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The Effects of Long-Term Storage on the Quality of Palm Oil Biodiesel and Canola Oil Biodiesel

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Highlights:

- After 12 months storage of biodiesel in a closed and dark container at 22 °C, density, kinematic viscosity, acid value, glycerol, and peroxide increased, while FAMEs compounds decreased.
- Storage of biodiesel under a closed and dark container at 22°C conditions helped minimize oxidation.
- In both POB and COB, the GCMS results showed decreases in 9-octadecenoic acid methyl ester and 9,12-octadecadienoic acid (Z,Z)-methyl ester, whereas there were increases in 9-octadecenoic acid and 9,12-octadecadienoic acid (Z,Z).
- FTIR results revealed the presence of methyl ester functional groups and negligible formation of ketones and aldehydes during biodiesel oxidation.

Abstract. Effective storage of biodiesel has proven to be a challenge, which the Indonesian government has invested billions of Indonesian rupiahs (IDR) in to overcome. It is thus important to investigate how different storage methods can affect the quality of biodiesel. The purpose of this study was to determine how storage at room temperature in the dark affects the quality of palm oil biodiesel (POB) and canola oil biodiesel (COB). POB and COB were stored in closed containers at 22 °C in the dark for 12 months. The results showed that POB was more significantly damaged than COB. This study found increases of density (POB by 51.52 kg/m³ and COB by 17.52 kg/m³), kinematic viscosity (POB by 0.67 mm²/s and COB by 0.32 mm²/s), acid value (POB by 0.27 mg-KOH/g and COB by 0.25 mg-KOH/g), total glycerol (POB by 0.58%-mass and COB by 0.60%-mass), and peroxide value (POB by 48 meq-O₂/kg and COB by 7.11%-mass and COB by 9.36%-mass). Gas chromatography-mass spectrometry results

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for POB and COB showed decreases in 9-octadecenoic acid methyl ester and 9,12octadecadienoic acid (Z,Z)-methyl ester, and increases in 9-octadecenoic acid and 9,12-octadecadienoic acid (Z,Z). Fourier transform infrared spectroscopy (FTIR) results revealed the presence of methyl ester functional groups. The storage of biodiesel in a closed container at 22 °C in the dark can minimize biodiesel oxidation, as evidenced by the findings of this study, namely, the insignificant formation of ketone and aldehyde groups in the biodiesel oxidation process during storage, based on the results of FTIR.

Keywords: biodiesel; palm oil; canola oil; oxidation; storage time.

1 Introduction

The main conventional energy sources are petroleum, other fossil fuels, and methane. Although they are currently our primary energy sources, they are set to run out given the increasing demand for such nonrenewable fuels. The main factor behind the decline in fossil fuel reserves has been increasing industrialization [1], and from 1970 to 2015 global consumption of fossil fuels was roughly 78% of the total production.

Biofuels are renewable sources of energy that can be defined as fuels produced through the chemical or natural processing of decomposed plants, animals, and other agricultural products. Biodiesel is a form of biofuel; it is extracted from plant oils and plant material through the chemical processes of transesterification and esterification [2]. As an alternative fuel, biodiesel has received attention worldwide for being renewable and having the potential to reduce life cycle emissions from diesel engines [3]. The life cycle of biodiesel production primarily consists of three processes, namely, oil palm plantation, palm oil production, and biodiesel production [4]. In 2011, biodiesel production in Indonesia was 1.8 million kL and in 2016, it reached 3.6 million kL. Indonesia's target for 2025 is 8.7 million kL. However, effective storage of biodiesel has proven to be a challenge, with the Indonesian government having invested billions of Indonesian rupiah (IDR) in overcoming this challenge [5].

The effect that storage has on the quality of biodiesel is important because biodiesel has to go through a storage process before reaching its destination, regardless of its type. Studies on the effects of storage on the quality of biodiesel have been performed, particularly focusing on storage and oxidation stabilities [6]; oxidation, thermal, and storage stabilities [7]; air-tight storage at two different temperatures (15 °C and 40 °C) with a light screen [8]; storage stability and corrosive characteristics of stabilized biodiesel exposed to carbon and galvanized steel [9]; the storage stability of biodiesel blends [10]; microbial storage stability [11]; long-term storage stability [12,13]; long-term storage at ambient temperature and 40 °C [14]; the long-term storage stability of biodiesel

blends [15]; and the effect of antioxidants on storage [16]. Quality tests carried out in previous studies focused on density [13,17]; viscosity, acid value [7,12,13,18]; peroxide content [19]; total glycerol, fatty acid methyl ester (FAME) content [20]; and Fourier transform infrared spectroscopy (FTIR) [21].

