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Influence of Transesterification Catalysts Synthesized with Citric Acid on the Quality and Oxidative Stability of Biodiesel from Black Soldier Fly Larvae

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Abstract: In biodegradable waste management, use of Black Soldier Fly Larvae (BSFL) is a promising method for bioconversion of waste into crude insect fat as feedstock for biodiesel production. Biodiesel is a renewable alternative to fossil fuel, but it is more susceptible to oxidative degradation over long-term storage. This study investigates the effectiveness of NaOH and CaO catalysts synthesized with citric acid (CA) in improving the oxidative stability of biodiesel. The biodiesel and biodiesel/diesel blends derived from BSFL were stored at 63 °C for 8 days. The quality of biodiesel was determined by analysis of the physicochemical and fuel properties by: Fourier transform infrared (FTIR) spectroscopy, ultraviolet visible spectrophotometer (UV-Vis), gas chromatography-mass spectroscopy (GC-MS), bomb calorimeter and titration methods. Properties that were analyzed included: peroxide value, acid value, iodine value, refractive index, density, calorific value, total oxidation (TOTOX), anisidine value and fatty acid profile. The results showed that catalysts synthesized with CA retarded the decomposition of unsaturated fatty acids, resulting in a significant delay in the formation of hydroperoxides. Besides, 10-oxo-octadecanoic acid, an antioxidant, was present in biodiesel produced using catalysts synthesized with CA, hence enhancing the stability of biodiesel against oxidation. Catalysts synthesized with CA slowed the decomposition of monounsaturated fatty acids by 6.11–11.25%. Overall, biodiesel produced using catalysts synthesized with CA was observed to degrade at a slower rate than biodiesel produced using commercial calcium oxide. The reduced degradation rates demonstrate the effectiveness of the synthesized catalysts in enhancing the oxidation stability and consequently the fuel qualities of biodiesel from BSFL under accelerated storage.

Keywords: biodiesel; Black Soldier Fly Larvae; catalyst synthesis; fatty acid methyl esters; oxidizability index; physicochemical properties; total oxidation

1. Introduction

Environmental concerns and depletion of fossil fuels have motivated the search for renewable fuel sources. Biodiesel, a clean alternative to fossil fuels, is commercially produced from edible oil, resulting in a high cost of production [1]. Bioconversion of waste to insect fat using Black Soldier Fly Larvae (BSFL) is a promising source of feedstock for biodiesel production which doubles as a biowaste management method [2,3]. Although

biodiesel is a clean fuel alternative with favorable benefits, such as lower environmental toxicity and biodegradability, it possesses poor fuel stability characteristics.

Fuel stability is defined as the ability of a fuel to resist degradation over a long storage period, mainly three months for biodiesel. Biodiesel is majorly composed of unsaturated fatty acid methyl esters (FAME), which are vulnerable to environmental conditions or autoxidation and which impair the fuel properties [4]. Degradation of the properties of biodiesel can be as a consequence of: oxidation, thermal decomposition, hydrolysis or microbial contamination [5]. The quality and stability of the biodiesel from various feedstock is mostly affected by oxidation.

The oxidative stability of oils and esters is primarily dependent on the composition of the fatty acids present in the biodiesel [6]. Fatty acids deteriorate with time, causing degradation of biodiesel, and hence oils with a higher composition of polyunsaturated fatty acids, such as linolenic acid, are more susceptible to rapid oxidation [7]. Other factors that affect the oxidation stability of biodiesel include: metal contaminants, primary and secondary oxidation products and the storage conditions of the fuel [5], while other factors that accelerate the degradation of biodiesel include the presence of impurities such as gums and exposure to metal surfaces [8,9].

Degradation through oxidation results from radical attacks on the unsaturated sites of the FAMEs chain. The initial stage of biodiesel degradation is termed primary oxidation or peroxidation, in which hydrogen is abstracted from carbon atoms to form a carbon-free radical ($R\cdot$). Oxygen then reacts with the carbon-free radical to form a peroxy radical, which in turn abstracts a hydrogen atom to form hydroperoxides ($ROOH$) and another carbon-free radical, as shown in Figure 1 [5–10]. The formed carbon-free radical reacts with oxygen and the propagation cycle continues.

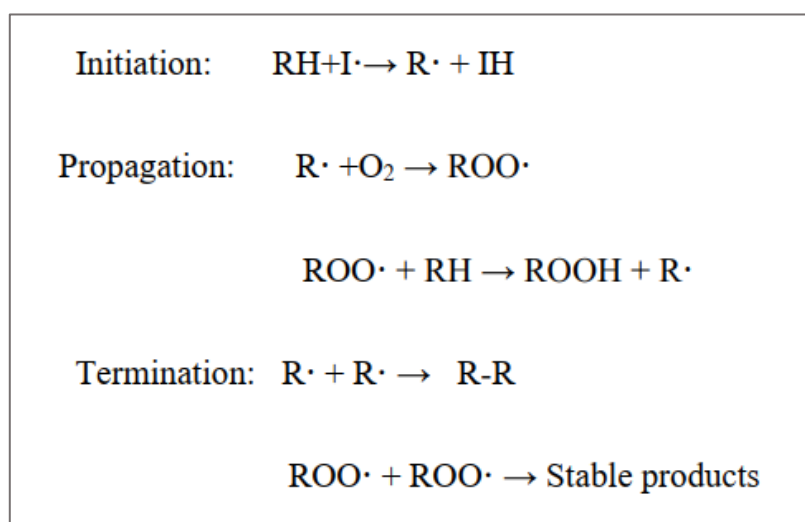


Figure 1. Oxidation chain reaction for hydroperoxide formation.

The formed unstable hydroperoxides, which are primary oxidation products in the biodiesel, then decompose to form secondary oxidation products such as ketones, aldehydes and/or carboxylic acids. These are short-chain hydrocarbons that attack the long-chain molecules of the biodiesel, as shown in Figure 2 [11]. Unsaturated fatty acids (UFA) composed of double bonds homolyze more readily at lower temperatures than saturated fatty acids (SFA); therefore, UFA are important initiators of oxidation in lipids [6,12].

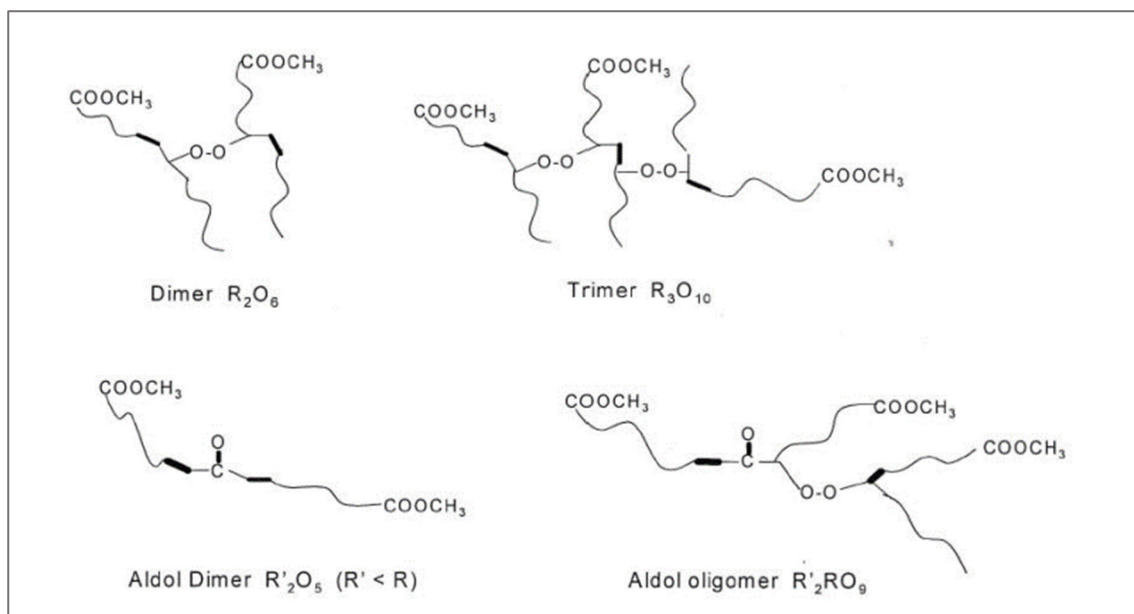


Figure 2. Types of hydroperoxide oligomers that can form, resulting in degradation of biodiesel.

Oxidation accelerates the aging of biodiesel and results in changes in the fuel's essential parameters, such as: viscosity, density, NO_x emission composition, acid value, insoluble sediments and engine fuel conversion efficiency [13]. Oxidation stability of biodiesel from various feedstock sources can be characterized by several methods, such as FAMES composition analysis by the oxidizability index (OX), primary oxidation products level by the peroxide value (PV), secondary oxidation products level by the anisidine value (AnV), physical properties, such as density and viscosity, and accelerated oxidation test methods [5]. The accelerated oxidation test methods include: the active oxygen method (AOCS Cd12-57), the Rancimat induction period (IP) or the oil stability index (OSI) and differential scanning calorimetry (DSC) [14]. Schaal's oven test method has been adopted by various researchers for accelerated degradation of biodiesel, taking 24 h at 63 °C or 1 week at 43 °C as equal to 1 month of storage under room temperature (21 °C) according to ASTM D6425 [15–18]. Schaal's oven test method has been reported as one of the best methods that correlate real-time aging of biodiesel and oils in oxidative stability experiments [19,20].

Other complementary techniques that have been used to determine the quality and oxidation stability of biodiesel include the Fourier transform infrared spectroscopy (FTIR) method of analysis of the spectrum vibration difference in the area of the carbonyl band (at approximately 1746 cm^{-1}) and analysis of the refractive index [13,21,22]. Typically, no single test method has been reported to be adequate for biodiesel oxidation analysis; hence, several techniques are used simultaneously to sufficiently characterize the quality and stability of biodiesel [5].

