Research Article / Review Article

FUPRE JOURNAL 6(3): 37-51 (2022)

FUPRE Journal of Scientific and Industrial Research

ISSN: 2579-1184(Print)

ISSN: 2578-1129 (Online)

https://fupre.edu.ng/journal

Corrosion Potentials of Biodiesel Formulated from Soapnut Seed *(Sapindusmukorossi)* Oil and Rapeseed (*Brassica Napus)* Oil

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ARTICLE INFO

Received: 20/03/2022
Accepted: 27/05/2022

Keywords

Biodiesel, Corrosion Potential, Extraction, Transesterification

ABSTRACT

The aim of this study is to investigate the corrosion potentials of biodiesel formulated from non-edible soapnut seed oil and rapeseed oil on copper, aluminum, and stainless steel, because of their usage in transportation and storage, and also because they are used either wholly, partially or as alloys in the manufacture of automobile parts like fuel pumps and filters, injectors etc. The oils were extracted from the oilseeds using mechanical engine driven screw press. Biodiesel was produced from them using methanol and alkaline catalyzed transesterification process. The physicochemical properties of the produced biodiesel were determined and a comparative study on the corrosion potentials of the produced biodiesel with commercial petroleum diesel on copper, aluminium, and stainless steel was carried out. The corrosion rate of copper in all the samples was more severe than those of aluminum and stainless steel. The result obtained shows that the corrosion rate of copper is 0.0002319 mm/year for biodiesel from rapeseed oil, 0.0003155 mm/year for biodiesel from soapnut seed oil, and 0.0000835 mm/year for petroleum diesel, the corrosion rate of aluminium is 0.0000773 mm/year for biodiesel from rapeseed oil, 0.0000869 mm/year for biodiesel from soapnut seed oil, and 0.0000386 mm/year for petroleum diesel, while the corrosion rate of stainless steel is 0.0000147 mm/year for biodiesel from rapeseed oil, 0.0000147 mm/year for biodiesel from soapnut seed oil, and 0.0000074 mm/year for petroleum diesel, respectively at room temperature. The results obtained also shows that biodiesel from soapnut seed oil has a higher corrosion potential than biodiesel from rapeseed oil, while petroleum diesel has the lowest corrosion potential when compared to the produced biodiesel samples. This work shows promise for the use of Biodiesel as an alternative to petroleum diesel.

1. INTRODUCTION
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Presently there are global moves towards renewable energy sources and there have also been research efforts towards the possibility of total or partial replacement of fossil fuel with fuels from bio-sources. Biodiesel has gained some prominence in this regard because it is a clean, safe and renewable fuel and can be produced by catalyzed transesterification reaction using methanol. However, there is concern about its corrosive potential and the presence of moisture coming from air, when it gets in contact with biodiesel can lead to corrosion of the metallic parts of the fuel system through the enhancement of microbes and also through the presence of unwanted impurities (Savita et. al., 2007).

The use of vegetable oil as fuel for running

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diesel engines has been practiced. Some of the challenges in its use include poor atomization, incomplete combustion and deposition of carbon on the injector system as a result of the presence of high viscosity of the vegetable oil which can be reduced through micro-emulsification, pyrolysis, dilution, and transesterification which is the method widely used for production of biodiesel on industrial scale because it gives a higher yield at low temperature and pressure and at reduced reaction time (Mathiyazhagan et. al., 2011).

Some of the advantages in using biodiesel include a. It's a renewable fuel and can be obtained from vegetable oils or animal fats, b. It has low toxicity, in comparison with normal diesel, c. The emission of contaminants like carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons etc is very low, d. There is reduced emissions of carcinogenic substances hence it has lower health risk, e. There is no sulfur dioxide (SO_2) emission, f. It has higher flash point (more than 100°C) and g. It has excellent lubricating properties. But for obvious reasons among whom is food security, attention is usually focused on non-edible sources. Some of the advantages of non-edible oil in the production of biodiesel are;

1. Plants from which they can be obtained can be grown in arid regions with rainfall up to 20 cm and above.
2. They do not compete with existing agricultural resources.
3. The competition for food is eliminated since they will not be suitable for human consumption because of the presence of some toxic substances in the oils made from them.

The by-products from the production of these oils can be used for making other useful products. The ASTM Biodiesel standards are shown in Table 1.

