INVESTIGATING THE EFFECT OF CASHEW NUT OIL (Anacardium Occidentale) BIODIESEL ON CORROSION OF METALS

ABSTRACT

The transition from fossil fuel to clean and renewable fuel is a burning issue in the global space as at present. In addition to other source of energy, renewable liquid fuels such as biodiesel are providing solution to this surging global need. Just like fossil fuels, these renewable fuels come with their own challenges of which corrosion is prime. In this study the corrosion behaviour of metals in cashew nut oil biodiesel was conducted. Oil extracted from Cashew nuts was characterized for acid value free fatty acid and fatty acid profile. The oil was further trans esterified into biodiesel and fuel properties were characterized. Corrosion test for selected metals in biodiesel using mass loss method was also conducted. The acid value and free fatty acid for the oil was observed to be 5.61 mg/g KOH and 2.26 mg/g KOH respectively. The fatty acid profile was observed to be more of monounsaturated fatty acid especially Oleic acid (68.2 wt %) for biodiesel. The corrosion test showed copper metals and mild steel have higher corrosion rate of 0.02896 mm/y and 0.02617 mm/y respectively. Hence the corrosion pattern of metal in cashew nut oil biodiesel is slightly higher than other edible oil biodiesel.

Keywords: Corrosion, Cashew nut oil, Biodiesel, Metals.

1. INTRODUCTION

Currently the global community is experiencing a significant energy transition, caused by increasingly severe decarbonization policies and speedy advances in low-carbon technologies (Eyl-Mazzega and Mathieu 2020). This transition to low-carbon energy is changing the global energy system, replacing traditional fossil energy sources with new, efficient and cleaner renewable sources of which biofuel is playing a significant role. Biofuel being a cleaner and environmentally friendly fuel has been proven of recent to be a feasible alternative to age-long fossil fuel that have contributed immensely to global warming and climate change (Khan et al., 2021).

Nigeria is among the top fifteen global producers of cashew nut with the potential to increase its capacity to surpass the current production capacity, having both favourable climatic condition and enough arable land to increase cultivation and productivity (Olife et al., 2013). Cashew nut is mainly consumed locally as snacks without large scale processing into other consumable goods resulting to its under-utilization. Cheaper alternative snacks such as peanuts reduce the consumption of processed cashew nut due to higher cost of cashew nut hence cashew nuts stay longer in the shelf leading to economic loss from rancidity and spoilage.

With the global transition of energy from fossil source to renewables and the need to maximize cashew cultivation and oil extraction as a rich sources of vegetable oil and feedstock for biodiesel production of which soya-beans is a present major contributor in developed economies such as the united states, developing nation will need to explore and domesticate oil crops for their energy need of which cashew nut is a promising option among other crops due to its minimal application.

Biodiesel is an also known as fatty acid methyl ester (FAME) is produced from renewable raw materials such as vegetable oils, animal fat, and algae. Recently, biodiesel is gaining utilization as a major biofuel and it is used in large quantities. The countries utilizing it include the U.S, Brazil, Indonesia, Malaysia, France, Germany and other European countries (Karabas 2022). This is due to the physiochemical properties of biodiesel such as High cetane number, clean combustion, good lubrication, low aromatic content, low sulfur content, and low pour point which gives biodiesel an edge over petroleum diesel (Sinha and Agarwal 2007). In addition, the unique features of biodiesel are that it reduces particulate matter (PM), carbon monoxide (CO), and hydrocarbon (HC) emissions in exhaust gas. Therefore, biodiesel is an environmentally friendly fuel[Atabani et at., 2012; Javidialesaadi and Raeissi 2013).

Corrosion is the degradation of metals due to their interactions with the environment. Metals usually corrode by chemical reactions. Materials which are refined have the tendency of reverting to their original forms, hence corrosion. For corrosion to occur, there has to be a cathode, anode the metallic material and an electrolyte. The principle and mechanism of corrosion of material in response to its environment is an essential knowledge in material usage. This knowledge can prevent accident and save cost and energy.

