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Effect of storage tank material on biodiesel stability under different environmental conditions

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KEYWORDS

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Fuel properties
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ABSTRACT

This study aimed to determine the effect of storage tank materials on fuel storage stability under different environmental conditions. Experiments on biodiesel blends (B10) were conducted using semi-transparent HDPE, clear glass, and stainless steel with various storage shapes under sun-exposed outdoor condition (28-32°C) and enclosed indoor condition (25-27°C) for 180 days. Oil samples from selected storage materials were monitored and the values of density, viscosity, acid value, flashpoint, and water content were recorded. In this study, the effect of storage tank material and environmental conditions were significant on biodiesel stability; oil samples placed indoor without exposure to sunlight recorded slight increase in data, regardless of storage material, while samples stored outdoor in clear glass containers showed a dramatic increase in viscosity, density, acid value, and water content by 23.7%, 9.7%, 150.4%, and 221.3%, respectively within 180 days of storage. Meanwhile, the flashpoint decreased by 6.58% with increasing storage duration. It also can be observed that discolouration was more rapid in glass storage tank compared to HDPE and stainless-steel tanks. From this study, it can be concluded that stainless steel is recommended as storage material due to its versatility to degradation for lower biodiesel blends.

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1.0 INTRODUCTION

Biodiesel is gaining popularity in the current market for its advantages over petrodiesel because of its sustainable benefits and unique features. This fuel can be used to cut costs for the currently expensive diesel in the market (S. Innocent et al., 2013). Biodiesel is blended with commercial diesel and is denoted as B (Yusof et al., 2015). For example, B10 fuel contains 90 percent petrodiesel and 10 percent palm methyl ester. Many countries are recommending the usage of biodiesel in the transportation, industrial, institutional, and commercial sectors. Usage of biodiesel can indirectly increase the economic sector in Malaysia as the country is the second biggest exporter of palm oil behind Indonesia (Shehu et al., 2020). The dependence on fossil fuels, greenhouse gas emissions (GHG), carbon monoxide, sulfur dioxide, and other pollutants are expected to reduce once biodiesel is executed at every petrol station around the world (Sudrajat et al., 2020). In Malaysia, B7 and B10 are already sold in local gas stations while B20 implementation is in an ongoing phase. For automotive applications, lower blends up to B20 can be used in the current engine without further modifications. Blends higher than B20 need engine modifications because higher blends have higher water content in their fuel (Zulqarnain et al., 2020). However, in general, biodiesel needs less engine modification than bioethanol. For example, rubber seals on the gasoline lines of certain older automobiles need replacement with a non-rubber alternative as biodiesel reacts with elastomers (Komariah et al., 2019).

Despite the benefits of biodiesel, this fuel has disadvantages due to its storage stability. During biodiesel production through the pyrolysis method, the fuel generates a certain amount of water but the fuel is safe to be used at that period. However, the fuel stability deteriorates throughout distribution and storage as a result of the lack of further care on the fuel. Reduction in the biodiesel quality can end up causing engine failures. Higher water content in the biodiesel can cause significant problems such as fuel degradation, fuel filter plugging, microbial growth, and corrosion to the engine compartment. Some researchers insisted on not storing the fuel for more than six months (180 days) due to its lower stability properties (Nurul Komariah et al., 2017; Pölczmann et al., 2016). Biodiesel contains unsaturated fats, which are contributed from vegetable oil. These fats make the fuel oxidizes, less stable, and degrades faster (Udomsap, Nuwong Chollacoop et al., 2009). Moreover, oxygen, water, exposure to light, contamination, and heat also contributes to degradation based on previous studies (Czarnocka & Odziemkowska, 2015; Ku et al., 2015; Rao & Chary, 2018; Weltschev et al., 2015). Kinematic viscosity, density, acid value, and water content were observed to be increased with longer storage duration(Ashraful et al., 2014; Khalid et al., 2015; Nanihar et al., 2019; Shahabuddin et al., 2012; Zakaria et al., 2014). The physicochemical properties of biodiesel also change over time. However, these changes also depend on the environmental conditions as the oxidation process is accelerated with heat, light, and air.