Table 1: Biodiesel Standard ASTM D6751

Property	Test Method	Limits
Flash Point	D 93	110 – 150 °C
Kinematic viscosity @ 40°C	D 445	1.9 – 6.0 mm^2 / s
Acid number	D 664	0.50 max mg KOH / g
Free glycerin	D 6584	0.020 % mass
Phosphorus content	D 4951	0.001 max % mass
Water and sediment	D 2709	0.050 max % volume
Density @ 25°C	D 445	800 – 900 Kg/m^3
Free Fatty Acid	D 664	1.10ax (% FFA)

Corrosion is mainly influenced by the nature of the metal, the environment of concern, the concentration of the electrolyte, and the temperature of the medium. This study therefore focused on investigating the corrosion potentials of some metals because they are broadly used in the field of transportation and storing of biodiesel, and also in the manufacturing of automobile parts like pistons, engine block, cylinder head etc and other ancillary parts like fuel pumps, injectors, nozzles, valves etc. Material selection would be very crucial depending on the level of contact with the diesel. In addition, biodiesel is believed to degrade plastics, natural rubber materials which are supposed to be alternatives for use as medium of storage.

1. Materials And Methods

2.1 Materials

The materials and reagents used for the

experiment include Soapnut Seed, Rapeseed, Acetone, Isopropanol, Potassium Hydroxide, Methanol, phenolphthalein, distilled water, and diesel.

2.1.1. Soapnut seed (SapindusMukorossi).

Soapnut Seed *(Sapindusmukorossi)* is a non-edible seed which belongs to the species of trees in the Sapindaceae family. The fruit is commonly referred to as soapberry or washnut, The soapnut contains saponin which has natural cleansing properties, making it useful as a cleanser a surfactant and also for production of insecticides.

Figure 1: Soapnut Seed *(Sapindusmukorossi)*

2.1.2 Rapeseed (Brassica napus)

Rapeseed (*Brassica napus*) is a bright-yellow member of the Brassicaceae family also referred to as the mustard or cabbage family and cultivated mainly for its oil-rich seed. The Rapeseed is one of the most important raw materials used in the production of biodiesel (Romano and Sorichetti, 2011).

Figure 2: Rapeseed (*Brassica napus*).

2.2 Apparatus

The apparatus used in this work are shown in Table 2.

Table 2: Apparatus used in Experiments

S/N	**Apparatus**	**Use**
02.	Beaker	For Sample Collection
05.	Measuring Cylinder	For Measuring Liquid Volumes
06.	Digital Weighing Balance	For Weighing Samples
07.	Water Bath	For Heating and Steaming
08.	Stop Watch	For Time measurement
10.	Separating Funnel	For Separating the Product
12.	Engine Driven Screw Press	For Mechanical Extraction
13.	Pycnometer	For Density Determination
14.	Pensky-Martens Cup Tester	For Flash Point Determination
15.	Mercury in Glass Thermometer	For Measuring Temperature
16.	Viscometer	For Viscosity Determination
17.	Sieve	For Physical Separation
18.	Metal Coupons	For Corrosion Analysis

2.3 Methods

i. Preparation of Seeds

The seeds were dried in the sun for about 7 days after being decorticated and then heated in an oven for 3 hours at 120ºC (Adebayo et. al., 2011).

ii. Extraction of Oil from the Seeds

1000gm of the prepared seeds was steam treated pretreated by steaming and introduced into the mechanical press to extract the oil. The extracted oil was heated mildly for about 30 minutes and filtered.

250 mL of oil was measured and poured into a 500mL conical flask and heated to a temperature of 54.4ºC (130ºF). A solution of potassium methoxide was prepared from 1.75g of KOH pellet and 50mL of anhydrous methanol and poured into the heated oil and stirred vigorously for 30 minutes and allowed to settle for 24 hours. After settling, the bottom layer which is glycerol was separated from the upper layer which was the biodiesel (Adebayo et. al., 2011).

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Figure 3: Solution before Separation

Figure 4: Solution after Separation

The catalyst potassium hydroxide, methanol, and glycerol were removed by successive rinsing of the produced biodiesel samples using equal volumes of warm distilled water. The mixture was heated to above 100ºC to remove any residual water (Adebayo et. al., 2011).