However, we did not find reports of studies on the extents of decreases of specific types of methyl ester during storage. Studies on the increase of total glycerol during biodiesel storage have also not been reported. As such, this study aimed to determine the effect of storage in the dark at room temperature on the quality of palm oil biodiesel (POB) and canola oil biodiesel (COB), by evaluating the density, viscosity, acid value, total glycerol, FAME, and peroxide values, and by performing gas chromatography-mass spectrometry (GCMS) and FTIR tests.

2 Materials and Methods

2.1 Materials

This study utilized palm oil and canola oil, which were obtained from local supermarkets. Other materials were methanol (99%; Merck), ethanol (95%; Merck), potassium hydroxide (KOH; Merck), chloroform (99%; Merck), acetic acid glacial (Brightchem), sodium thiosulfate (Merck), potato starch solution, phenolphthalein, hydrochloric acid (HCl; Merck), periodic acid (Merck), sodium hydroxide (NaOH; Merck), and potassium iodide (KI).

2.2 Characterization of Raw Materials

The density, viscosity, and acid value of the raw materials were identified before transesterification. These elements were chosen from previous work conducted by Hadiyanto, *et al.* [22]. Raw materials with low acid values – not exceeding 2.0 mg-KOH/g – were ready for transesterification [23].

2.3 Transesterification

We found two oils with low acid values, allowing the transesterification process to proceed. KOH (1% of the mass of the oil mixture (1% wt)) was used as a catalyst. The transesterification process lasted for 2 h at 65 °C, and the molar ratio of oil to methanol was 1:6. The result was left in a separating funnel for 24 h, resulting in the formation of two layers. The top layer was biodiesel, containing FAMEs, and the bottom layer was glycerol as a by-product. The biodiesel was then washed with distilled water (at 60 °C), to remove residual potassium hydroxide catalyst and methanol until the washing water reached neutral pH. Finally, the washed biodiesel was heated to 105 °C to remove residual water. The final product was pure biodiesel.

2.4 Biodiesel Storage

POB and COB samples were stored for 12 months in closed plastic bottles at 22 °C in the dark. All test parameters were measured before and after storage, to determine the effects of temperature, darkness, and the duration of storage on the density, viscosity, acid value, glycerol levels, and FAME levels of the samples. Samples were extracted once a month for quality testing.

2.5 Testing Methods

2.5.1 Density

The mass of an empty 5 ml pycnometer was weighed. Each biodiesel sample was then preheated to 40 °C and inserted into the pycnometer. The filled pycnometer was weighed using a Pioneer Ohaus scale with an accuracy of 0.0001 g. The mass of the biodiesel was obtained by subtracting the mass of the empty pycnometer from the total mass of the filled pycnometer. The density of the biodiesel sample was calculated using the following equation:

$$\rho = \frac{m}{v} \tag{1}$$

where ρ , m, and v are the density (g/ml), mass (g), and volume (5 ml) of biodiesel, respectively.

2.5.2 Kinematic Viscosity

Kinematic viscosity was tested using an NDJ-5S digital rotary viscometer in accordance with standard operating procedures. Before the kinematic viscosity test, 30 ml of biodiesel was heated to 40 °C. The viscometer was set at 60 rpm, and its rotor was allowed to rotate until the measured values were stable. Lastly, the kinematic viscosities displayed on the viscometer were recorded.

2.5.3 Acid Value

Acid value was examined in accordance with the Association of Official Analytical Chemists (AOCS) Cd 3d-63 in 2009 [24], which was ratified in Indonesian National Standard (SNI) 7182 in 2015 [25].

2.5.4 Total Glycerol

Total glycerol content was determined in accordance with AOCS Ca 14–56 in 2011 [26], which was ratified in SNI 7182 in 2015 [25].

2.5.5 FAMEs and Yield

FAMEs and yields were tested in accordance with SNI 7182 in 2015 [25].

2.5.6 GCMS

GCMS is an analytical technique to identify substances contained in a test sample, which combines the features of gas chromatography and mass spectrometry [27]. In the present study, GCMS was performed to determine the reduction of the percentage of methyl ester compounds and their identities in biodiesel.