Acid value and flashpoint remain constant when the biodiesel storage tank is placed in a dark surrounding without any light exposure. Compared to dark surrounding storage, biodiesel stored in storage tank placed under sun exposure shows a crucial change in its properties, mainly due to higher temperature (Azizul et al., 2020). Water content during this condition can be observed to be higher. Based on previous research, for storage in a lower temperature, fuel properties were below the normal values during the observation duration, which was stored in the duration range of 3 to 52 weeks (Nanihar et al., 2019). Biodiesel, which is hygroscopic, absorbs atmospheric moisture quickly due to methyl ester during air exposure. The presence of a double bond in the fatty acid molecule increases the level of reactivity with oxygen. Higher concentrations of various acids or polymers produced during oxidation corrode the storage tanks and engines which can lead to engine malfunction.

Most biodiesel properties tests were done on oil stored in metal storage tanks which is the common practice to store biodiesel. Stainless steel and aluminium are recommended metallic components to be used for storage. The most compatible material is stainless steel due to its resistance to chemicals with higher blends of biodiesel (Torsner, 2010). Another common material used by researchers for biodiesel storage tanks is glass for biodiesel stability tests. High-density polyethylene (HDPE) is a thermoplastic polymer made of petroleum. This plastic is resistant to most chemicals, durable, and withstands higher temperature. It is also stiffer and opaque. Thompson et al. (2013) observed that fuel in the polyethylene storage tank is stable for 380 days at 23°C, but during higher temperature storage (80°C), the production of acids and peroxides was observed. For instance, LN Komariah et. al. (2017) used HDPE, stainless steel, and glass to observe the density, kinematic viscosity, and water content of B20 for 12 weeks. As expected, the parameters increased with the storage period (Nurul Komariah et al., 2017). Higher water content is noticed in higher temperature storage. Unfortunately, previous studies using HDPE and other plastic materials for storage tanks are limited as the research done were more on biodiesel raw materials type, blends, and storage period observations (Khalid et al., 2015; Nurul Komariah et al., 2017)

The environmental conditions have to be considered for storage tanks, mainly during transportation as the climate can be unstable in actual situations. Ideally, storage tanks have to be able to keep the fuel in its optimum properties for a longer period. Meanwhile, for oil storage at temperatures greater than 30°C for a duration of 180 days, the fuel must be treated with antioxidants to delay the deterioration process. It has been shown that most experimental investigations of the storage tank were done outdoor under sun exposure to consider the safety and environmental circumstances. However, the degradation results obtained by previous research within 90 days storage period are still acceptable (Czarnocka & Odziemkowska, 2015; Humairak et al., 2015; Thompson et al., 2013). Other than that, non-metal storages show a major increase in the value of acid number compared to metal storage. The main aspects that should be considered for the best storage tank are material type and location of the tank placed. Steel and concrete are the most popular materials for storage tanks. Moreover, polyethylene materials gain popularity to be used in storage tanks due to their chemical resistance and cheap production.

In this study, the selected biodiesel blend was placed in storage tanks made from various materials and shapes under two environmental conditions: indoor and outdoor condition for the duration of 180 days.

2.0 EXPERIMENTAL PROCEDURE

The Euro 5 Diesel (B10) sample was used in this experimental investigation. This sample was stored for 180 days under two different surrounding conditions: enclosed indoor space (25-27°C) and outdoor space under sun exposure (28-32°C). Outdoor temperature and humidity were recorded daily. The illustrated test setup and real test setup were as shown in Figure 1 and Figure 2, respectively. The results of outdoor and enclosed indoor space storage tank data were recorded on the first and final days of the experiment. Three different materials were used: glass, HDPE, and stainless steel. Semi-transparent HDPE and clear glass were used to ensure storage tanks received total exposure during observation. Rectangular and cylindrical storage tanks were utilized in this experiment to observe the effect of storage tank shape. The acid number (AN), density, kinematic viscosity, water content, and flashpoint properties were observed and recorded according to ASTM D6751 and EN14214 regulations, with the used apparatus presented in Table 1.