The products of secondary oxidation can be detected by a sensitive wet chemistry method using UV absorption with p-anisidine according to ISO 6885 [23]. The AnV is a measure of secondary oxidation that indicates the extent to which 2,4-alkadienals and 2-alkanals are generated as a result of hydroperoxide decomposition, while the PV gives a measure of early indication of rancidity [14]. Hence, the total oxidation value (TOTOX) is used as a measure of PV in conjunction with AnV as an indicator of both the oxidative stability and the deterioration potential of FAMES [5]. The AnV measures the secondary oxidation content, making it a more suitable predictor of oxidation stability for thermally stressed oils by the accelerated storage method.

Developing novel methods to realize biodiesel yield with high oxidative stability is an important aspect for successful breakthrough in enhancing biodiesel fuel quality. Among the experimented biodiesel feedstock, Black Soldier Fly Larvae (BSFL) oil has

been reported to have high oxidative stability potential due to its high composition of SFA (60–70%) and low polyunsaturated fatty acids (PUFA) at 2–9% [24,25]. However, experimental reports regarding the oxidative stability of the biodiesel and biodiesel/diesel blends from BSFL oil have not been adequately documented. Various techniques that have been reported to improve the oxidation stability of biodiesel include: the use of additives and antioxidants [26,27], blending biodiesel with petroleum diesel and higher alcohols such as propanol and pentanol [28] and washing biodiesel with antioxidants such as citric acid (CA) [29]. Washing biodiesel with CA has been reported to improve the oxidation stability of the biodiesel from IP of 8 to 25 h and also act as a chelating agent to prevent oxidation due to metal contaminants [30,31].

CA is a tricarboxylic acid commonly found in citrus fruit and commercially produced through fungal fermentation [32]. Synthesizing catalysts with citric acid has been reported to improve the catalytic activity of catalysts as well as the quality of methanol produced in methanation [33–35]. Our previous study investigated the effects of synthesizing transesterification catalysts with CA on biodiesel yield and reported that CA improved the catalytic activity of the catalysts by enhancing the crystallite size and dispersion of the particles [36]. The effects of synthesizing transesterification catalysts with CA on the quality of the produced biodiesel have not been adequately reported.

The choice of catalysts in transesterification reaction depends on the free fatty acid (FFA) content of the oil. While homogenous catalysts such as NaOH and KOH have higher reaction rates than heterogenous catalysts, their application is limited to oils with a low FFA of less than 1% due to the formation of soap [37,38]. Besides, homogenous catalysts are difficult to separate from biodiesel and glycerol, leading to high water consumption during product recovery [39]. BSFL has a high composition of FFA, and therefore the use of a heterogenous catalyst can increase the biodiesel yield by impeding saponification [40].

Biodiesel from BSFL is composed of saturated and unsaturated fatty acids. The unsaturated fatty acids are prone to oxidation when exposed to air, leading to fuel degradation, which in turn compromises the quality of the biodiesel. This study evaluates the effectiveness of synthesizing transesterification catalysts (NaOH and CaO) with citric acid on the quality and oxidative stability of biodiesel produced from BSFL that were fed on kitchen waste. The two catalysts were chosen based on their catalytic type: NaOH is a homogenous catalyst while CaO is a heterogenous catalyst. Synthesizing NaOH with CA forms a heterogenous catalyst for performance comparison with CaO.

2. Materials and Methods

2.1. Catalyst Preparation

NaOH and CaO catalysts were synthesized with CA by precipitation and impregnation methods, respectively, following the procedure reported by Kathumbi et al. [36]. The catalysts, NaOH and CaO, were synthesized with 130% and 40% CA loading weight percent (wt.%) at 80 °C, respectively. The modified catalysts were then dried at 110 °C for 12 h in an oven. Thereafter, the synthesized catalysts, NaOH/CA and CaO/CA, were calcined in a furnace at 600 and 900 °C, respectively, for 4 h. In this study, the synthesized catalysts, NaOH/CA and CaO/CA, as well as the commercial CaO (AR Grade, 98%) catalyst, were used for biodiesel production for a quality comparison of the biodiesel under accelerated thermal storage.

2.2. Oil Extraction from BSFL and Transesterification into Biodiesel

BSFL were reared on organic kitchen waste at Jomo Kenyatta University of Agriculture and Technology (JKUAT), in Kenya. After feeding the larvae for 28 days, they were harvested, washed, dried in an oven at 85 °C for 8 h and then ground using a domestic blender. Oil was extracted from the 500 g of ground BSFL biomass using hexane at a biomass to solvent ratio of 1:3.

A two-step esterification followed by transesterification method was used to produce biodiesel. Esterification was carried out by boiling 100 mL of BSFL oil in 220 mL of methanol

and 1% H₂SO₄ at 100 °C for 1 h on a temperature-controlled hotplate equipped with a magnetic stirrer, followed by transesterification of 100 mL of oil in methanol and 1.8% of the catalyst at 90 °C for 1 h under stirring. Once the reaction was complete, the catalyst was separated from biodiesel and the by-products by centrifugation. Then, a funnel separator was used to separate biodiesel, methanol and glycerol. The biodiesel was then washed with warm distilled water, separated and filtered to remove impurities, and then dried in a rotary evaporator. Biodiesel was stored in a dark bottle away from light prior to experimental analysis.

2.3. Sample Preparation and Oxidation by Accelerated Thermal Storage

Schaal's oven test was applied for oxidation at 63 ± 3 °C (AOCS method Cd 12-57) to accelerate the aging of biodiesel and biodiesel/diesel blends. Biodiesel blends with petroleum diesel were made by mixing the two fuels using a Voltex ultrasonic mixture for 30 s. For each catalyst used (NaOH/CA, CaO/CA and CaO) in biodiesel production, five biodiesel/diesel blends: B2.5, B5, B10, B20 and B100, were made by volume ratios, where, for example, B2.5 represents a 2.5% volume of biodiesel in the sample and B100 is pure biodiesel at 100%.

The samples were placed in an oven with an air fan at 63 °C for 8 days. After every 24 h, 10 mL of a sample was removed from the oven and flushed with nitrogen. The samples were covered and stored in a dark place at room temperature prior to testing.

2.4. Analysis of Physiochemical Properties of Biodiesel and Biodiesel/Diesel Blends

Biodiesel and biodiesel/diesel blends' properties were analyzed according to the methods summarized and presented in Table 1.

Table 1. Analytes and test methods for quality of biodiesel and biodiesel blends.

Analyte	Apparatus	Method	Source
Iodine value (g/100 g)	Titration	AOAC (920.158)	[41]
Acid value (mg KOH/g)	Titration	AOAC (993.20)	[41]
Peroxide value (meq/kg)	Titration	AOAC (965.33)	[42]
FFA (%)	Titration	AOAC (940.28)	[4]
Kinematic viscosity at 40 °C (mm ² /s)	Fensky viscometer	ASTM D445	[27]
Density at 40 °C		Analytical method	
Calorific value	Bomb calorimeter (CAL2K)	ASTM D240	
Refractive index	Refractometer (RFM330)	AOAC 977.17	[41]

2.4.1. Determination of Peroxide Value (PV)

Biodiesel samples (0.5–1 g) were dissolved in 10 mL of chloroform-acetic acid mixture in a volume ratio of 2:3. Then, 1 mL of potassium iodide was added, and the flask was covered and stored in the dark for 5 min. After incubation, 20 mL of distilled water was added, and the sample was agitated for 1 min. Then, 1 mL of 1.5% starch solution was added. The liberated iodine was titrated with 0.01 N sodium thiosulphate. The PV was then expressed in terms of milliequivalent (meq) of O₂ per kilogram of the sample, as presented in Equation (1):

$$\text{PV (meq/kg)} = \frac{V \times N \times 1000}{W} \quad (1)$$

where:

V = volume of sodium thiosulphate used in titration (mL),

N = normality of sodium thiosulphate,

W = weight of the biodiesel sample (g).

2.4.2. Determination of Acid Value (AV) and Iodine Value (IV)

The AV and IV of biodiesel were determined by titrations following the procedure described by Ishmail and Ali [41]. AV was determined by dissolving 1 g of the sample in 10 mL of ethyl alcohol and boiling in a water bath for 2 min, and thereafter titrated against 0.1 N KOH solution using a phenolphthalein indicator. A blank sample was tested without the biodiesel and the AV was then expressed as mg KOH required to neutralize 1 g of biodiesel.

The IV was determined by dissolving 0.5 g of biodiesel in 20 mL of chloroform. Then, 10 mL of Wijs solution was added and the mixture was stored in the dark for 30 min. Afterwards, 100 mL of distilled water was added followed by titration with 0.1 N sodium thiosulphate, using starch solution as an indicator. Similarly, a blank sample was used and the IV was computed as grams of I₂ per 100 g of biodiesel sample.

2.4.3. Determination of p-Anisidine Value (AnV)

The pigments present in the biodiesel and biodiesel/diesel blends were analyzed using an ultraviolet visible spectrophotometer (Cary 60) by measuring the absorbance in the range of 200–600 nm. The p-anisidine value (AnV) was determined following the method described by Neto et al. [43]. The samples were prepared using a 10 mL volumetric flask, a micropipette and a volumetric pipette. Specifically, a known amount (0.5–1 g) of the biodiesel samples was dissolved in 2.8 mL of hexane (sample solution) and the absorbance was measured at 350 nm (A₀). Next, 1 mL of p-anisidine solution (2.5 mg/mL in glacial acetic acid PA) was added to the sample solution, homogenized and kept in the dark for 10 min. The absorbance was measured at 350 nm (A₁). The AnV was then calculated using Equation (2) and the total oxidation (TOTOX) of biodiesel and biodiesel/diesel blends was then computed using Equation (3):

$$\text{AnV} = 25 \times \frac{(1.2 \times A_1) - A_0}{W} \quad (2)$$

$$\text{TOTOX} = \text{AnV} + 2\text{PV} \quad (3)$$

where:

W = weight of the biodiesel sample (g).

2.4.4. Determination of Fatty Acids' Composition

The samples of biodiesel and biodiesel blends were analyzed using gas chromatography-mass spectrometry (GC-MS) (Shimadzu QP2010SE series) equipped with a BPX5 capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas. The schematic diagram of the GC-MS setup is shown in Figure 3.