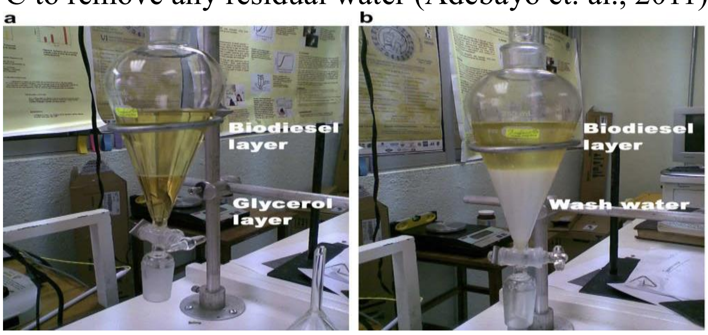


Figure 5: Separation of Wash Water from Biodiesel after Washing

iii. Determination of Corrosion Rate by Weight Loss Method.

Corrosion characteristic of copper, aluminium, and stainless steel in both petroleum diesel and the produced biodiesel samples was investigated using the non-electrochemical metal immersion test. The following Equation was used in determining corrosion rate (Xianguo et. al., 2012):

Corrosion rate (mm/year) =

$$\frac{\text{Weight Loss (g)} \times 24\text{hrs} \times 365 \text{ days}}{\text{Density of the Metal Coupon} \left(\frac{\text{g}}{\text{cm3}}\right) \times \text{ Exposure Time(hr)} \times \text{Exposed Surface Area (Cm2)}} \quad (1)$$

Figure 6: Metal Immersion Test

3. Results And Discussion

3.1 Results Presentation

2.	**Total Acid Number (TAN) (mgKOH/g)**	**4.457**	**3.463**

Table 3: Properties of the Oil used in Biodiesel Production.

S/N	Seed	Weight of Seed Extracted (g)	Weight of Oil Recovered (g)	Percentage Yield (%)
1.	Soapnut Seed	1000	384	38.4
2.	Rapeseed	1000	556	55.6

Table 4: Percentage Yield of the Extracted Oil from the Various Seeds

S/N	Properties	Biodiesel (Soapnut Seed oil)	Biodiesel (Rapeseed Oil)
1.	Viscosity (mm^2/s @40°C)	5.44	4.19
2.	Density @ 25°C (Kg/m^3)	869	847
3.	Flash Point (°C)	116	98
4.	Free Fatty Acid ($^o/_o$FFA)	0.0216	0.0165
5.	Total Acid Number (TAN) (mgKOH/g)	0.0432	0.0330

Table 5; Properties of the Produced Biodiesel Samples

Table 6: Percentage Yield of Biodiesel from the Various Seed Oil

S/No.	Seed	Volume of Oil Used in Making Biodiesel (mL)	Volume of Biodiesel Recovered (mL)	Percentage Yield of Biodiesel (%)
1.	Soapnut Seed	250	132.1	52.84
2.	Rapeseed	250	184.2	73.68

Table 7: Corrosion Results for Biodiesel from Rape Seed, Soapnut Seed and Petroleum Diesel

S/No	Time (Hrs)	Metal	Rape seed Diesel			Soapnut Diesel			Petroleum Diesel		
			Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)
01	24	Cu	39152	39151	1	38528	38527	1	39077	39077	0
		Al	21833	21833	0	22106	22106	0	21833	21833	0
		S/S	10032	10032	0	09228	09228	0	10032	10032	0
02	48	Cu	38320	38317	3	38201	38196	5	38180	38179	1
		Al	22362	22361	1	21828	21827	1	22362	22362	0
		S/S	09237	09237	0	10039	10039	0	09237	09237	0
03	72	Cu	39045	39035	10	38554	38542	12	38524	38522	2
		Al	22108	22106	2	22351	22349	2	21831	21830	1
		S/S	09238	09238	0	09238	09238	0	09773	09773	0
04	96	Cu	38551	38539	12	38198	38183	15	38550	38545	5
		Al	22102	22099	3	22369	22366	3	21834	21833	1
		S/S	10033	10033	0	09776	09776	0	10033	10033	0
05	120	Cu	38782	38766	16	39049	39028	21	38173	38166	7
		Al	22370	22366	4	21831	21826	5	22363	22362	1
		S/S	10040	10039	1	09238	09237	1	09238	09238	0
06	144	Cu	38434	38412	22	38499	38472	27	39408	39402	6
		Al	22109	22102	7	22111	22105	6	21832	21828	4
		S/S	10021	10020	1	09771	09770	1	09774	09774	0
07	168	Cu	38552	38528	24	23181	23146	35	38193	38185	8
		Al	22110	22103	7	21852	21842	10	21835	21832	3
		S/S	09229	09228	1	10039	10036	3	10034	10033	1