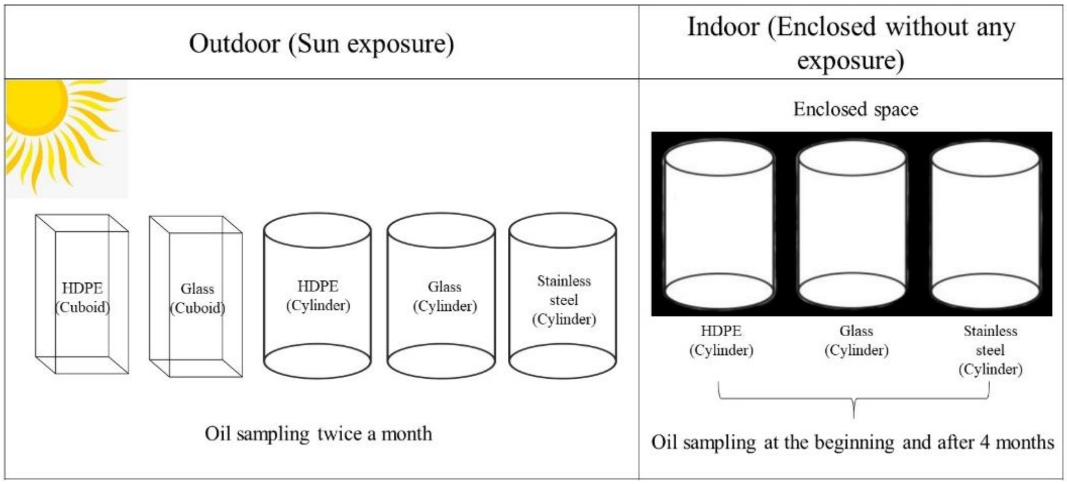


Figure 1: Experimental setup illustration.

(a) (b)

Figure 2: Real experimental setup (a) Outdoor storage and (b) Indoor storage.

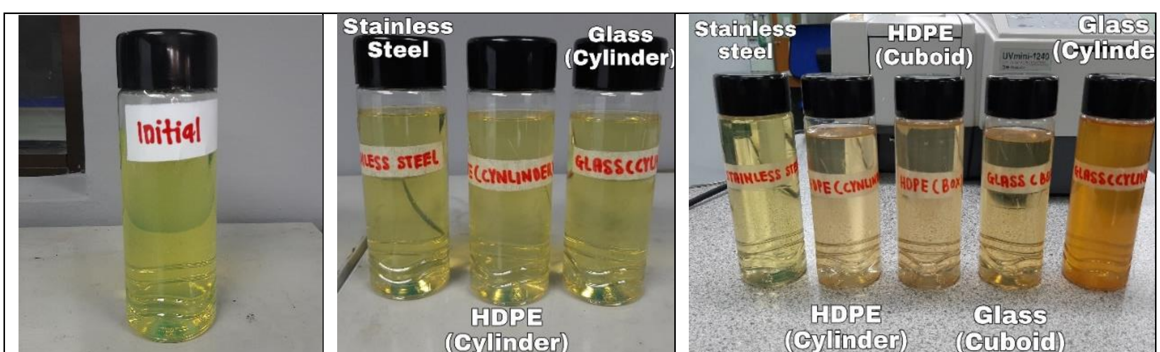
Table 1: Fuel properties analysis method.