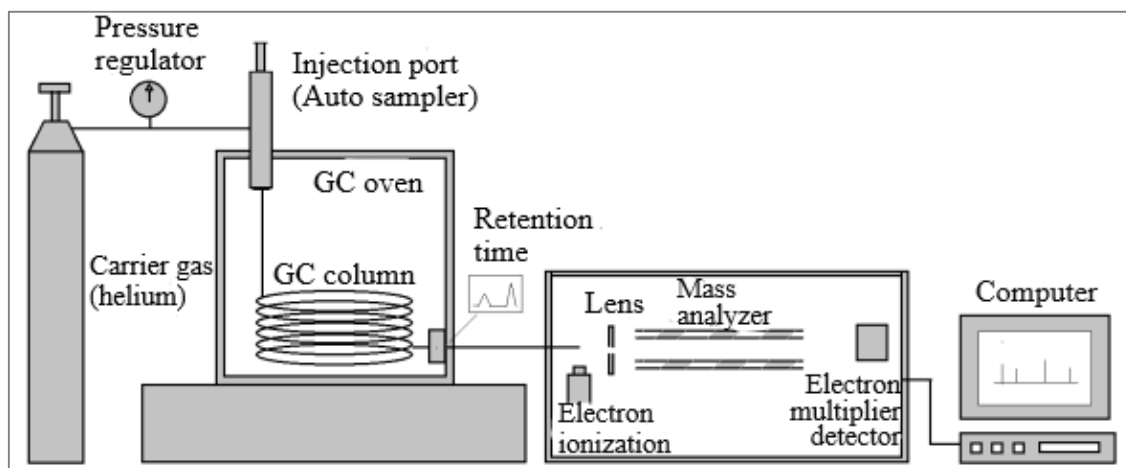


Figure 3. Block diagram of GC-MS setup.

The column temperature program was 80–260 °C, with a temperature ramp at 5 °C/min, helium carrier gas flow rate of 1.0 mL/min and a split injector (1:100) temperature of 250 °C. The NIST standard reference library was used for identification of the present fatty acids. Heptadecanoic acid was used as the internal standard (IS). The IS solution was prepared as described by Wang et al. [4]. Specifically, biodiesel sample (0.5 g) was added to 5 mL of methanol to make the sample solution. Then, 0.1 mL of sample solution (with IS) was put into a vial, diluted with 1 mL of methanol and injected using an autosampler into the GC-MS instrument for analysis.

The percentage of ester content (C) was calculated using Equation (4), as described by Suraj et al. [44]:

$$C = \frac{\sum A + A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100 \quad (4)$$

where: $\sum A$ = total area of peaks corresponding to FAME (mV/s), A_{IS} = peak area of IS (mV/s), C_{IS} = concentration of the IS (mg/mL), V_{IS} = volume of IS (mL) and m = mass of the biodiesel sample (mg).

Oxidizability (OX) was determined as an indicator of the relative rate of oxidation for the biodiesel and blends based on the composition of oleic acid (C18:1), linoleic acid (C18:2) and linolenic (C18:3) using Equation (5) [45,46]:

$$OX = \frac{[0.02(\%C18 : 1) + (\%C18 : 2) + 2(\%C18 : 3)]}{100} \quad (5)$$

2.4.5. Determination of Functional Groups of Biodiesel and Blends

The functional groups of neat biodiesel and its blends were analyzed at room temperature using a Bruker Alpha FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a temperature-controlled diamond attenuated total reflectance (ATR) accessory. Spectra were obtained in a range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} .

2.5. Statistical Analysis

Data were computed as mean $\pm$ standard deviation (SD) from three replicates. Excel spreadsheet was used to subject the results to an analysis of variance (ANOVA). A probability of 0.05 ($p \leq 0.05$) was set to define the significance level of the test result.

3. Results and Discussion

The changes in chemical properties and composition of BSFL biodiesel and blends with diesel during accelerated storage were used to evaluate the effectiveness of transesterification catalysts synthesized with CA in the quality and oxidative stability of the biodiesel. The physiochemical properties of BSFL oil and biodiesel are presented in Table 2.

All properties of biodiesel were improved in comparison to those of BSFL oil, indicating the effectiveness of the transesterification process. Acid value, kinematic viscosity and peroxide value showed the greatest improvements, by 63.9–69.1%, 44.0–44.2% and 13.6–15.2%, respectively. The properties of biodiesel produced by the modified catalysts closely compared to those of biodiesel produced by the CaO catalyst. Some properties, such as viscosity, calorific value and TOTOX, were improved by an average of 0.22%, 0.11% and 17.8%, respectively, when NaOH/CA and CaO/CA were used as catalysts, in comparison to the CaO catalyst. These results indicate that the synthesized catalysts (NaOH/CA and CaO) were effective in the transesterification of BSFL oil into biodiesel.

Table 2. Physiochemical properties of BSFL oil and biodiesel.

Properties	BSFL Oil	BSFL Biodiesel			EN 14214 Limits *
		NaOH/CA	CaO/CA	CaO	
Moisture content (%)	3.63	1.88	1.92	1.87	-
Density (kg/m ³)	885.26	868.14	868.01	868.22	860–900
Iodine value (g/100 g)	92.38	89.44	88.01	89.78	120 max.
Acid value (mg KOH/g)	3.1	1.118	1.112	1.02	0.8 max
Peroxide value (meq/Kg)	5.19	4.48	4.42	4.46	-
FFA (%)	1.33	0.68	0.53	0.46	-
Kinematic viscosity (mm ² /s)	7.97	4.44	4.46	4.46	2.5–6
Calorific value (MJ/kg)	39.17	39.28	39.31	39.25	-
Refractive index	1.4667	1.4566	1.4565	1.4566	-
% Ester content	97.74	98.66	98.82	98.66	96.5
TOTOX	3.88	3.92	4.06	4.856	-
Oxidizability (OX)	0.051	0.0342	0.0349	0.0344	-

* Biodiesel specification limits according to European standards [47].

3.1. Peroxide Value (PV)

PV indicates the primary oxidative degradation trail of biodiesel. The peroxide value of biodiesel from BSFL was found to range between 4.4 and 4.86 and 57.42 and 65.33 meq/kg at the beginning and at the end of the accelerated storage, respectively. The PV of BSFL oil was 5.19 meq/kg, which compares to that of non-edible oils, which has been reported to range between 4.36 and 9.82 meq/kg [48]. The accuracy of determining the PV of a sample has been of great concern in research [23]. In this study, the standard deviations for PV determination ranged from 8% to 10%, showing great reliability of the results obtained. Similar deviations have been reported by Guillen and Cabo [23] due to the high rates of hydroperoxides' generation and degradation, making it difficult to reproduce the PV values. The PV increased rapidly from Day 1 to a maximum value on Day 3 for biodiesel catalyzed with CaO and Day 4 for biodiesel from the synthesized catalysts, as shown in Figure 4.

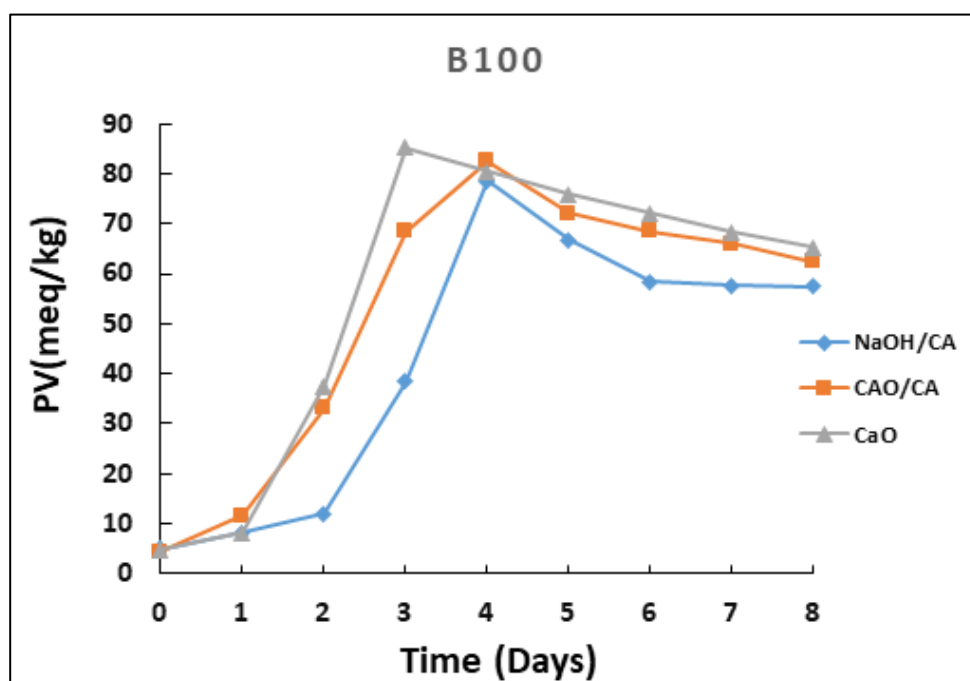


Figure 4. Peroxide value of B100 on different days under accelerated storage at 63 °C.

This is in agreement with findings by Guillén and Cabo [23], who reported that the PV of sunflower oil, rapeseed oil and safflower increased sharply during the initial days of accelerated storage at 70 °C. The rapid increase in PV may be a result of the high composition of oleic acid (11.29–14.29%), which could be the initiator of hydroperoxide formation. Previous studies have reported that even though oleic acid is monounsaturated, it is highly prone to thermal oxidation compared to linoleic and linolenic acid [49]. After Day 4, the PV curve started to decrease, indicating the propagation stage in the formation of hydroperoxides. This phenomenon indicating the different stages in hydroperoxides' formation has also been reported in [15,23,50].