2.5.7 FTIR

FTIR is a technique used to obtain the infrared spectrum of the absorption or emission of solids, liquids, or gases. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectrum range [28]. In the present study, FTIR was conducted to determine the methyl ester, alcohol, ketone, and aldehyde functional groups contained in the biodiesel.

3 Results and Discussion

3.1 Characteristics of the Raw Materials

The characteristics of the raw materials for biodiesel production need to be studied to determine whether this process requires only transesterification or if esterification is also required. Table 1 shows the characteristics of the raw materials.

Test parameters	Raw material samples		
	Palm oil	Canola oil	
Density (kg/m ³)	912	902	
Kinematic viscosity (mm ² /s)	61.2	35.6	
Acid value (mg-KOH/g)	0.561	0.494	

Table 1Characteristics of the raw materials.

The acid value represents the amount of free fatty acids contained in raw material. The higher the acid value, the more free fatty acids it contains [29]. The acid value of high-value raw materials should not exceed 2.0 mg-KOH/g, and if it does, it should be reduced through esterification [23]. The transesterification process is inefficient for raw material with a high acid value, with most of it forming soap and a little producing methyl esters [30]. As demonstrated in Table 1, both palm oil and canola oil were below the acid value limit, so the transesterification process alone was sufficient for the efficient production of biodiesel, which created methyl esters, with very little soap forming [30,31].

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3.2 Density during Storage

Figure 1 shows the density of POB and COB during 12 months of storage; it was directly proportional to the storage time. After 12 months of storage, the density of POB had increased by 51.52 kg/m³, from 837.94 kg/m³ to 889.46 kg/m³. The density of COB after 12 months of storage had increased by 17.52 kg/m³, from 858.12 kg/m³ to 875.64 kg/m³. This is in line with Ashraful, *et al.* and Jose and Anand [17,13]. Ashraful, *et al.* [17] reported that the density of POB of storage for 3 months increased by 3.2 kg/m³, from 864.9 kg/m³ to 868.1 kg/m³. Jose and Anand [13] reported that the density of Karanja oil biodiesel after 10 months of storage increased by 30 kg/m³, from 880 kg/m³ to 910 kg/m³. The increase in density is mainly the result of oxidation and depends on the concentration of fatty acids in biodiesel. Oxidation is followed by a polymerization reaction, in which smaller molecules combine to form larger ones, thus tending to increase the density of the fuel as the storage period extends [13,32].

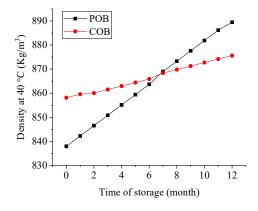


Figure 1 The density of POB and COB during 12 months of storage.

3.3 Kinematic Viscosity during Storage

Figure 2 shows the kinematic viscosities of POB and COB over the 12-month storage period. Kinematic viscosity is directly proportional to the storage time, which means that, as storage time passes, the viscosity increases. The kinematic viscosity of POB after 12 months of storage increased by $0.67 \text{ mm}^2/\text{s}$, from 5.80 mm²/s to $6.47 \text{ mm}^2/\text{s}$. The kinematic viscosity of COB after 12 months of storage increased by $0.32 \text{ mm}^2/\text{s}$, from $5.58 \text{ mm}^2/\text{s}$ to $5.90 \text{ mm}^2/\text{s}$. This is in line with the findings of Bouaid, *et al.* [12] and Jain and Sharma [7]. According to Bouaid, *et al.* [12], the viscosity of sunflower oil biodiesel (SFOB) after 30 months of storage increased by 7.5 mm²/s, from 5 mm²/s to 12.5 mm²/s. Jain and Sharma [7] reported that the viscosity of Jatropha curcas biodiesel (JCB) after 6 months

of storage increased by 1.9 mm²/s, from 4.4 mm²/s to 6.3 mm²/s. The kinematic viscosity of biodiesel indicates an oxidizing effect during storage that causes the viscosity to increase. The formation of oxidized polymers is a major contributor to the increase in viscosity of biodiesel during storage [17,33]. Mittelbach and Gangl [34] compared the effect of bright and dark storage conditions and closed and open containers on the viscosity of biodiesel; they found that storage in open containers and bright conditions increased viscosity the most.

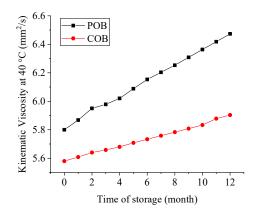


Figure 2 Kinematic viscosity of POB and COB during 12 months of storage.