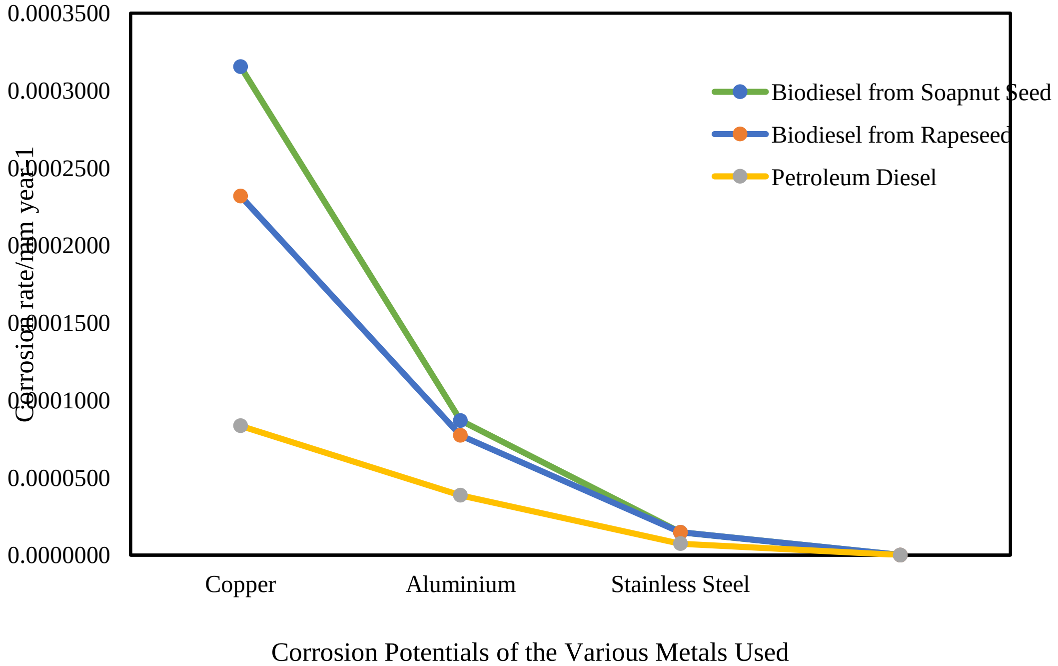


Figure 7: Corrosion Rate of the Metals in Petroleum Diesel and Biodiesel Samples

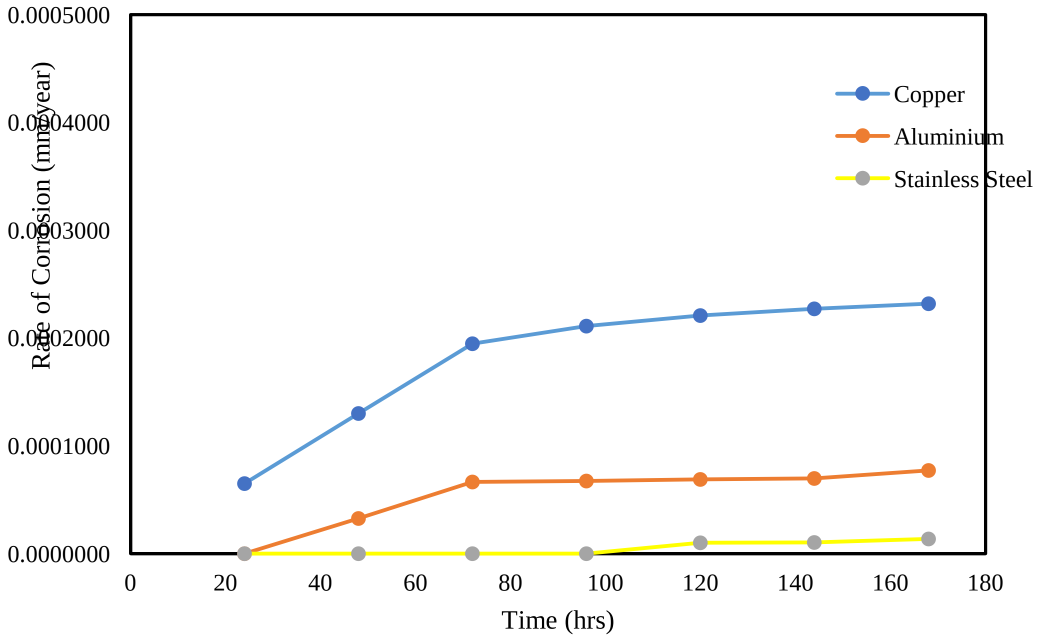


Figure 8: Corrosion Rate of Copper, Aluminium, and Stainless Steel in Rapeseed Biodiesel

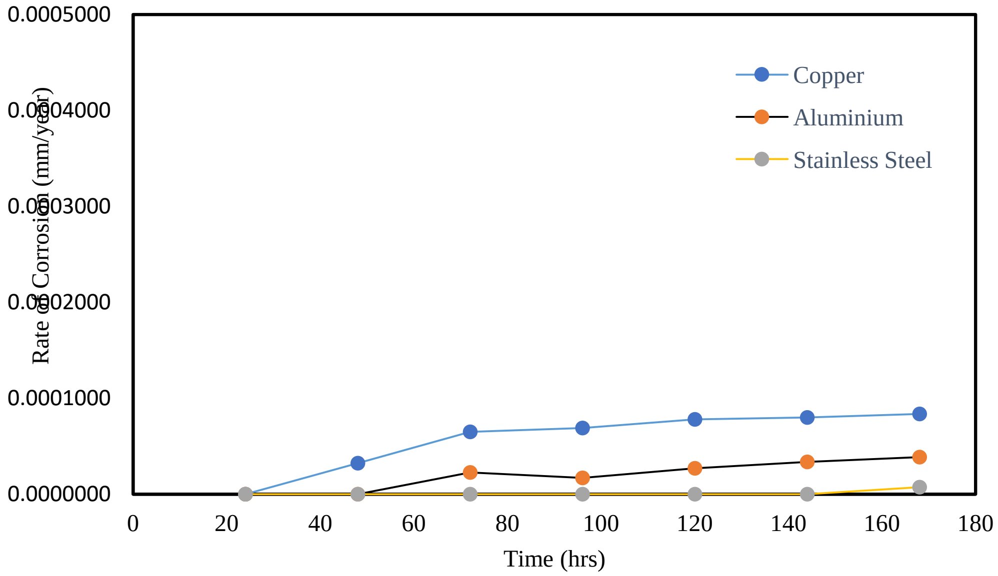


Figure 9: Corrosion Rate of Copper, Aluminium, and Stainless Steel in Commercial Petroleum Diesel

3.2 Discussions

i. Percentage Yield of the Extracted Oil Samples from the Various Seeds

From Table 4, it is observed that for the same weight (1000g) of seeds crushed for the extraction of oil, rapeseed yielded 55.6% while soapnut seed yielded 38.4% of hence rapeseed yields more oil than soapnut seed.

ii. Percentage Yield of Biodiesel from the Extracted Oil Samples

The yields of biodiesel from the various oils are presented in Table 6 with rapeseed oil having the highest percentage yield of 73.68% biodiesel, compare to soapnut seed oil with 52.84% biodiesel and rapeseed oil yields more biodiesel with a percentage difference of 20.84%.