Diesel fuel in general is any liquid fuel used in diesel engines, whose fuel ignition takes place, without spark, as a result of compression of the intake of fuel mixture and then ingestion of the fuel. The most common type is a specific distillate of petroleum fuel oil but alternation that are not derived from petroleum fuel include Biodiesel

Biodiesel can be produced in a transesterification process where vegetable oils or animal fats are reacted with excess short-chain alcohol such as methanol or ethanol in the presence of a catalyst (Atabani et al., 2012). According to Tamalampudi and Fukuda, (2011), Biodiesel is not corrosive initially, but the fatty acid methyl esters it contains are readily hydrolyzed by microbes, which transform it into organic acids and highly corrosive hydrogen sulfide.

Corrosion behavior in petroleum diesel environment is well understood and methods of preventing it is well developed (Fazal et al., 2010; Hu et al., 2012). The use of biodiesel changes the environment which may lead to corrosion and failures. Although a substantial study on biodiesel supported corrosion of metals is available in literature, such studies have excluded cashew nut oil biodiesel. Currently edible oil provides 95% of feedstock for biodiesel production due to its high oil content and domestication over time (Atabani et al., 2012; Atabani A. E. (2012). Some sources of this oil have the potential for future food scarcity and deforestation. With the growing global population from urbanization which eventually will lead to increase in food demand, it is necessary to avoid future disaster of food competition and seek alternative oil as feedstock for biodiesel research and production. This study will focus on corrosion behavior of metals in cashew nut oil biodiesel which is a non-common edible oil.

2. MATERIALS AND METHODS

The oil used was extracted from cashew nut using soxhlet extractor. Acid value and free fatty acid were analyzed for the oil. The oil was pretreated by esterification reaction using concentrated tetraoxosulphate (vi) acid and methanol to reduce the free fatty acid content and increase biodiesel yield. The cashew biodiesel was produced from the pretreated cashew nut oil. Mild steel, aluminium and copper plate were obtained from local metal artisans, they were cut to size (length of 0.025m, breath of 0.020m and 0.002 m thickness), abraded and cleaned with acetone before use.

1.1. Experimental Set-up

Methanol to oil ratio was 6:1 for transesterification. The catalyst used was sodium hydroxide. 100ml the treated CNO was measured using a measuring cylinder. The measured oil was poured into a clean dry Erlenmeyer flask and then placed on a magnetic stirrer with heating maintained at 500C. 20 ml of 99.8% methanol was measured also using another clean measuring cylinder. The methanol was poured into a clean, dry beaker. Then, 0.35g of sodium hydroxide (NaOH) was weighed using the analytical weighing balance. The sodium hydroxide was transferred into the beaker containing the methanol to form Sodium Methoxide. The sodium methoxide solution in the beaker was stirred vigorously using a glass rod until the entire sodium hydroxide pellets were completely dissolved. After thorough mixing, the sodium methoxide solution was poured into the heated TCNO. The heating and stirring of the mixture of sodium methoxide and oil at 500C was continued for 1 hour, after which the mixture was poured into a separating funnel and allowed to stand for 18 hours for complete separation with the top layer being the biodiesel and the bottom layer being glycerol. The glycerin layer was separated from the biodiesel by gently opening the funnel's tap.

1.2. Corrosion analysis

Corrosion test procedure as reported in Fazal et al., (2012) was used in this study. Corrosion of mild steel, stainless steel, aluminium and copper metals in cashew nut oil biodiesel (B100) was investigated by immersion test at room temperature (25–27 °C) for a period of 1440 hours. The metals used for this study, their dimension and density are shown in Table 1. Test coupons of mild steel, aluminium and copper were cut for a length of 0.025m, breath of 0.020m and 0.002 m thickness. A hole of diameter 0.002 m was drilled near the edge of each specimen for hanging it into the fuels. The samples were then abraded with 100C–220C-grit silicon carbide papers, washed by deionized water and degreased with acetone. Glass beakers were used for the immersion test. These beakers were kept open during the test. Two duplicate coupons were immersed in each of the test fuels. For each immersion time, new duplicate coupons were used. Upon completion of immersion test, the samples were cleaned carefully in a water stream by using a polymer brash in order to remove the corrosion products. The weight of each sample was recorded prior to and after immersion test by using a balance with a four decimal accuracy. The obtained data from weight loss measurement were converted into corrosion rate (lm/y) by following the Eq. (1).