3.4 Acid Value During Storage

Figure 3 shows the acid value of POB and COB during 12 months of storage. Acid value describes the amount of acid in biodiesel. The acid value of POB after 12 months of storage increased by 0.27 mg-KOH/g, from 0.11 mg-KOH/g to 0.38 mg-KOH/g. For COB, there was a corresponding increase of 0.25 mg-KOH/g, from 0.16 mg-KOH/g to 0.40 mg-KOH/g. This is in line with the findings of Bouaid, et al. [12], and Jain and Sharma [7,18]. Bouaid, et al. [12] reported that the acid value of SFOB after 30 months of storage increased by 1.4 mg-KOH/g, from 0.1 mg-KOH/g to 1.5 mg-KOH/g. Meanwhile, Jain and Sharma [7] reported that the acid value of JCB after 6 months of storage increased by 0.32 mg-KOH/g, from 0.18 mg-KOH/g to 0.5 mg-KOH/g. POB and COB acid values increase with storage time, making the biodiesel more easily oxidized [18,35], and the oxidation of biodiesel causes the formation of acid compounds. The acid value increases with the formation of peroxide because esters are first oxidized to peroxides [36]; they then undergo complex reactions including separation to aldehydes [37,38], which are more reactive and further oxidized to acid. The acid value also increases with storage time because of the hydrolysis of the methyl esters to fatty acids [12].

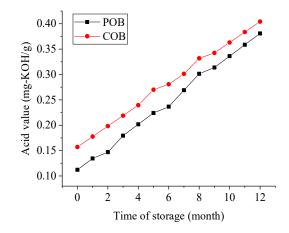


Figure 3 Acid value of POB and COB during 12 months of storage.

3.5 Total Glycerol Content during Storage

Figure 4 shows the total glycerol of POB and COB during 12 months of storage; it also shows how it increased with storage time.

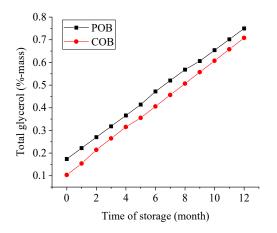
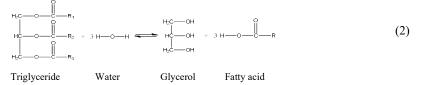


Figure 4 Total glycerol of POB and COB during 12 months of storage.

The total glycerol of POB increased by 0.58%-mass, from 0.17%-mass to 0.75%-mass, while that of COB increased by 0.60%-mass, from 0.10%-mass to 0.71%-mass. This is in line with Silviana and Buchori [20]. Silviana and Buchori [20] reported that, owing to the length of the storage process, a transesterification

reaction occurs in residual methanol contained in biodiesel. This results in an increase in the glycerol content of biodiesel that has been stored for too long (>3 months). Methanol can also form from the hydrolysis of methyl esters [12], as seen in the hydrolysis reaction in Eq. (6). As the acid value and the glycerol value increase, the triglyceride hydrolysis reaction starts producing glycerol and fatty acids [39]. Eq. (2) represents the hydrolysis reaction of triglycerides.



3.6 FAME Content During Storage

Figure 5 shows the FAME content of POB and COB during 12 months of storage; it decreased with storage time for both biodiesels. The FAME content of POB after 12 months of storage decreased by 7.11%-mass, from 98.22%-mass to 91.11%-mass, while that of COB decreased by 9.36%-mass, from 98.78%-mass to 89.43%-mass. This is in line with Silviana and Buchori [20], who reported that the FAME content of POB after 6 weeks of storage decreased by 3.27%-mass, from 98.07%-mass to 94.80%-mass. The decrease in ester levels is caused by oxidation [36] and hydrolysis [12], as shown in Eq. (6); this results in the degradation of biodiesel. The ester contained in biodiesel turns into acid via degradation, as shown in Figure 3; the longer the storage time, the higher the acid value. The increasing acid value proves the decrease in the methyl ester levels contained in biodiesel [20].

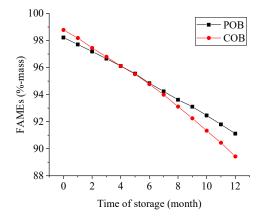


Figure 5 FAME content of POB and COB during 12 months of storage.

3.7 Peroxide Value During Storage

Figure 6 shows the peroxide values of POB and COB during 12 months of storage; it also shows how it increased with storage time. The POB peroxide value increased by 48 meq-O₂/kg, from 18 meq-O₂/kg to 66 meq-O₂/kg, and that of COB increased by 54 meq-O₂/kg, from 20 meq-O₂/kg to 74 meq-O₂/kg. This is in line with the work of Bondioli, *et al.* [19].