Parameters	Units	Apparatus	Method
Density	kg/m^3	Hydrometer	ASTM E100
Kinematic viscosity	cSt (mm^2/s)	HK-265A Kinematic Viscosity Apparatus	ASTM D445
Water content	mg/kg	899KF Coulometer Titrator	ASTM D6304
Flash point	°C	SetaFlash Series 3 Plus Closed Cup Flashpoint Tester	ASTM D3828
Total acid number	mg KOH/g	KOH Titration	ASTM D664

3.0 RESULTS AND DISCUSSION

3.1 Observation on Biodiesel Appearance

Figure 3 shows the discolouration that occurred after the 180 days storage period for oil samples that were stored in indoor and outdoor conditions; initially, the oil samples in all storage tanks were greenish in colour. For oil samples that were stored in outdoor condition, the 180 days storage duration did affect the appearance of the oil. Samples taken from the glass storage tanks discolourised the most by turning into dark brown, followed by oil samples stored in HDPE tanks that turned light orange. However, the oil sample from the stainless-steel tank was still greenish in colour which showed it managed to maintain the biodiesel quality despite the outdoor condition. The contamination intensity can be assumed by observing the colour clarity of the fuel (Elkelawy et al., 2019). On the other hand, the fuel in indoor condition showed no obvious colour changes indicating that oxidation may had slightly took place or even possibly did not occur at all during the 180 days storage period (Mohamed Shameer & Mohamed Nishath, 2019). The colour change in the biodiesel was not further investigated in this work; though previous research had observed biodiesel discolouration occurrence due to bacterial contamination in the storage tank (Jain & Sharma, 2010).

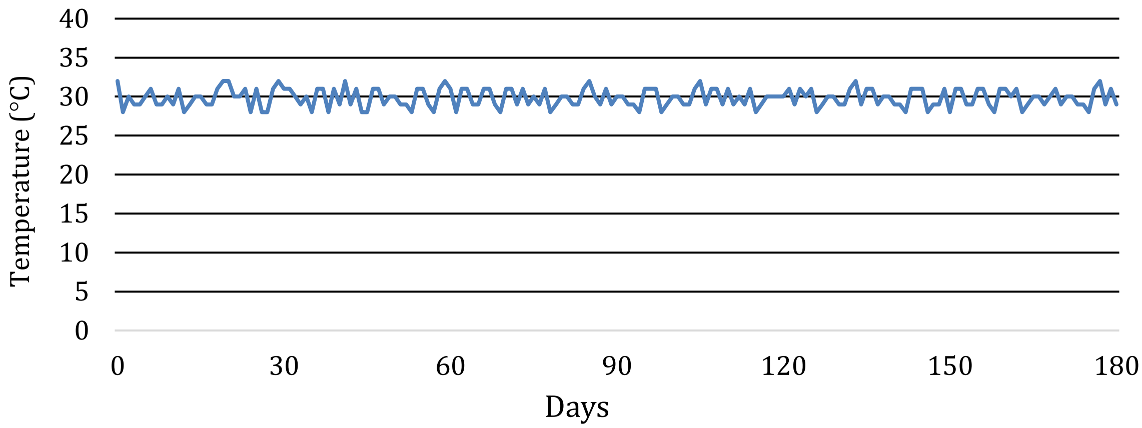


(a) (b) (c)

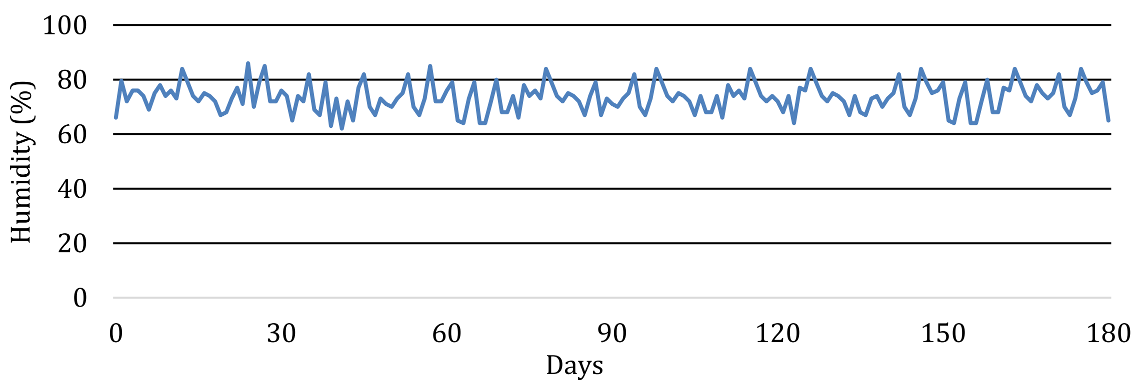
Figure 3: Colour changes in biodiesel (a) initial, (b) indoor after 6 months and (c) outdoor after 6 months.