Corrosion rate (mpy) = $(\frac{8.76 \text{ x w}}{\text{DtA}})$

where corrosion rate is in micrometer per year (mm /y), w is the weight loss (kg), D is the density (kg/m^3), A is the exposed surface area (m^2) and t is the exposure time (h).

2. Result and discussion

In this study, oil was extracted from cashew nut, pretreated and trans-esterified into biodiesel. Fatty acid profile and Fuel properties of biodiesel was analyzed using G-C MS. Corrosion test using weight lost method was conducted for mild steel, aluminium and copper metals using biodiesel produced from cashew not oil.

Table 1 Properties of CNO Biodiesel

PROPERTIES	UNITS	CNO	BIODIESEL	EN 14214[a]	ASTM D6751[a]
Yield of extracted oil	%		37.2	-	-
Biodiesel yield	%		85	-	-
Density @ 25^{0}C	g/cm^3	0.9200	0.8600	0.850-0.900	-
Free Fatty acid	(mg KOH/g)	2.28	0.4	0.2	0.2
Cetane Number	-	-	46	51	47
Acid Value	(mg KOH/g)	5.61	0.4	0.5	0.5
Pour point	(^{0}C)	-	-15	-	-
Flash point	(^{0}C)	-	150	101	130
Specific gravity (60/60^{0}F)	-	0.9200	0.8600	0.850-0.900	-
Kinematic Viscosity @ 40^{0}C	(mm^2/sec)	11.67	3.2	3.5 -5	1.6 - 6

2.1. Yield of extracted oil and biodiesel

From table 1, the yield of extracted oil was observed to be 37.2% which is slightly lower than the 40.0% obtained by Aremu &Akinwumi,(2014) but higher than 32.0 % obtained by Bello, et al., (2013). This study found that the oil content of cashew nut seed is higher than those recorded for soya bean (23%), corn (15%) and tiger nut (24%) (Atabani, 2012). This high oil content and the liquid nature at room temperature gives cashew nut seed a high potential as feedstock for biodiesel production. The percentage yield of biodiesel observed in this study was 85% which is higher than 75% reported by Aremu &Akinwumi, (2014) but lower than 85 % reported by Bello, et al., (2013).

2.2. Specific gravity

The specific gravity obtained for cashew nut oil in this study is 0.92. this is similar to 0.902 reported by Bello, et al., (2013). Specific gravity is commonly used in addition to other properties in assessing the purity of oil. The specific gravity of cashew nut oil falls within the narrow range of 0.900 – 0.925 for vegetable oils. This value is close to those of some well-known edible oils like sesame, soya beans and corn oils of 0.916 – 0.921 and cottonseed and sunflower oils of 0.916 – 0.918 (Venkatachalan and Sathe 2006). Idah and Simeon, (2014) have reported 0.962 in a similar assessment of physicochemical properties of cashew nut oil.

It is an important parameter for the vehicle injection system. Biodiesel has a density higher than petroleum diesel. The density of biodiesel differs as the oil used for production is changed. High values may indicate the presence of contaminants such as soap and/or vegetable oil. Excess alcohol excess decreases its density. The European standard specification for biodiesel is between values of 860-900 kg m^{-3} while the ANP gives the specification range of values between 850 to 900 kg m^{-3}.

2.3. Acid Value and free Fatty Acid

Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids that occur naturally in fats and oils but are not attached to glycerol backbones. Acid value is expressed as mg KOH required for neutralizing 1 g of FAME. The free fatty acid value and acid value in this study was 2.8 mg KOH/g and 5.6 mg KOH/g respectively. These values are not much different from 2.26 mg KOH/g and 4.56 mg KOH/g reported by Bello, et al., (2013) for free fatty acid value and acid value of cashew nut respectively. Another study also reported a free fatty acid value and acid values of 2.24 mg KOH/g (Aremu and Akinwumi, 2014).