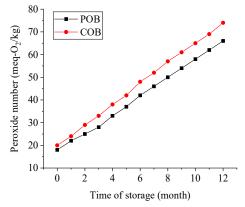


Figure 6 Peroxide values of POB and COB during 12 months of storage.

The oxidation of biodiesel is caused by unsaturation of the fatty acid chains and reflects the presence of double bonds in the fatty acid molecules, which indicates a high level of reactivity with O₂, especially upon exposure to air or water. Highly unsaturated fatty compounds disproportionately reduce the stability against oxidation [40]. Hence, the oxidation mechanism can be divided into two categories: primary and secondary oxidation. Primary oxidation occurs in three stages, namely, initiation, propagation, and termination [41]. The initiation involves removing hydrogen from carbon atoms to create carbon free radicals. If diatomic oxygen is present, the reaction that forms peroxy radicals occurs rapidly, not even allowing a substantial alternative to carbon-based free radicals [42]. Carbon free radicals are more active than peroxy ones. However, peroxy free radicals are reactive with hydrogen atoms to form carbon and other fatty acid hydroperoxide (ROOH) radicals. The newly formed carbon free radicals can react with diatomic oxygen and continue the propagation cycle. The equation representing the initiation for basic oxidation is as follows:

$$RH + I \rightarrow R + IH$$
 (3)

Throughout the oxidation system, the ROOH levels increase very rapidly after the induction period has been reached [36]. During the induction period, ROOH can directly or indirectly change the properties of fatty oils and biodiesel. Fatty

acids react with oxygen molecules, to produce unstable peroxide radicals (ROO), which in turn react with the fatty acids (RH) of the original substrate. The transfer of hydrogen atoms from fatty acids to peroxide radicals will result in the formation of ROOH. The radical chain reaction is shown in Eqs. (4) and (5), where the reaction with oxygen results in the formation of new fatty acid radicals (R) due to the addition of ROOH and maintains the chain reaction [41].

$$R \cdot + O_2 \to ROO \cdot \tag{4}$$

$$ROO \cdot + RH \rightarrow ROOH + R \cdot$$
 (5)

ROOH levels can peak and then decrease or increase and stabilize when oxidation takes place. The disintegration of ROOH continues due to its peak concentration. Insufficient oxygen levels can slow or even stop the formation of ROOH. In our study, the storage containers were kept closed, to minimize the exposure to oxygen. As a result, the peroxide value remained below the maximum of previous studies, namely 300 to 400 meq O_2/kg [36,43].

Secondary oxidation comprises various products, including short-chain carboxylic acids, alcohols, high-molecular-weight oligomers, and aldehydes; they are formed even at room temperature during the secondary oxidation stage, whereas ROOH continues to decompose and interact [44]. Several studies observed various secondary oxidation products from different experiments using biodiesel, such as aldehyde compounds, during the oxidation of vegetable oils, including 2,4-heptadienal, pentane, propane, heptenals, and hexenal [37,38].

3.8 GCMS Test Results

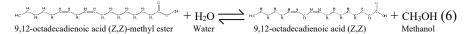
The GCMS test aimed to determine the %-area and identities of methyl esters contained in the biodiesel. Table 2 shows the profile of chemical compounds.

Name	%-area			
	POB	POB after 12 months of storage	СОВ	COB after 12 months of storage
9-octadecenoic acid methyl ester (CAS) \$\$ oleic acid methyl ester	48.55	47.58	57.73	40.11
9-octadecenoic acid (CAS) \$\$ oleic acid	0.77	0.79	0.42	0.88
9,12-octadecadienoic acid (Z,Z)-methyl ester (CAS) \$\$ linoleic acid methyl ester	13.81	12.67	20.46	16.25
9,12-octadecadienoic acid (Z,Z)-(CAS) \$\$ linoleic acid	0.22	0.25	0.15	0.26

 Table 2
 Profile of chemical compounds in the biodiesel samples.