Considering the effects of synthesizing the catalyst with citric acid, it was evident that NaOH/CA was the most effective in delaying the peak for hydroperoxide formation. The CaO/CA catalyst also resulted in a lower PV and a delayed hydroperoxide peak compared to commercial CaO. This indicated that synthesizing catalysts with CA was effective in retarding the degradation of biodiesel. This is in agreement with a study by Serrano et al. [51], who reported a lower PV for biodiesel that had been washed with citric acid during the purification step. The lower PV observed from biodiesel produced using catalysts synthesized with CA can be explained by the fact that CA chelates metal ions that stimulate decomposition of hydroperoxides in lipids [31].

3.2. *p*-Anisidine Value (AnV)

The AnV value is an indicator of secondary oxidation, which results in the formation of aldehydes (α and β -alkenals) that react with *p*-anisidine reagent and can be detected using UV-VIS spectroscopy. The results of the AnV of B100 and the blends under accelerated storage are presented in Figure 5 and Table 3, respectively.

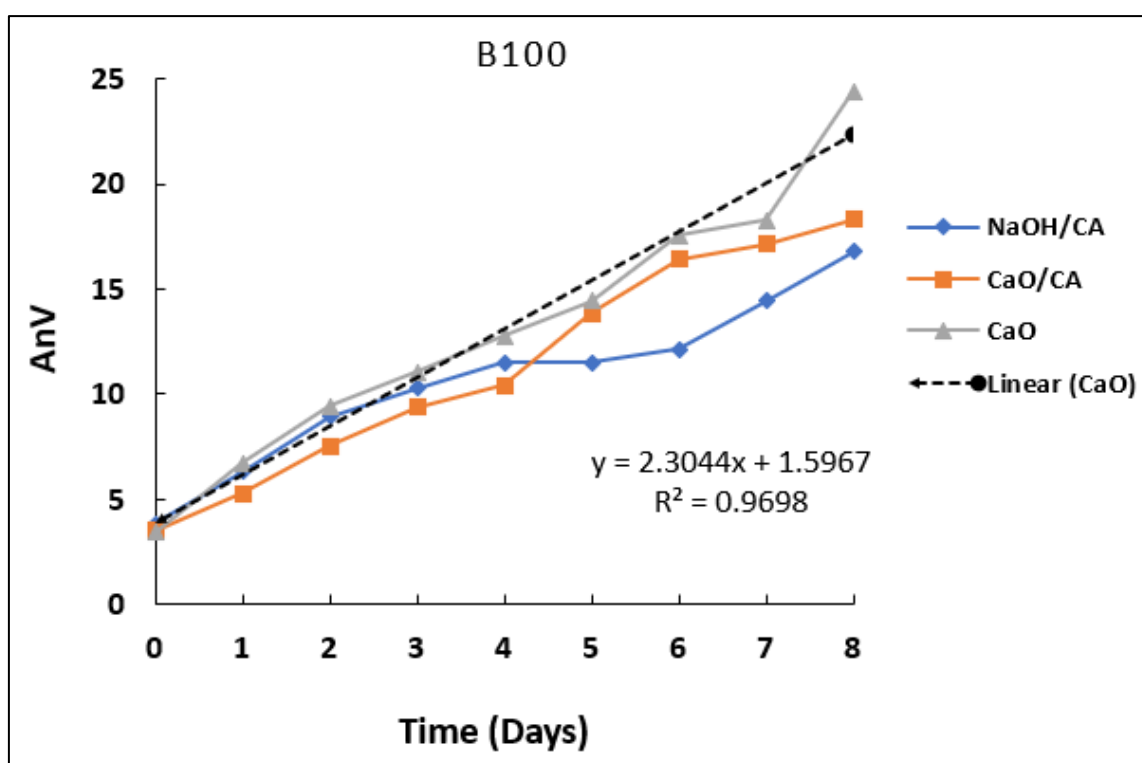


Figure 5. *p*-Anisidine values of biodiesel and biodiesel/diesel blends under accelerated storage. The R^2 value applies to the curve of the CaO catalyst.

Table 3. p-Anisidine values (AnV) of biodiesel and biodiesel blends under accelerated storage at 63 °C.

Storage Period	Biodiesel and Blends	p-AnV		
		NaOH/CA	CaO/CA	CaO
Day 0	B2.5	2.41 ± 0.49	2.45 ± 0.06	2.56 ± 0.11
	B5	2.46 ± 0.15	2.46 ± 0.41	2.47 ± 0.52
	B10	2.82 ± 0.81	2.82 ± 0.83	2.81 ± 0.51
	B20	2.88 ± 0.93	2.88 ± 0.14	2.87 ± 0.61
	B100	3.85 ± 0.11	3.53 ± 0.24	3.41 ± 0.96
Day 4	B2.5	3.56 ± 0.04	3.55 ± 0.46	3.58 ± 0.23
	B5	3.55 ± 0.53	3.56 ± 0.23	3.55 ± 0.48
	B10	3.84 ± 0.84	3.89 ± 0.13	3.86 ± 0.71
	B20	6.21 ± 0.61	6.45 ± 0.66	6.80 ± 0.94
	B100	11.51 ± 0.91	10.44 ± 0.41	12.76 ± 0.63
Day 8	B2.5	6.11 ± 0.44	6.50 ± 0.12	6.44 ± 0.13
	B5	6.44 ± 0.65	6.44 ± 0.32	6.40 ± 0.43
	B10	6.88 ± 0.16	6.92 ± 0.41	6.99 ± 0.67
	B20	9.86 ± 0.91	10.12 ± 0.09	11.61 ± 0.48
	B100	16.79 ± 0.42	18.33 ± 0.44	24.40 ± 0.94

The AnV for B2.5, B5 and B10 was below 10 over the 8 days of accelerated storage, while that of B100 was seen to increase from 3.53 to 24.4 (Table 3). The AnV of fresh biodiesel (B100) was 3.85, 3.53 and 3.41 for NaOH/CA, CaO/CA and CaO, respectively, which is comparable to that reported by Guillen and Cabo [23]. The effect of different catalysts on oxidation degradation was not noticeable for B2.5, B5 and B10 due to the high volumetric composition of diesel (Table 3). This could also be attributed to the low unsaturation in biodiesel blends leading to low accumulation of oxidation products. However, for B20 and B100, the effect of synthesizing the catalysts with CA was evident. Biodiesel produced by CaO showed a constant increase of AnV from Day 5, indicating advanced oxidation and accumulation of decomposed hydroperoxides in comparison to biodiesel from CaO/CA and NaOH/CA (Figure 5). The rate of increase of the AnV was lowest in biodiesel produced by NaOH/CA. In general, biodiesel produced by NaOH/CA and CaO/CA recorded a lower AnV in the long run, indicating that the synthesis played an effective role in retarding the formation of aldehydes in the produced biodiesel.

3.3. Total Oxidation Index (TOTOX)

The TOTOX indicates the overall oxidative state of FAMES by analysis of cumulative primary and secondary products of oxidation. It describes the quality of biodiesel. The TOTOX of biodiesel produced from BSFL using the three catalysts is presented in Figure 6.

The trend for TOTOX values (Figure 6) was seen to compare to that of PV (Figure 4) rather than to the AnV trend (Figure 5), indicating that primary oxidation was more noticeable than secondary oxidation in BSFL biodiesel. The TOTOX value of fresh biodiesel from BSFL was observed to range between 8.6 and 9.3, indicating high oxidation stability [52]. After Day 1 of accelerated storage, the TOTOX was seen to rapidly increase, which can be linked to the rapid formation of hydroperoxides, as previously shown by PV results. For biodiesel synthesized by CaO, the peak TOTOX value was attained on Day 3, while that for biodiesel from CaO/CA and NaOH/CA catalysts was reached on Day 4. At the end of the storage period, the TOTOX values of biodiesel produced by NaOH/CA and CaO/CA decreased by 17.9% and 8.26%, respectively, in comparison to the biodiesel produced by CaO. Lower TOTOX values indicate better quality of biodiesel [42]. Catalysts synthesized with CA delayed the TOTOX value peak and resulted in lower values over the entire storage period, a strong indication that the CA synthesis had a preservative effect against primary and secondary oxidation in biodiesel.

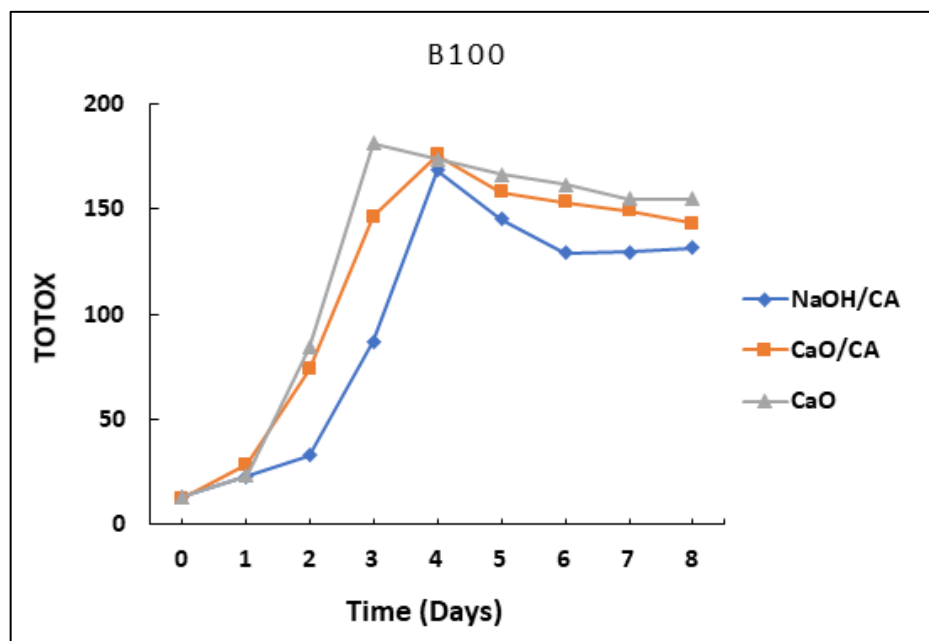


Figure 6. The TOTOX value for degraded biodiesel for increasing times based on PV and AnV.