Table 2: Fatty acid profile of CNO, TCNO and CNO FAME

No	Fatty acid	Abbreviation [a]	Formula	Composition of CNO (wt%)	Composition of TCNO (wt%)	Composition of Biodiesel (wt%)
1	Myristic	C14	$C_{14}H_{28}O_2$	-d	-d	-d
2	Palmitic	C16	$C_{16}H_{32}O_2$	7.84	16.07	10.03
3	Palmitoleic	C16 :1	$C_{16}H_{30}O_2$	-d	-d	-d
4	Stearic	C18:0	$C_{18}H_{36}O_2$	-d	3.85	10.92
5	Oleic	C18:1 **Δ**6	$C_{18}H_{34}O_2$	-d	-d	4.9
6		C18:1 **Δ**9	$C_{18}H_{34}O_2$	92.16	77.70	74.14
7		C18:1 **Δ**11	$C_{18}H_{34}O_2$	-d	-d	-d
8	Linoleic	C18:2 **Δ**9,12	$C_{18}H_{32}O_2$	-d	2.38	-d
9	Linolenic	C18:3 **Δ**9,12,15	$C_{18}H_{30}O_2$	-d	-d	-d

[a] For example, C18:1 Δ9 signifies an 18 carbon fatty acid with one cis double bond located at carbon 9-d Not detected

2.4. Fatty acid profile of CNO, TCNO and CNO FAME.

Figure 1,.2 and 3 shows the GC-MS chromatogram for CNO, TCNO and the FAME of CNO. Table 3 shows the compositional data of fatty acid profile of the cashew nut oil, TCNO and the CNO FAME.

Fig. 1. GC-Chromatogram for Cashew Nut Oil (CNO)

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Fig. 2. GC-Chromatogram for Treated Cashew Nut Oil (TCNO).

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Fig. 3. GC-Chromatogram for Cashew Nut Oil Fatty Acid Methyl Ester (CNO-FAME)

2.4.1. Fatty acid profile of CNO

Table 2 shows Oleic acid as the major fatty acid with 92.16 wt%. This suggest that crude cashew nut oil from this study is majorly composed of mono-saturated fatty acid (MUFA) which is Oleic acid. Palmitic acid which is a saturated fatty acid (SFA) is 7.84 wt% of the total amount of the oil. Other common SFA and MUFA observed in other vegetable oils such as stearic and palmitoleic acids were not detected in the crude cashew nut oil. Also Polyunsaturated fatty acids (PUFA) such as linoleic and linolenic acids were not observed. Perhaps the reason for the difference from previous studies might be due to environmental processing and genetic factors.

2.4.2. Fatty acid profile of TCNO

The fatty acid profile for TCNO showed some differences from that of the crude CNO as seen in Table 2. The oil was treated to reduce the free fatty acid value to increase biodiesel yield. The high oleic acid was reduced to 77.7 wt%. Palmitic acid and stearic acid were found to be 16.07 wt% and 3.85 wt% respectively. Another major difference is the observation of palmitic acid methyl esters, oleic acid methyl esters and linoleic acid methyl esters that were not present in the crude CNO. This validate the reduction of free fatty acid value observed after the treatment of the oil. This result is expected to increase the yield of biodiesel produced in the trans-esterification reaction.

2.4.3. Fatty acid profile of CNO-FAME

From the GC- analyses of the CNO-FAME, Oleic acid is observed to be 79.04 wt %. Palmitic acid and stearic acid content were observed to be 10.03 wt% and 10.92 wt% respectively. There is an increase in the SFA in the CNO-FAME as against the TCNO and CNO. This is probably due to the transesterification reaction. This in addition to palmitic acid ethyl ester and stearic acid ethyl esters show the increase in the FAME produces, hence the conversion of CNO to CNO-FAME is confirmed. The implication is that the properties of the oil has being changed and it free fatty acid reduced hence a corrosive property is greatly reduced.