iii. Corrosion Rate

The corrosion potential of the produced biodiesel samples is one of the most important parameters of consideration in the use of biodiesel as engine fuel. The corrosion effects of biodiesel from rapeseed oil, soapnut seed oil, and petroleum diesel were determined by calculating their corrosion rates on the different metals used (i.e. copper, aluminium, and stainless steel) using the non-electrochemical process which involves weight loss measurements through metal immersion test. The corrosion rate of copper in all the samples was observed to be more severe than those of aluminum and stainless steel. The result obtained shows that the corrosion rate of copper is 0.0003155 mm/year for biodiesel from soapnut seed oil, 0.0002319 mm/year for biodiesel from rapeseed oil, and 0.0000835mm/year for commercial petroleum diesel, the corrosion rate of aluminium is 0.0000869 mm/year for biodiesel from soapnut seed oil, 0.0000773 mm/year for biodiesel from rapeseed oil, and 0.0000386 mm/year for commercial petroleum diesel, while the corrosion rate of stainless steel is 0.0000147 mm/year for biodiesel from soapnut seed oil, 0.0000147 mm/year for biodiesel from rapeseed oil, and 0.0000074 mm/year for commercial petroleum diesel, respectively. The corrosion effects of the produced biodiesel samples and petroleum diesel on aluminium was minor, while the corrosion effects of the produced biodiesel samples and petroleum diesel on stainless steel was very insignificant. These corrosion effects of the biodiesel samples on the metals were caused basically by the oxidation of the biodiesel samples leading to the creation of metal oxides. Copper easily oxidizes hence its higher corrosion rate, while aluminium and stainless steel do not easily oxidize and thus their lower corrosion rates.

The results obtained also show that biodiesel from soapnut seed oil has a higher corrosion potential than biodiesel from rapeseed oil, while petroleum diesel has the lowest corrosion potential when compared to the produced biodiesel samples. In addition, the corrosion effect of the produced biodiesel samples and commercial petroleum diesel on copper was more severe than those of aluminum and stainless steel as shown in Figure 10.

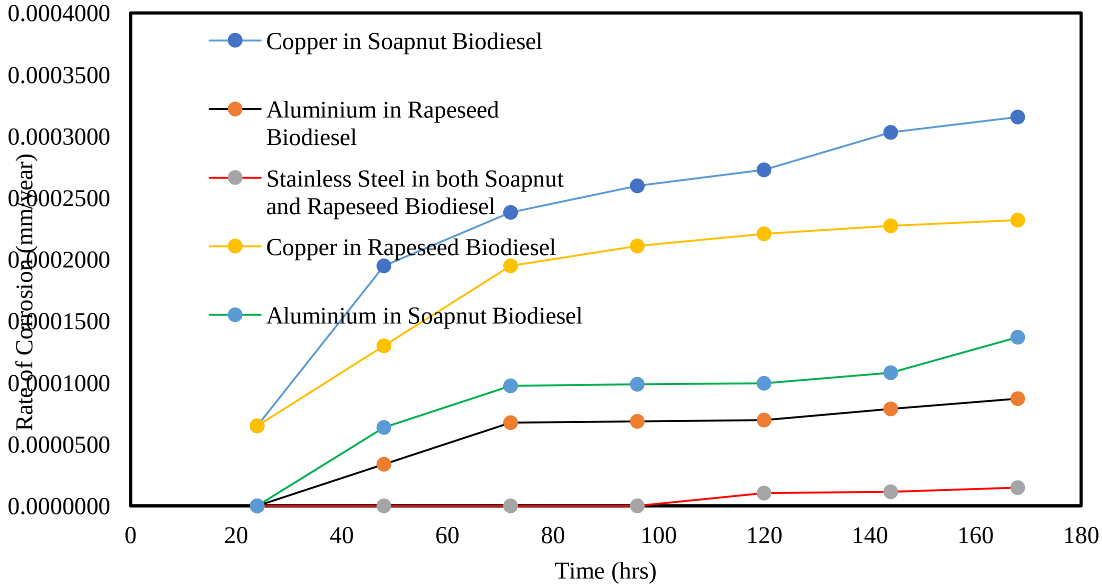


Figure 10: Corrosion Rate of Copper, Aluminium and Stainless Steel in Soapnut and Rapeseed Biodiesel

iv. Properties of the Produced Biodiesel Samples

a) Kinematic Viscosity of the Produced Biodiesel Samples

Table 5 shows that the fuel property for the produced biodiesel samples (i.e. kinematic viscosity) is in line with the standard ASTM value. The biodiesel produced from soapnut seed oil has a higher value of kinematic viscosity (5.44 mm^2/s at 40ºC) when compared to biodiesel produced from rapeseed oil (4.19 mm^2/s at 40ºC). The values of the kinematic viscosity obtained were all within the specified limits for diesel making it suitable use in diesel engines.