3.2 Temperature and Humidity Recording

The temperature and humidity of outdoor environmental conditions are presented in Figure 4 (a) and Figure 4 (b) respectively. The overall surrounding temperature values were observed to be between 28°C to 32°C and the humidity values were between 65% to 87%. In this range of temperature and humidity, the changes on the parameters were significant throughout 180 days storage period. The humidity was monitored as biodiesel is hygroscopic; the higher the humidity, the quicker it will absorb moisture from the atmosphere.



(a)



(b)

Figure 4: Outdoor environment data on: (a) temperature and (b) humidity.

3.3 Evaluation on Biodiesel Properties

In this paper, the effect of storage materials placed in two different storage conditions was observed for 180 days of storage period, using several tanks shapes which data is presented in Tables 2 and 3. As observed from the data in the tables below, biodiesel properties change correlate to the different types of storage tank materials and the different surroundings. This is also concluded by previous researchers (Azizul et al., 2020; Ku et al., 2015; Nanihar et al., 2019; Zakaria et al., 2014). On the other hand, there is no significant impact of the tank shape on the biodiesel properties.

It can be seen that density in indoor storage after 180 days period exhibits a constant trend in Table 2. For oil samples stored in outdoor condition, the presence of saturated fatty acid and oxidation process was observed, shown by the increase in density value in Table 3. The increase in density was significant in outdoor condition by a maximum of 10.51% (0.09 kg/m^3) for the glass storage, but for indoor, the difference was observed at about 0.12% (0.001 kg/m^3) for HDPE material. This is due to higher surrounding temperature and humidity as presented in Figure 4 for outdoor storage condition. Oxidation products can increase biofuel density; a higher rate of oxidation increases the mass of oil and fat due to the formation of sediments at the bottom of the storage tanks. An increase in density can be hazardous because it can affect fuel injection equipment which influences the combustion process.

Table 2: Initial and final properties of indoor biodiesel B10 stored in cylindrical storages made from various materials after 180 days of storage duration.

Physical properties of B10		**Initial reading**	**Final reading (Day 180)**		
			HDPE	**Glass**	**Stainless steel**
Density	kg/m^3	0.828	0.829	0.828	0.828
Flashpoint	°C	76	73	74	75
Viscosity	cSt	2.8768	2.8786	2.8774	2.879
Acid value	mgKOH/g	0.1789	0.2231	0.2236	0.2178
Water content	%	0.0122	0.0135	0.0135	0.0139

Table 3: Initial and final properties of outdoor biodiesel B10 stored in storages made from various materials with various shapes after 180 days of storage duration.

Physical properties of B10		**Initial reading**	**Final reading (Day 180)**				
			HDPE		**Glass**		**Stainless steel**
			Cylindrical	**Cuboid**	**Cylindrical**	**Cuboid**	**Cylindrical**
Density	kg/m^3	0.828	0.875	0.866	0.908	0.915	0.844
Flashpoint	°C	76	70	69	71	70	70
Viscosity	cSt	2.8768	3.4169	3.3923	3.5588	3.5151	3.0675
Acid value	mgKOH/g	0.1789	0.4155	0.4149	0.4479	0.4381	0.3758
Water content	%	0.0122	0.0324	0.0318	0.0392	0.0388	0.0256

Table 4: Percentage change properties of biodiesel B10 after observation for 180 days in indoor and outdoor condition.