Table 2 shows that there were decreases in 9-octadecenoic acid methyl ester and 9,12-octadecadienoic acid (Z,Z)-methyl ester in both POB and COB after 12

months of storage. The 9-octadecenoic acid methyl ester content of POB decreased by 0.97%-area, from 48.55% to 47.58%-area. In COB, it decreased by 17.62%-area, from 57.73% to 40.11%-area. The 9,12-octadecadienoic acid (Z,Z)-methyl ester content of POB decreased by 1.14%-area, from 13.81% to 12.67%-area. The 9,12-octadecadienoic acid (Z,Z)-methyl ester content of COB decreased by 4.21%-area, from 20.46% to 16.25%-area. Increasing acid values are indicative of decreased methyl ester levels. Increasing acid value was caused by the conversion of methyl esters into fatty acids through the hydrolysis process [12]. Minami and Saka [39] reported that the hydrolysis reaction of 9,12-octadecadienoic acid (Z,Z)-methyl ester turns it into 9,12-octadecadienoic acid (Z,Z), as per Eq. (6).



3.9 FTIR Test Results

FTIR aimed to determine the methyl ester functional groups in biodiesel. Figure 7 shows the FTIR spectra of POB and COB.

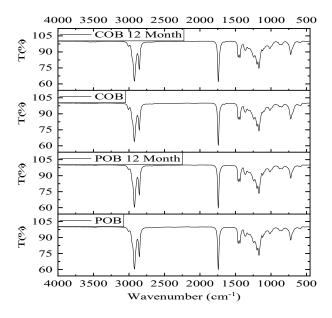


Figure 7 The FTIR spectra of the biodiesel samples.

The FTIR graph (Figure 7) shows the characteristic bands that the spectra of the optimal methyl esters contained for POB and COB. The absorption band at 3007 to 2854 cm⁻¹ represents asymmetric and symmetric CH₃ stretching vibrations (-CO-O-CH₃), and the characteristic absorption band at 1742 cm⁻¹ represents the carbonyl ester group (C=O). The presence of C=C represents the characteristic stretching mode of the olefin, which was found at 1656 cm⁻¹. The band at 1461 to 1437 cm⁻¹ was due to bending (-C-H) in the alkanes, and the band at 1196 to 1016 cm⁻¹ was associated with the strain vibration of the ester (-C-O-) group. This is in line with Fadhil and Abdulahad [45] and Al-dobouni, *et al.* [46]. Al-dobouni, *et al.* [46] and Fadhil, *et al.* [47] studied the conversion of oil to a suitable ester and found that the area under the peaks of the C=O band, the stretch of the C-H band, and the C-H band of binder were smaller in the methyl ester than those found in the oil. This can be explained by the substitution of glycerol by methoxy radicals [48].

Saluja, *et al.* [49] reported that, during oxidation, peroxide and hydroperoxide were formed, developing short-chain compounds, such as ketones and aldehydes. The absorption of ketones occurs at 1750 to 1660 cm⁻¹, while the absorption of aldehydes occurs at 2900 to 2700 cm⁻¹. After 12 months of storage, the POB and COB samples in our study did not exhibit increases in absorption intensity at 1742 cm⁻¹ (ketone) and 2854 cm⁻¹ (aldehyde) and instead stayed the same as before storage. This shows that the formation of ketones and aldehydes during biodiesel oxidation is negligible. According to Furlan, *et al.* [21], oxidation strongly influences the IR spectrum, as it results in the formation of hydroperoxides, alcohols, acids, aldehydes, and ketones.

4 Conclusions

In this study, all test parameters of POB and COB were affected by storage time. After 12 months in a closed container at 22 °C in the dark, POB showed increases in density of 51.52 kg/m³, kinematic viscosity of 0.67 mm²/s, acid value of 0.27 mg-KOH/g, total glycerol of 0.58%-mass, and peroxide value of 48 meq-O₂/kg, along with a decrease in FAMEs of 7.11%-mass. Meanwhile, COB exhibited increases in density of 17.52 kg/m3, kinematic viscosity of 0.32 mm²/s, acid value of 0.25 mg-KOH/g, total glycerol of 0.60%-mass, and peroxide value of 54 meq-O₂/kg, along with a decrease in FAMEs of 9.36%-mass. In both POB and COB, the GCMS results showed decreases in 9-octadecenoic acid methyl ester and 9,12-octadecadienoic acid (Z, Z)-methyl ester, whereas there were increases in 9octadecenoic acid and 9,12-octadecadienoic acid (Z, Z). The FTIR results revealed peaks showing low formation of ketone and aldehyde groups in the biodiesel oxidation process during storage. Based on these results, the quality of POB and COB after the storage period remained adequate. The most suitable conditions for the long-term storage of biodiesel are room temperature, a closed container, and dark conditions. The storage of biodiesel under these conditions helps minimize oxidation.

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