b) Density of the Produced Biodiesel Samples

It is observed from Table 5 that the results of the fuel property for the produced biodiesel samples (i.e. Density) is in line with the standard ASTM value. The biodiesel produced from soapnut seed oil had a higher value of density (869 kg/m^3 at 25ºC) when compared to biodiesel produced from rapeseed oil (847 kg/m^3 at 25ºC). The values of the density obtained were all within the specified limits for diesel and at such can be used for diesel engines.

c) Flash Point of the Produced Biodiesel Samples

From Table 5 above, the results of the fuel property for the produced biodiesel samples (i.e. Flash Point) is in line with the standard ASTM value. The biodiesel produced from soapnut seed oil had a higher value of flash point (116ºC) when compared to biodiesel produced from rapeseed oil (98ºC). The value of the flash point for rapeseed oil biodiesel is slightly lower when compared to the standard ASTM values (110ºC – 150ºC). This could be due to the number of times the biodiesel is washed with warm water (the produced biodiesel samples was washed with warm water twice). Nevertheless the values of the flash point obtained are all within the specified limits for diesel and at such can be used for diesel engines.

d) Percentage FFA of the Produced Biodiesel Samples

From Table 5, the Free Fatty Acid (FFA) percentage is in line with the standard ASTM value and the biodiesel produced from soapnut seed oil had a higher value of percentage FFA (0.0216 %) when compared to biodiesel produced from rapeseed oil (0.0165 %). The values of the percentage FFA obtained are all within the specified limits for diesel and at such can be used for diesel engines.

e) Total Acid Number (TAN) of the Produced Biodiesel Samples

From table 5, the results of the Total Acid Number (TAN) is in line with the standard ASTM value. The biodiesel produced from soapnut seed oil had a higher acid value (0.0432 mg KOH/g) when compared to biodiesel produced from rapeseed oil (0.0330 mg KOH/g). The acid values of the produced biodiesel samples obtained are all within the specified limits for diesel and at such can be used for diesel engines.

3.2.1 Statistical Modelling of the Results Obtained.

Table 8: Numerical Statistical Analysis for Rapeseed Biodiesel

Descriptive Statistical Analysis for Rapeseed Biodiesel	
Column 1	
Mean	0.000107967
Standard Error	6.45479E-05
Median	0.0000773
Mode	#N/A
Standard Deviation	0.0001118
Sample Variance	1.24993E-08
Kurtosis	#DIV/0!
Skewness	1.141472577
Range	0.0002172
Minimum	0.0000147
Maximum	0.0002319
Sum	0.0003239
Count	3

Table 9: Numerical Statistical Analysis for Commercial Petroleum Diesel

Descriptive Statistical Analysis for Petroleum Diesel	
Column 2	
Mean	4.31667E-05
Standard Error	2.20865E-05
Median	0.0000386
Mode	#N/A
Standard Deviation	3.8255E-05
Sample Variance	1.46344E-09
Kurtosis	#DIV/0!
Skewness	0.529529968
Range	0.0000761
Minimum	0.0000074
Maximum	0.0000835
Sum	0.0001295
Count	3

Table 10: Numerical Statistical Analysis for Soapnut Seed Biodiesel

Descriptive Statistical Analysis for Soapnut Biodiesel	
Column 3	
Mean	0.000139033
Standard Error	9.06616E-05
Median	0.0000869
Mode	#N/A
Standard Deviation	0.00015703
Sample Variance	2.46586E-08
Kurtosis	#DIV/0!
Skewness	1.329310233
Range	0.0003008
Minimum	0.0000147
Maximum	0.0003155
Sum	0.0004171
Count	3
Bin	*Frequency*
0.0000147	1
0.0001147	1
0.0002147	0
0.0003147	0
0.0004147	1
More	0