3.4. Iodine Value (IV) and Acid Value (AV)

The IV of biodiesel indicates the degree of unsaturation (number of double bonds). The IV of biodiesel from BSFL was observed to range between 88 and 89.78 g I₂/100 g, showing a lower degree of unsaturation compared to edible oils and non-edible oils, such as sunflower (126.9 g I₂/100 g), Cucurbita pepo (150.37 g I₂/100 g) and Jatropha (102 g I₂/100 g) [48,53,54]. From these results, it can be seen that BSFL fed on kitchen waste have the ability to produce high-quality biodiesel.

The IV was observed to decrease with the increase in the storage period, indicating decomposition of the unsaturated fatty acids (USFA), as shown in Figure 7a.

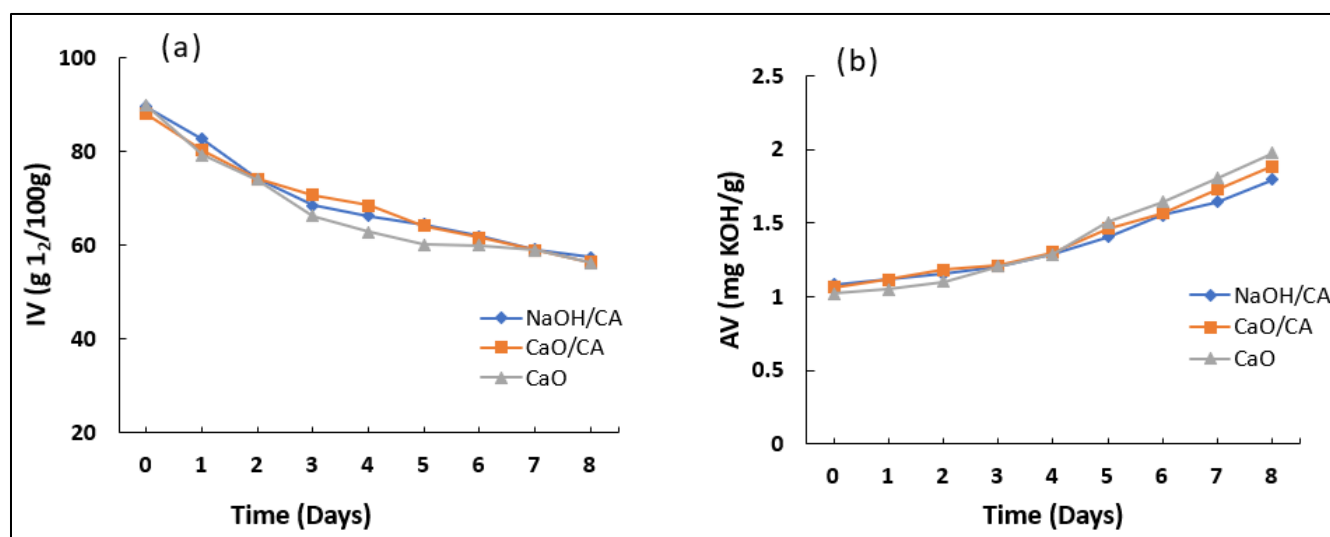


Figure 7. Results of the accelerated storage stability of B100: (a) iodine value and (b) acid value.

A rapid decrease in IV was observed from Day 0 to Day 3, which may indicate the initiation stage of lipid peroxidation, while the gradual decrease after Day 3 could indicate slight changes as the termination stage was reached [55]. Besides, the slow rate of

decrease in IV after Day 3 may be due to the low composition of USFA in BSFL biodiesel in comparison to SFA, as shown by the analysis from GC-MS (Section 3.6). Overall, the IV decrease was 37.77%, 35.93% and 37.42% in biodiesel produced using NaOH/CA, CaO/CA and CaO, respectively, after 8 days of accelerated storage. The effect of synthesizing the catalyst with CA on the degree of unsaturation in reference to the IV was not conclusive.

On the other hand, the AV (Figure 7b) increased with the accelerated storage period by 1.66-, 1.77- and 1.93-fold for biodiesel produced using NaOH/CA, CaO/CA and CaO, respectively, after 8 days of accelerated storage. Interestingly, the AV of fresh biodiesel produced from CaO was lower compared to the synthesized catalysts. However, after Day 4 of accelerated storage, the rate of increase in the AV of biodiesel from the synthesized catalysts was lower by 2.11% and 1.38% for NaOH/CA and CaO/CA, respectively, compared to that of biodiesel produced by CaO. These results indicate that synthesizing catalysts with citric acid could be effective in improving the AV of biodiesel in long-term storage. A rapid increase in AV was observed from Day 5, indicating an advanced stage of degradation, which may be attributed to the hydrolysis of biodiesel. Similarly, the sharp increase in AV was accompanied by a rapid increase in the density of the biodiesel, indicating hydrolysis and degradation of biodiesel due to increased moisture content. The AV of all samples increased over storage at 63 °C, and the rate of increase was slower for catalysts that were synthesized with citric acid.

3.5. Refractive Index (RI)

The RI of BSFL oil was determined as 1.4613, which was higher than that of the biodiesel (1.4429–1.4436). These results are in agreement with findings by Santos et al. [56]. The decrease in the RI shows the removal of some unsaturated compounds from the oil [41]. The RI of the biodiesel under accelerated storage was observed to range between 1.4566 and 1.4563 for fresh biodiesel and between 1.4508 and 1.4522 on Day 8 of the storage period, as shown in Figure 8.

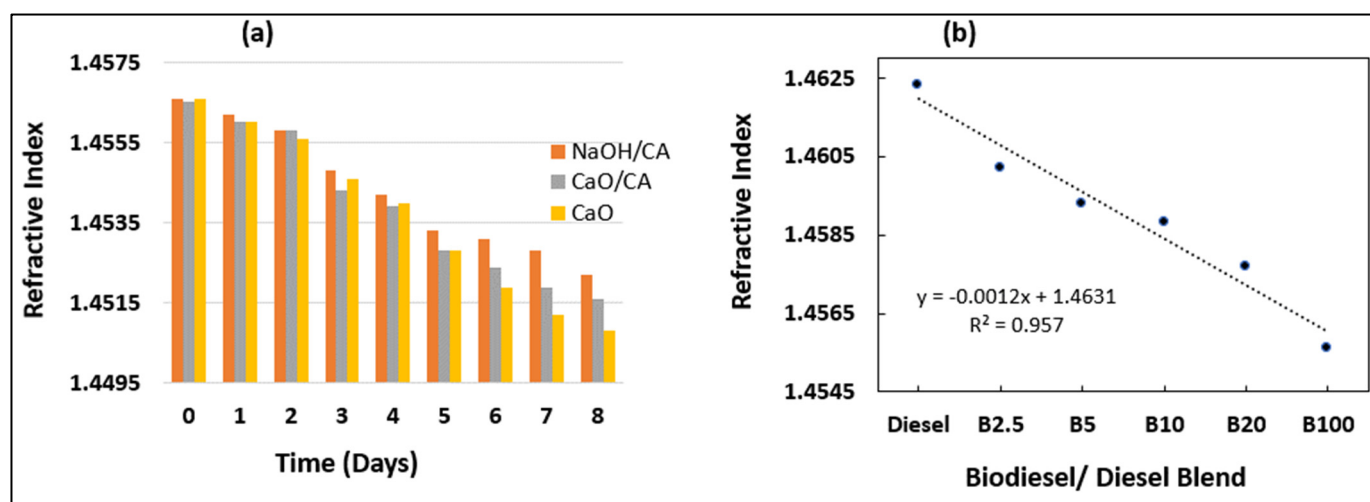


Figure 8. Refractive index of (a) biodiesel under accelerated storage, and (b) biodiesel, diesel and biodiesel/diesel blends.

The RI decreased with the increased storage period, which may relate to the reduction in the degree of unsaturation in degraded biodiesel. The RI of biodiesel produced using the NaOH/CA catalyst was seen to decrease at a lower rate compared to that produced by CaO/CA and CaO, indicating the effectiveness of synthesizing the catalysts with CA in inhibiting thermal oxidation of USFA in long-term storage of biodiesel. The RI of diesel and biodiesel/diesel blends was observed to be higher than that of B100, confirming the higher degree of unsaturated compounds in biodiesel, as shown in Figure 8b. These results are consistent with previous studies by Avlviso et al. [57], Santos et al. [58] and Santos et al. [56].

RI is an easy technique that does not require sophisticated equipment and analysis to determine the quality of biodiesel and oxidative rancidity in oils [59–61].

3.6. Fatty Acids' Composition Profile

The characteristics of the fatty acid composition of BSFL oil and its extracted biodiesel are presented in Table 4.

Table 4. Fatty acid composition of biodiesel synthesized from BSFL.

Fatty Acid	Number of Carbons and Double Bonds	Relative Composition (%)			
		Oil	Biodiesel		
			NaOH/CA	CaO/CA	CaO
Nonanoic acid	C9:0	1.08	0.04	Nd	Nd
Decanoic acid	C10:0	1.09	1.02	0.48	1.00
Dodecanoic acid	C12:0	28.55	43.84	45.36	48.68
methyl myristoleate	C14:1	Nd	0.35	0.22	0.29
Methyl Z-11-tetradecenoate	-	Nd	0.07	0.03	Nd
Methyl tetradecanoate	C14:0	5.03	8.48	8.83	7.29
Pentadecanoic acid	C15:0	Nd	0.03	Nd	Nd
9-Hexadecenoic acid	C16:1	Nd	0.19	Nd	0.15
10-Nonadecenoic acid	-	3.92	4.26	4.68	3.41
Hexadecanoic acid	C16:0	23.76	16.57	17.6	13.61
cis-10-Heptadecenoic acid	-	Nd	0.06	0.03	Nd
Heptadecanoic acid	C17:0	3.2	3.8	5.07	8.6
9,12-Octadecadienoic acid	C18:2	9.57	4.15	4.04	4.05
9-Octadecenoic acid	C18:1	21.92	14.94	11.36	11.29
Methyl stearate	C18:0	1.03	1.61	1.85	1.28
9,11-Octadecadienoic acid	C18:2	Nd	0.2	0.29	0.32
5,8,11,14-Eicosatetraenoic acid	C20:3	Nd	0.03	Nd	0.03
Nonadecanoic acid	C19:0	0.85	0.06	Nd	Nd
10-oxo-octadecanoic acid	-	0	0.3	0.16	Nd
Saturated fatty acids (SFA)		64.59	75.45	79.19	80.46
Monounsaturated fatty acids (MUFA)		21.92	15.48	11.58	11.73
Polyunsaturated fatty acids (PUFA)		9.57	4.38	4.33	4.4

Nd = Not detected.

