evolution of very thin films with deep indents. The growth rate of pitting corrosion is only time-dependent. In the present work, the acidic conditions that occurred in biodiesel stored in SS tanks showed a major tendency to create pit corrosion.

3.5. Corrosion characteristics from the metal surface morphology

The corrosion on the metal surface may also be observed from physical changes on the coatings. Thicker coatings allow the pass of the electrolyte due to the stresses generated during coating deposition and the corresponding crack formation between different layers. While, thinner coating let the electrolyte permit through the coating then may create a surface damage (Reddy et al., 2017).

After exposure to biodiesel in certain storage conditions, GS, SS and CS metal specimens were analysed using SEM. Under the same magnification, the morphology view of each metal surface was examined, as seen in Fig. 6.

The surface morphology of each part of the base of the steel tank was influenced by the type of metals element that coats each surface. The oxide layer appeared to be very apparent on the surface of the GS and SS. Meanwhile, on the surface of the GS tank, visible pores and cracks that are heterogeneous were found in addition to the oxide crust on almost all metal surfaces. According to (Groysman, 2014), organic acids can be formed in biodiesel as a result of its oxidation by dissolved oxygen during long-term storage. As known, acids can increase the corrosiveness of biodiesel (Setiawan et al., 2017; Chew et al., 2013) and trigger deposition onto CS and GS tank surfaces. From the morphological observations shown in Fig. 6, the corrosion that most likely occurred on SS and

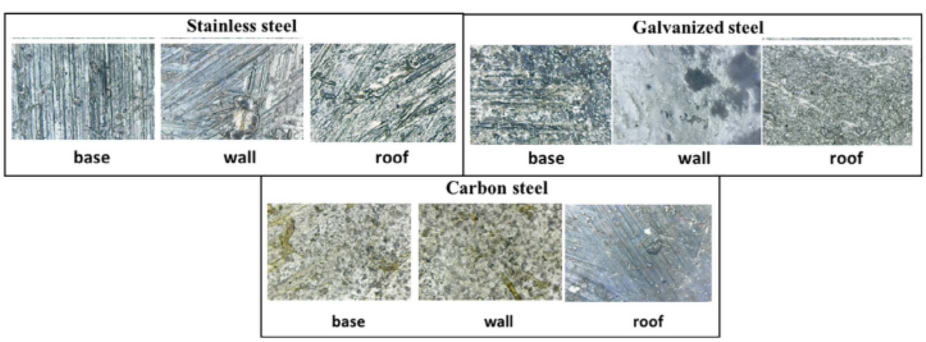

Fig. 5. Low magnification optical microscope images of the three zones of metal surface after exposure to biodiesel.

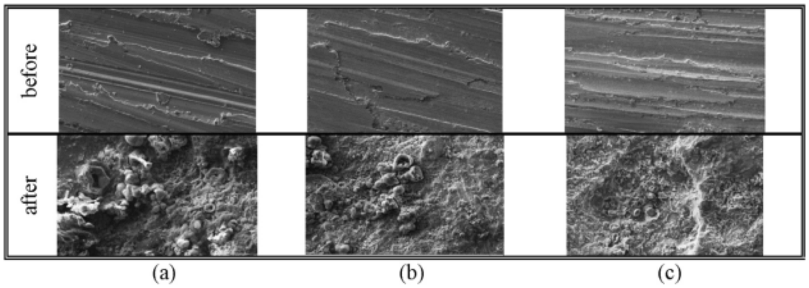

Fig. 6. SEM image of the base of biodiesel storage steel tanks; (a) SS, (b) GS, and (c) CS

GS surfaces is local, because it occurred on definite parts of the metals' surface. Under longer exposure time with biodiesel, which has high acidity conditions, the oxide layer forms rust and crust, which can then erode and potentially cause crevice and pitt. The surface of CS tanks was rough and covered with cavities, which was thought to be on the surface of CS with the potential to experience uniform corrosion.

3.6. Cost analysis of corrosion in biodiesel storage tanks

For many industrial and commercial users, the equipment downtime, repair, and replacement due to corrosion may lead to bundle and high cost bundle. As known, corrosion investigations are a fraction of equipment design costs, while corrosion assessment or evaluation is a major part of the maintenance cost. For most industrial countries, the average corrosion cost is 3.5–4.5% of the GNP (Ahmad, 2006). They also estimated that than 2–10% of maintenance cost is spent on corrosion remediation.

From this work, it is known that in order to deal with the aggressiveness of corrosion triggered by the presence of biodiesel and its blends with petrodiesel, high performance metal alloys are a priority. Besides that, it needs to be equipped with a specific and reliable protective layer or coatings due to potential pitting and uniform corrosion occurred. A worldwide consultant Kennedy-Jenks mentioned in a report that interior recoating costs for water storage tank is about 10–22 $/sq ft. The cost factor will be influenced by the properties of fluid stored, the resistivity of the coating element selected, and the life expectancies. The corrosion behavior in each tank materials, locations that are vulnerable to being damaged and the length of time exposed to biodiesel will determine varying resistance of tank materials and its coating. As a consequence, the corrosion protection cost increases with the increase of improvement in corrosion resistance.

4. Conclusions

The corrosion of biodiesel is occurred due to the specific properties and its interactions with the oxide layer formed on the surface of each metal. Storage conditions contribute more to contamination and corrosion, but the type of metal coating element influences the type of corrosion that occurs on metal surfaces. Stainless steels and metal alloys in galvanized steel are susceptible to pitting, galvanic corrosion or localized corrosion. Uniform corrosion is most likely to occur in CS tank types, whereas GS and SS tanks show the potential for localized corrosion. The bottom zone or bottom of the tank is the part that shows the most corrosion symptoms, including pitting corrosion. In the future, it is very important to measure the potential and corrosion rate in each segment of the tank by considering the typical of corrosion and its behaviour along with the complexity of the interactions that arise due to the extreme changes in the properties of biodiesel.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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