In this study CNO, TCNO and CNO-FAME are more of MUFA than saturated fatty acids. This is a little different from what was obtained by Bello, et al., (2013) where the fatty acid profile of CNO is 63% unsaturated consisting mainly of 20.97% linolenic acid with triple bond, 34.48% oleic acid with single bond and 28.87% palmitic saturated fatty acid. Aside the reduction of the free fatty acid in CNO-FAME which is a factor for corrosion another possibility of corrosion is the oxidation of the unsaturated compounds in the biodiesel. The result reveals the conversion of triglycerides and free fatty acids to methyl esters form CNO, through TCNO and then the CNO-FAME. This confirms that the two step transesterification reaction reduced the free fatty acid present and hence reduces the corrosive nature of the CNO-FAME obtained.

Table 3: Corrosion rate of metals in biodiesel

Sample	Metal Coupons					
	Mild steel		Aluminium		Copper	
	A1	A2	B1	B2	C1	C2
Density (g/cm^3)	7.85	7.85	2.69	2.69	8.96	8.96
Area (mm^2)	750	750	1000	1000	1000	1000
Initial weight	4.4594	4.2809	2.8577	2.9635	6.3798	6.5999
Final weight	4.4565	4.2777	2.8576	2.9633	6.3754	6.5956
Weight loss (mg)	0.0029	0.0032	0.0001	0.0002	0.0044	0.0043
Corrosion rate (mm/y)	0.02625	0.02896	0.00198	0.00396	0.02617	0.02557
Corrosion rate (mpy)	1.03342	1.14033	0.07799	0.15599	1.03028	1.00687

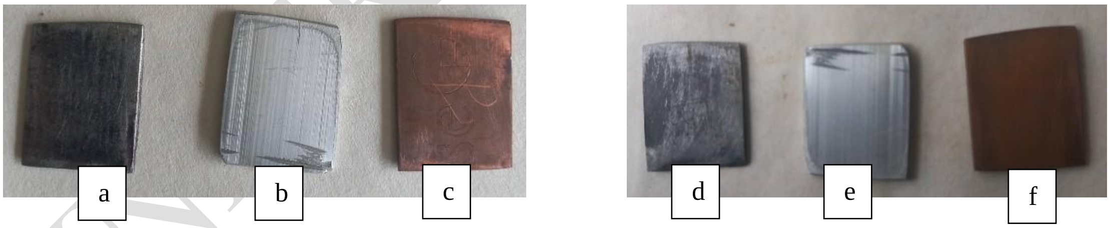

Figure 4: Metal samples before and after corrosion test

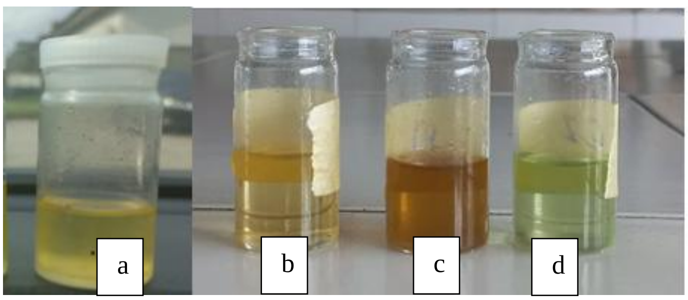

Figure 5: Biodiesel samples before and after corrosion test; (a) before test (b) after mild steel test (c) after aluminium test (d) after copper test.

2.5. Corrosion rate

The corrosion reaction of metals is one of the most important preconditions of biodiesel when used as engine fuel. The variable corrosion behaviors and effects on different metals of biodiesel from cashew nut oil were determined by calculating their corrosion rates, as shown in Table 3. Figure 4 shows the metals coupon used before and after the corrosion test. With Figure 4 a-c as mild steel, aluminium and copper respectively before immersion and Figure 4 (d-f) of same metal coupons after corrosion test. The change in biodiesel colour was also observed before and after the immersion test with the different metals as shown in figure 5 (a-d).

2.5.1. Corrosion rate of mild steel

Table 3 shows the corrosion rate of mild steel upon exposure to CNO biodiesel for a test periods of 1440 h. The corrosion rates obtained from the duplicate test coupons are 0.02625 mm/y and 0.02896 mm/y. Figure 4 a & d shows the appearance of the mild steel test coupons before and after exposure to biodiesel for the test period. Darker patches are seen to appear on the surface of the coupon (Figure. 4 a & d). It is further observed that the color of biodiesel changes from yellow to pale yellow before and after immersion for 1440 h. (Figure.5b).