The biodiesel was mainly composed of saturated fatty acids (SFA) (74.4–80.5%), monounsaturated fatty acids (MUFA) (11.5–15.4%) and polyunsaturated fatty acids (PUFA) (4.4–4.33%). The fatty acid composition was seen to vary from one catalyst to another, which is in agreement with a previous study by Allami and Nayebyzadeh [62]. The low composition of PUFA is an indication that biodiesel from BSFL is of high quality [10]. The major SFA that were observed included: dodecanoic, hexadecenoic and tetradecanoic acids. Three main MUFA present in BSFL biodiesel were: 10-nanodecenoic, hexadecenoic and 9-octadecenoic acids. A very low composition of PUFA was observed for 9,12-octadecadienoioc, 9,11-octadecadienoic and 5,8,11,14-eicosatetraenioc acids.

Comparing the fatty acid profile of oil to that of biodiesel, the transesterification was observed to result in a decrease in the composition of MUFA and PUFA, while that of SFA increased, indicating the effectiveness of the catalysts in the esterification reaction. The lower composition of MUFA and PUFA can be attributed to the fact that they are more prone to thermal decomposition as a result of high temperatures during the transesterification reaction. The decrease in the composition of UFA also indicates that the biodiesel produced was of better quality and was stable compared to the BSFL oil. B100 was mainly composed of saturated, monounsaturated and a low composition of polyunsaturated fatty acid methyl esters, and the biodiesel blends were observed to majorly contain alkane hydrocarbons with 14, 15 and 16 carbon atoms. Low compositions of SFA and MUFA were observed

in blends with a very low biodiesel volume ratio (B2.5 and B5). The absence of PUFA in B2.5 and B5 revealed the high stability of these two blends in accelerated storage. B10 and B20 showed 25% and 45% of FAMES, respectively, while the rest of the composition was mainly alkanes.

The oxidizability index (OX) of oils and biodiesel is an important measure as it determines the rate of reactivity of unsaturated lipids under oxidation [31]. The OX value of B100 ranged between 0.0460 and 0.0468 for fresh biodiesel and between 0.0269 and 0.0296 on Day 8 of accelerated storage, as presented in Figure 9.

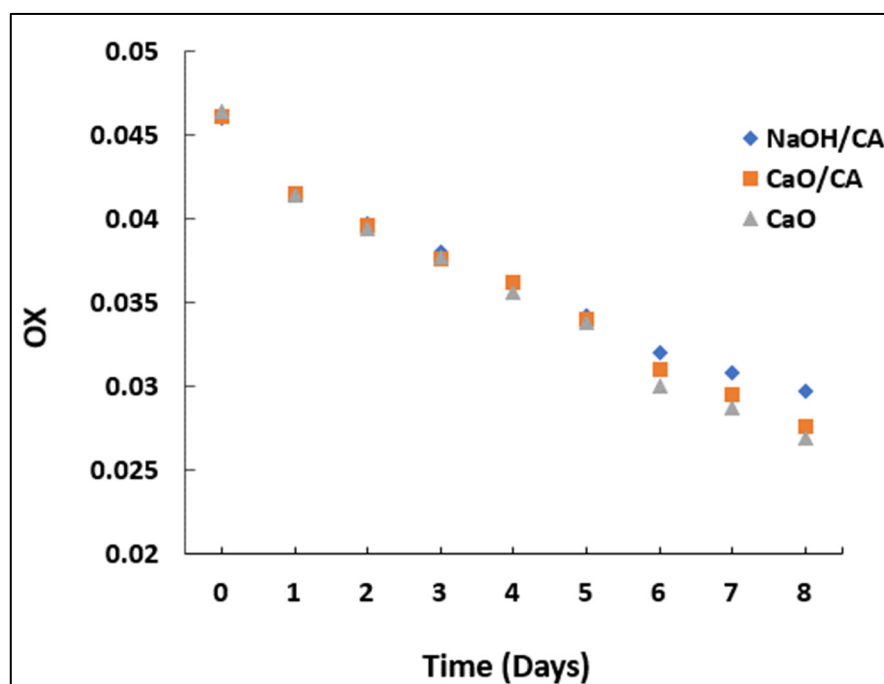


Figure 9. Oxidizability index of B100 under accelerated storage on different days.

The low OX can be attributed to the fact that BSFL biodiesel contains a very high composition of SFA, moderate MUFA and very low PUFA. Serrano et al. [51] demonstrated that oils with a low PUFA have a very high induction period as compared to those with a high PUFA composition. The OX increases with the degree of unsaturation. Kumar and Sharma [63] reported that vegetable oils with a very high PUFA of above 80% have an OX of 0.65–0.74. Likewise, high-oleic sunflower oil containing 8% SFA, 78% MUFA and 12.2% PUFA has been reported to have an OX of 0.12 [31]. This indicates that biodiesel from BSFL is more stable under storage compared to biodiesel from high-oleic vegetable oils.

PUFA play a major role in computation of the OX. The decrease in the OX of the biodiesel under accelerated storage indicates that the PUFA degraded with time. The OX of biodiesel produced using catalysts synthesized with CA decreased at a lower rate after Day 5, indicating slow degradation of PUFA in long-term storage. Overall, the OX was observed to decrease by 35.49%, 40.09% and 42.08% in biodiesel synthesized by NaOH/CA, CaO/CA and CaO catalysts, respectively.

On exposure to thermal degradation, the linoleic acid was observed to isomerize to methyl 10-trans,12-cis-octadecadienoate and methyl 9-cis,11-trans-octadecadienoate. These results are in agreement with previous reports that have reported the decomposition pathway for methyl linoleate into 9c,11t-18:2 and 10t,12c-18:2 [64]. The formation of these conjugated linoleic acids (CLA) was observed on the first, third and fourth days of accelerated storage for biodiesel produced using CaO, CaO/CA and NaOH/CA, respectively. The results indicated that catalysts synthesized with CA lagged the isomerization process of PUFA, which are prone to thermal oxidation. Additionally, 10-oxo-octadecanoic acid

methyl ester (KetoB), a CLA, was present in biodiesel produced using NaOH/CA and CaO/CA but absent in biodiesel produced using CaO. The oxo-methyl esters (KetoA, KetoB and KetoC) that are derived from linoleic acids in the presence of lactic acid have been reported to possess antioxidative effects that protect cells from oxidative stress [65]. This may explain why the OX value of biodiesel synthesized by NaOH/CA and CaO/CA was higher than that of biodiesel from CaO. The results indicated that 10-oxo-octadecanoic acid methyl ester can be formed in the presence of CA and has the ability to retard the degradation of PUFA, thus improving the oxidation stability of biodiesel in accelerated storage.

Overall, the FAME content of all samples decreased with the increased storage period. The change in fatty acid composition in relation to C12:0, C14:0, C16:0, C18:1 and C18:2 over the storage period is presented in Figure 10. The percentage composition of SFA (Figure 10a) was observed to slightly increase by 2.3–3% over the storage period, while that of USFA decreased due to degradation.

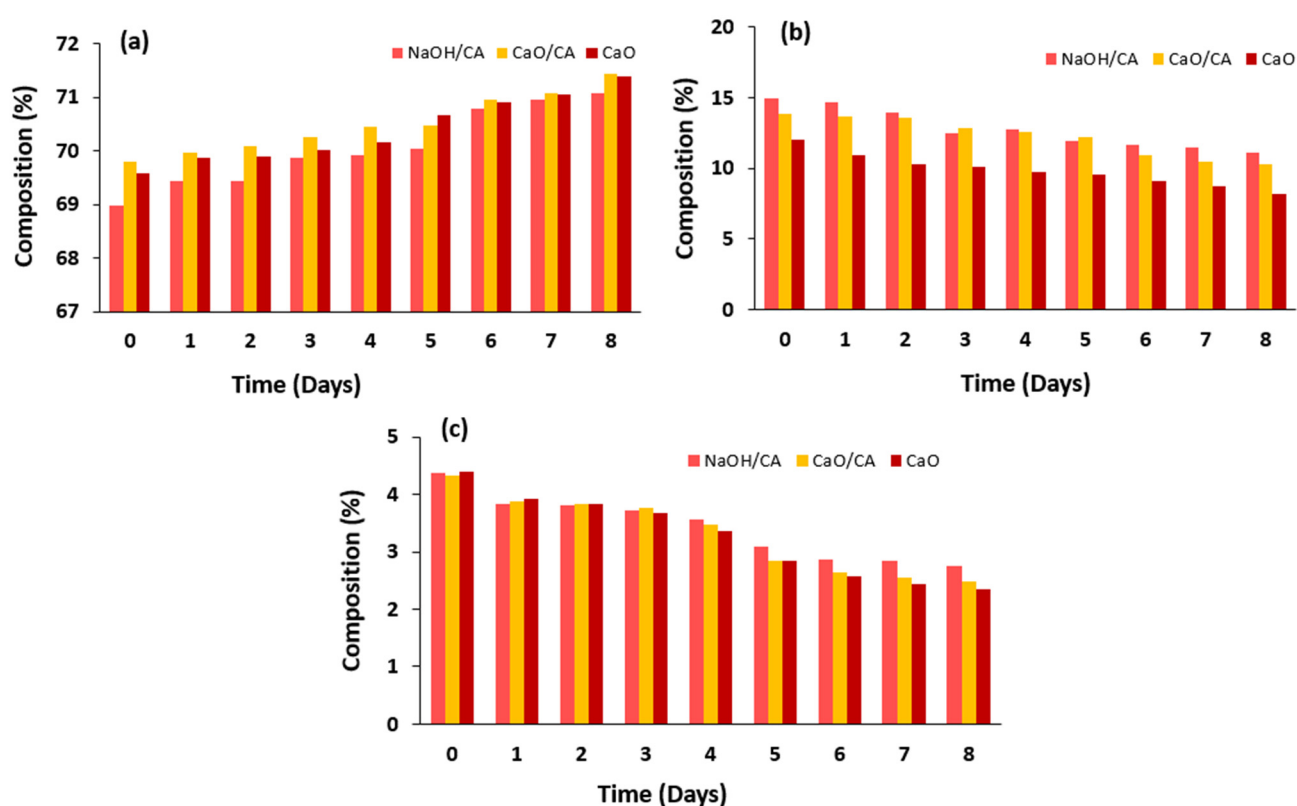


Figure 10. Composition of fatty acids in degraded biodiesel. (a) Saturated fatty acids, (b) monounsaturated fatty acids and (c) polyunsaturated fatty acids.