Physical properties of B10	Percentage change, % (Day 180)							
	HDPE			Glass			Stainless steel	
	Outdoor		Indoor	Outdoor		Indoor	Outdoor	Indoor
	Cylindrical	Cuboid	Cylindrical	Cylindrical	Cuboid	Cylindrical	Cylindrical	
Density	5.68	4.59	0.12	9.66	10.51	0	1.93	0
Flashpoint	7.89	9.21	3.95	6.58	7.89	2.63	7.89	1.32
Viscosity	18.77	17.92	0.06	23.71	22.19	0.02	6.63	0.08
Acid value	132.25	131.92	24.71	150.36	144.88	24.99	110.06	21.74
Water content	165.57	160.66	10.66	221.31	218.03	10.66	109.84	13.93

Kinematic viscosity had also undergone increment during the storage period similar to density. The main contributor to the rise in biodiesel viscosity during storage is the production of oxidized polymeric. Oxidized products can initiate the production of gums and sediments, which can block engine filters. Other than that, higher molecular weight leads to greater viscosity. The viscosity of methyl esters increases by the formation of more polar and oxygen-containing molecules. The viscosity increases as peroxides reach a certain level which starts the oxidation process. The oxidation process leads to the formation of double bond isomerization and free fatty acids which increased the kinematic viscosity and density.

The flashpoint of a substance must be considered when determining its overall flammability danger. For the flashpoint parameter, the reduction was not that significant, though compared to the environmental conditions, flashpoint in outdoor conditions was reduced by 23.71% as presented in Table 4. The chemical properties of flashpoints are influenced by the number of carbon atoms and double bonds. Therefore, the flashpoint of biodiesel drops as the length of the carbon chain of the compound molecules decreases in length. This is because larger molecules have fewer interactions with one another. Smaller molecules are more easily converted into vapors (Jafarihaghighi et al., 2020). Meanwhile, the rate of change for acid value in indoor conditions was lower compared to outdoor conditions as presented in Table 2. This increment is also proven in previous research (Nanihar et al., 2019; Yusof et al., 2015). An increase in acid value indicates the degradation of methyl esters. The hydroperoxide which is obtained from oxidation undergoes complex secondary reactions into aldehydes which further oxidizes into acids. Acids may also be generated when traces of water cause the esters to hydrolyze into alcohols and acids. When subjected to high operating temperatures, biodiesel oxidizes due to the reactivity of biodiesel molecules with oxygen in the air (Ashraful et al., 2014). Moreover, diesel is more stable than biodiesel in terms of oxidation due to the higher oxygen content in biodiesel.

Another reason of these increments in biodiesel properties stored in outdoor conditions as presented in Table 3 was the storage tank materials. Compared to HDPE and stainless steel, glass is transparent and has direct exposure to sunlight or any kind of light. Sun exposure increases fuel degradation especially on unsaturated components of the biodiesel (Blanchfield, 2016). The same phenomenon applies to water content. Light exposure and higher humidity increase the water content rate. Besides that, biodiesel has a stronger polarity than petroleum diesel due to the presence of ester bonds. The water content increases when exposed to the sun because biodiesel has hygroscopic properties which can absorb water 6.5 times more than diesel under similar relative humidity which leads to higher corrosivity (B. B. He et al., 2007).

It was also observed that the container shapes did not have any major impact on the parameters in this study. Moreover, the storage tank was not corroded in this paper due to using a lower biodiesel blend (B10).

CONCLUSION

This study shows that, as the storage period increases in outdoor conditions, the kinematic viscosity, density, water content, and acid values increase; meanwhile, flashpoint decrease in all high-temperature storage cases. However, in indoor condition, the parameters have only a slight increment; the effect of storage material and storage period on biodiesel stability is minimal as the indoor condition delays the degradation process of the biodiesel. Nevertheless, the increase in value of oil samples properties in outdoor condition is not only caused by molecular structure but also affected by higher temperature and humidity. Although only five parameters were observed, they are sufficient to prove that the oxidation has taken place in storage tanks placed in outdoor conditions during the testing period. It is also shown that the shape of storage tanks does not have any major impact on biodiesel properties. It can be concluded that glass is a good storage material for chemical resistance, but it has to be placed in an enclosed space to reduce its degradation. Stainless steel can also be considered as a potential storage material but shall only be used to store lower biodiesel blends.

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