2.5.2. Corrosion rate of Aluminium

The corrosion rate of aluminium upon exposure to CNO biodiesel for a test periods of 1440 h is reported to 0.0780 mpy and 0.1560 mpy in Table 3. A study by Chew et al., (2013) shows the corrosion rate of aluminum upon exposure in biodiesel for 1440 h at room temperature gave a corrosion rates 0.0527 mpy. The values obtained in this study are higher than that obtained by the above stated study. This may be as a result of the different feedstock used for biodiesel production (Atabani et al., 2012; Munoz et al., 2012). Figure 4 b & e shows the appearance of the mild steel test coupons before and after exposure to biodiesel for the test period. It was observed that the lustrous nature of aluminium test coupon diminishes after the immersion test (Figure 4 b & e). It is further observed that the color of biodiesel changes from yellow to darker yellow before and after immersion for 1440 h. (Fig.5c)

2.5.3. Corrosion rate of Copper

Table 3 shows the corrosion rate of copper upon exposure to CNO biodiesel for a test periods of 1440 h. The corrosion rates obtained from the duplicate test coupons show 1.0303 mpy and 1.00687 mpy. In an interesting study, Fazal, et al.,(2010) studied the effects of palm oil-based biodiesel on the corrosion behavior of Copper when immersed in biodiesel samples at temperature 80ºC with a stirring speed of 250 rpm by a magnetic stirrer. They observed corrosion for copper after 1200h of test time to be 0.586 mpy. This is lower than what was obtained in this study may be due to lower test time. Figure. 4 shows the appearance of test coupons before and after exposure to biodiesel for the test period. A light blue-greenish layer is seen to appear on the coupon (Figure 4 c & f) while the rest is reddish in color. It is further observed that the color of corrosion product layer changes with immersion time from yellowish to blue-greenish before and after immersion for 1440 h (Fig. 5c). This demonstrates the conversion of copper compounds on the exposed surface with time.

2.5.4. Change in composition of biodiesel

The colour and density change of the biodiesel observed in this study signifies compositional change in the biofuel in form of the presence of metal species or increase in TAN number (Tabish, 2018). This is confirmed by Ahmmad et al., (2018) in a study which showed a GC-MS analysis of the fatty acid profile with increase in palmitic, stearic and oleic acid as against linoleic and linolenic acids after the immersion test. This change the fatty acid profile of the fuel to more of saturated compounds.

3. CONCLUSION AND RECOMMENDATION

3.1. Conclusion

The corrosion characteristics of selected metals such as Cu, Al and mild steel in Cashew nut oil biodiesel were investigated at room temperature over a period of 1440 hours using an immersion test. The following key conclusions can be drawn from the current investigation.

(1) The corrosion rate of metals in CNO biodiesel follows a similar behavior to that observed in biodiesel of other feedstock. The highest corrosion rate was observed with the presence of Cu, while the lowest was using Aluminium.

(2) The higher corrosiveness of cashew nut biodiesel was due to its physicochemical properties such as unsaturated fatty acid, higher oxygen moieties, and hygroscopic nature.

(3) The degraded fuel samples after the immersion test showed that all properties such as composition and fatty acid profile were changed as compared to the initial conditions.

(4) The change in chemical compositions also played a crucial role to enhance the corrosion rate of the materials in biodiesel.

(5) The auto-oxidative properties of biodiesel resulted in the formation of acidic and water contents, which led to increasing the corrosion rate of the materials.

3.2. Recommendation

For further study of corrosion in biodiesel other advanced methods like Scanning Electron Microscope (SEM) can be used to confirm presence and rate of corrosion of cashew nut oil biodiesel in metallic storage materials and elastomers used in compression Injection engines.

3.3. Contribution of study

Despite the many advantages of biodiesel over petroleum diesel, it is important to know that it also have disadvantages that impact on production equipment, storage tanks, transportation vessels and automotive engines and parts that use biodiesel. This study will enhance the production and usage of biodiesel as an alternative to petroleum diesel form alternative source and also report its corrosion behavior which is economically expensive to prevent and the need to inhibit it if considered to be used as fuel.

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