BSFL biodiesel has a very low composition of PUFA of 4.33–4.4%. Therefore, it can be said to be more stable over storage as compared to edible oils such as soybean and rapeseed oil that have been reported to contain high compositions of PUFA of 61.3% and 32.6%, respectively [51,66]. The effect of the catalysts synthesized with CA was more pronounced in slowing down the decomposition of MUFA (Figure 10b) as compared to PUFA (Figure 10c) by 6.11–11.25% and 5.24–6.01%, respectively, indicating a greater antioxidant effect on oleic acid in the FAMES. In addition, the linoleic acid decomposed 1.4–1.6 times more than the oleic acid, which is in agreement with previous studies by Frankel [31].

3.7. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The FTIR spectrum of biodiesel derived from BSFL before accelerated storage is presented in Figure 11a.

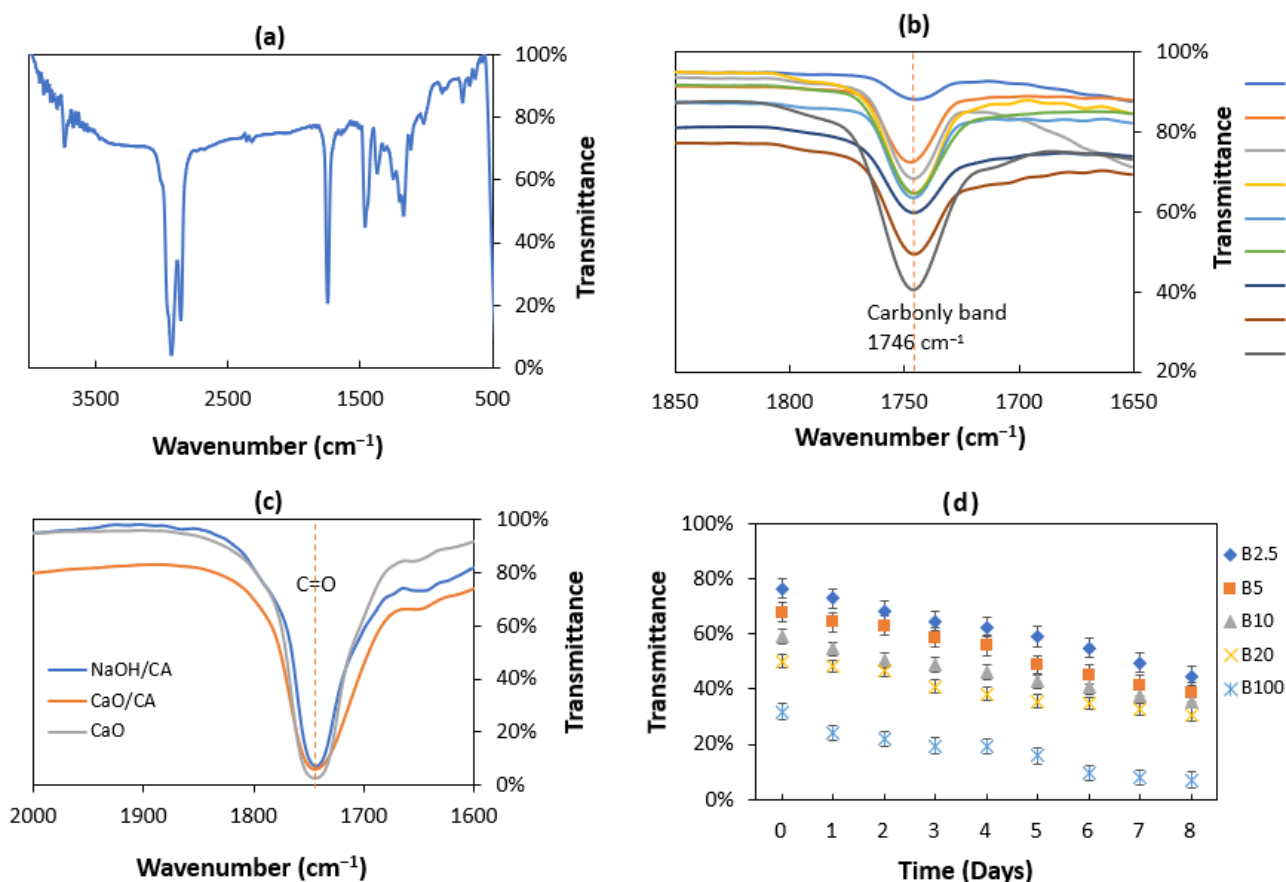


Figure 11. Changes in FTIR spectra of biodiesel and biodiesel/diesel blends under accelerated oxidation. (a) Fresh BSFL biodiesel, (b) B2.5 spectra, (c) comparison spectra of B100 on Day 8 for different catalysts and (d) transmittance strength at 1746 cm^{-1} of biodiesel and blends.

Changes were observed in the region of the O-H band ($3630\text{--}3250\text{ cm}^{-1}$) and the carbonyl band at 1746 cm^{-1} with accelerated storage due to the accumulation of acids, aldehydes and other oxidation products, due to the reaction of hydroperoxides [11]. The most prominent and consistent changes were observed in the carbonyl band (1746 cm^{-1}), as shown by Figure 11b,c. This region was used to analyze the level of oxidation of the biodiesel samples by evaluation of the transmittance strength.

Use of the FTIR spectra for evaluation of oxidative degradation of biodiesel by comparison of the carbonyl band region has been reported to be effective by several researchers [11,21,23,67]. A study by Fang and McCormick [11] showed that the build-up (absorbance strength) in the carboxyl group increased with the increase in the degradation period of biodiesel. The rate of increase in the area of the carboxyl group with oxidation time was reported to be similar to that of PetroOxy and the Rancimat method [21].

Accelerated storage led to build-up of the carboxyl group, where transmittance strength at 1746 cm^{-1} was observed to dwindle with increased storage. A continuous decrease in transmittance strength with the storage period was observed in all samples, as shown in Figure 11d, indicating accumulation of oxidation products. As expected, the lowest transmittance strength was observed for B100, confirming that blending biodiesel with diesel improved the fuel resistance towards oxidation. A rapid decrease in transmittance was observed from Day 1 to Day 2 and after Day 5 in B100, which may be linked to the rapid formation of hydroperoxides at the initiation stage and the termination stage. Comparing the increase in the carbonyl band for biodiesel synthesized with different catalysts after 8 days of storage (Figure 11c), catalysts synthesized with CA resulted in a higher transmittance strength. These results indicate lower levels of accumulated products of hy-

droperoxides in biodiesel produced using the synthesized catalysts, showing the catalysts' efficiency in producing quality biodiesel with improved resistance towards oxidation.

3.8. Kinematic Viscosity and Density

Kinematic viscosity of biodiesel is higher than that of diesel and therefore an important determinant of fuel quality. High viscosity presents a setback in fuel atomization by clogging of injector nozzles, resulting in poor engine performance [68]. The viscosity of neat biodiesel was 1.76-fold higher than that of diesel. High viscosity has a negative impact on the biodiesel engine performance as it results in increased fuel consumption [69]. Blending biodiesel with diesel fuel lowered the viscosity of biodiesel by 57.44%, 53.63%, 50.51% and 46.05% for B2.5, B5, B10 and B20, respectively, as shown in Figure 12a.

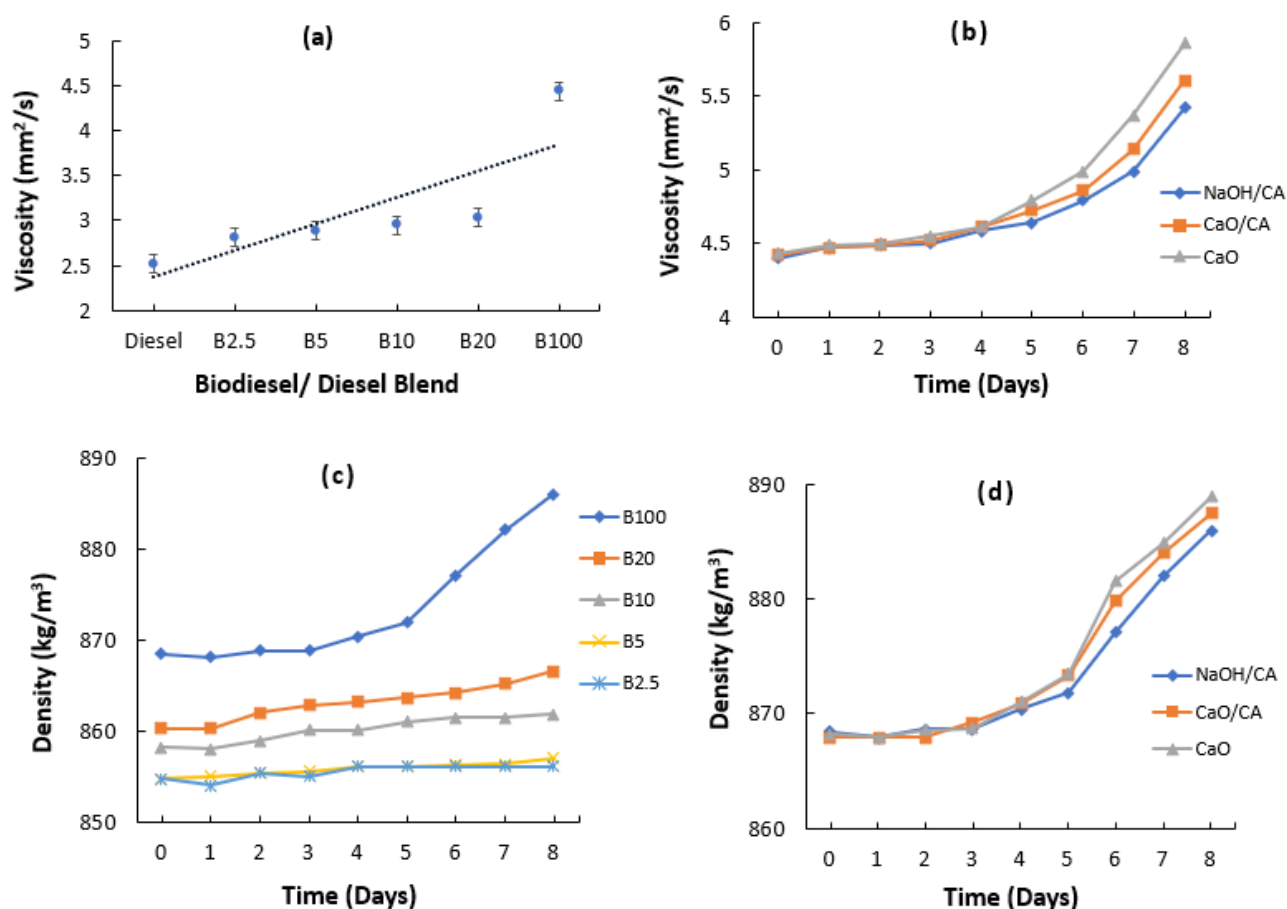


Figure 12. Fuel properties of biodiesel and blends. (a) Viscosity of biodiesel/diesel blends and diesel, (b) viscosity of biodiesel under accelerated storage, (c) density of biodiesel/diesel blends and diesel and (d) density of biodiesel.

The viscosity of biodiesel was observed to increase gradually from Day 0 to Day 4. After Day 4, the viscosity of all the samples increased rapidly, as presented in Figure 12b. The rapid increase corresponded to an increase in the previously discussed acid value as well as the density, as presented in Figure 12d. The swift increase in density after Day 4 is attributed to hydrolysis of the biodiesel due to oxidation, which in turn resulted in increased viscosity. Besides, the increase in density could be attributed to the fact that biodiesel absorbs moisture under accelerated storage [70]. Although moisture absorption can lead to accelerated degradation of the biodiesel, the effect has been reported to be minimal [8]. As earlier observed, synthesizing catalysts with CA slowed the rate of biodiesel oxidation, resulting in a lower rate of increase in AV, implying that the rate of increase of viscosity and density would also be lower, as depicted in Figure 12b,d. Oxidation forms FFA

that have greater AV and viscosity compared to FAMES [71]. As previously observed from fatty acid profile results, degradation resulted in isomerization of linoleic acid to cis–trans (conjugate linoleic acids), which are solid fats at room temperature and can be linked to the increase in density and viscosity of biodiesel [72]. Therefore, catalysts synthesized with CA delayed the formation of conjugate linoleic acids, which in turn improved the viscosity of the biodiesel in accelerated storage. For all the samples tested, the ASTM D445 viscosity limit of $6 \text{ mm}^2/\text{s}$ was not exceeded over the entire storage period, indicating that biodiesel from BSFL has high stability with long storage due to the low composition of linoleic acid.

3.9. Calorific Value

The calorific value of biodiesel from BSFL was observed to be within the range of 39.22–39.32 MJ/kg, which is lower than the reported value for biodiesel derived from sunflower oil (41.33 MJ/kg) [73]. The calorific value of biodiesel has been reported to be dependent on the ash and the extractive content of biodiesel [1]. Comparing the percentage linolenic composition of biodiesel from BSFL ($4.41 \pm 0.42\%$) to that of sunflower oil (62.5%), it is clear that the calorific value increased with the increase in the degree of unsaturated double bonds [71,72]. Therefore, even though a high degree of unsaturation is undesirable for biodiesel storage, moderate composition is required for improved fuel properties, such as viscosity. The calorific value of biodiesel was observed to decrease with the storage period at a rate linear to the increase in the biodiesel viscosity, as shown in Figure 13a,b.

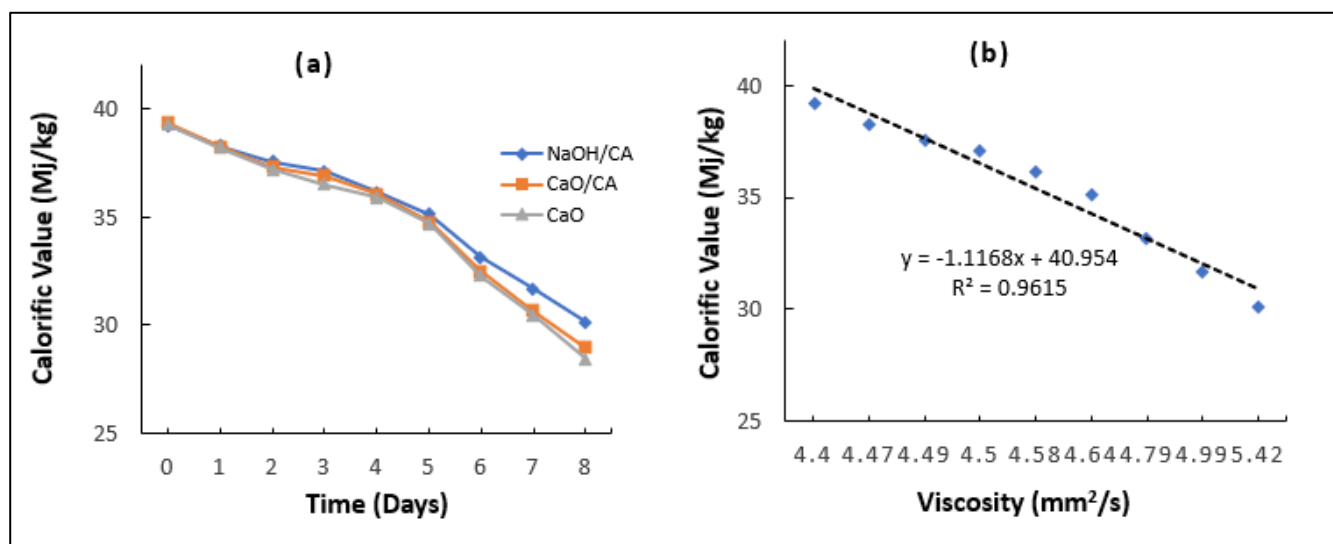


Figure 13. Physical properties of oxidized biodiesel: (a) calorific value and (b) correlation between calorific value and viscosity of B100 from BSFL.

The resultant Equation (6) for the calculation of the calorific value of biodiesel from BSFL compares to the equation derived for vegetable oils [74]:

$$\text{Calorific value} = -1.116v + 40.95 \quad (6)$$

where: v = kinematic viscosity of biodiesel at 40°C .

The calorific value was seen to rapidly decrease after Day 5, which was directly linked to the increase in viscosity and the decrease in the composition of PUFA. Samples of biodiesel synthesized using NaOH/CA showed the slowest rate of decrease in calorific value compared to CaO/CA and CaO. The overall decrease in calorific value was observed to be 23.2%, 26.3% and 27.5% for biodiesel synthesized with NaOH/CA, CaO/CA and CaO, respectively, after 8 days of accelerated storage, indicating that the NaOH/CA catalyst was the most effective in the preservation of the physical properties of biodiesel over the storage period.

4. Conclusions

The changes in the chemical properties and composition of BSFL biodiesel and biodiesel blends during accelerated storage were used to evaluate the effectiveness of transesterification catalysts synthesized with CA in the preservation of the quality and oxidative stability of biodiesel.

From the results, the calorific value, fatty acid composition, analysis of the carbonyl band by FTIR and the TOTOX index were the best indicators of oxidation degradation of biodiesel and biodiesel/diesel blends. Biodiesel from BSFL has a very low composition of polyunsaturated fatty acids. While very high levels of unsaturated fatty acids are undesirable for fuel qualities, very low levels result in poor fuel qualities, such as calorific value. Therefore, there is a need to improve the resistance of the unsaturated fatty acids against oxidation during storage to maintain the quality of the biodiesel. Synthesizing the catalysts with CA exhibited antioxidation characteristics of unsaturated fatty acids. Here, 10-oxo-octadecanoic acid was present in biodiesel produced using NaOH/CA and CaO/CA catalysts but absent in biodiesel produced using the CaO catalyst. The oxo-methyl esters possess antioxidative properties which can be linked to the retarded degradation of polyunsaturated fatty acids, thus improving the oxidation stability of biodiesel in accelerated storage.

The quality of biodiesel produced from BSFL was seen to improve when the catalysts were synthesized with CA. The peak of hydroperoxide formation was delayed by 24 h in biodiesel produced using the synthesized catalysts. Biodiesel samples for the synthesized catalysts showed an improved calorific value, viscosity and transmittance strength with accelerated storage in comparison to samples for biodiesel produced using the CaO catalyst. Overall, the NaOH/CA catalyst was the most effective in improving the biodiesel's resistance to oxidation, with the minimum decrease in OX of 35.49% over the entire storage period, followed by the CaO/CA catalyst with 40.09%, while that of the CaO catalyst was 42.08%. The results of this study show the ability to improve the resistance of biodiesel against oxidation by synthesizing transesterification catalysts with CA. Biodiesel produced by the synthesized catalysts had a higher oxidation resistance under accelerated storage, which resulted in improved fuel qualities.

BSFL biodiesel has a high composition of saturated fatty acids, which may indicate poor cold flow properties. Further studies can be performed to monitor the effects of low storage temperatures on the fatty acid composition and cold flow properties of biodiesel from BSFL.

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