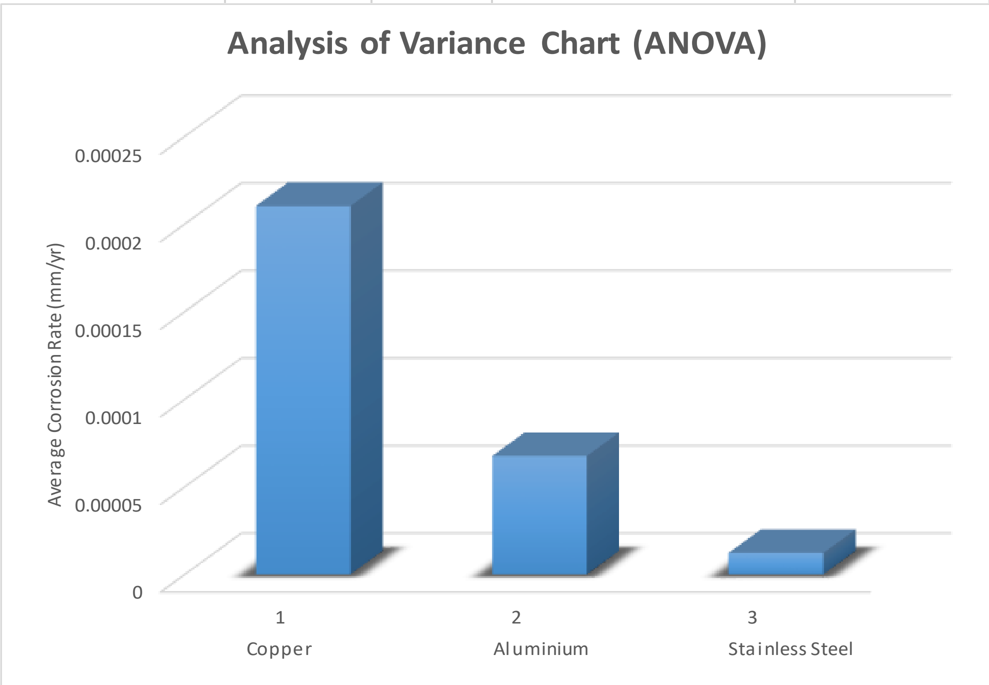
Table 11: Statistical Analysis Using ANOVA

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Copper	3	0.0006309	0.0002103	1.38059E-08
Aluminium	3	0.0002028	0.0000676	6.5379E-10
Stainless Steel	3	0.0000368	1.22667E-05	1.77633E-11
Soapnut Seed Biodiesel	3	0.0004171	0.000139033	2.46586E-08
Rapeseed Biodiesel	3	0.0003239	0.000107967	1.24993E-08
Petroleum Diesel	3	0.0001295	4.31667E-05	1.46344E-09

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	6.26423E-08	2	3.13211E-08	8.580926364	0.035728	6.94427191
Columns	1.43546E-08	2	7.1773E-09	1.966335665	0.254262	6.94427191
Error	1.46004E-08	4	3.65009E-09			
Total	9.15972E-08	8				



From the statistical modeling of the results obtained, Tables 8, 9 and 10 show that the descriptive statistical analysis for soapnut biodiesel gave a mean value of 0.000139033, median value of 0.0000869, standard deviation of 0.00015703, sample variance of 2.46586×10^{-8}, skewness of 1.329310233, and a standard error of 9.06616×10^{-5}. Also the descriptive statistical analysis for rapeseed biodiesel gave a mean value of 0.000107967, median value of 0.0000773, standard deviation of 0.0001118, sample variance of 1.24993×10^{-8}, skewness of 1.141472577, and a standard error of 6.45479×10^{-5}, while the descriptive statistical analysis for commercial petroleum diesel gave a mean value of 4.31667×10^{-5}, median value of 0.0000386, standard deviation of 3.8255×10^{-5}, sample variance of 1.46344×10^{-9}, skewness of 0.529529968, and a standard error of 2.20865×10^{-5}. The results show that Soapnut biodiesel which has the highest corrosive effect on copper, aluminium, and stainless steel also has the highest descriptive statistical values (i.e. mean, median, standard deviation, sample variance, skewness, and standard error) compared to rapeseed biodiesel, while the commercial petroleum diesel which has the lowest corrosive effect on coopper, aluminium, and stainless steel has the lowest descriptive statistical values (i.e. mean, median, standard deviation, sample variance, skewness, and standard error). The analysis of variance (ANOVA) chart using two-factor without replication as shown in Figure 11 indicate that copper coupons have more corrosive effect than aluminium coupons, while stainless steel coupons have the least corrosive effect when immersed in the produced biodiesel samples and the commercial petroleum diesel sample over the same time.

Conclusion

The corrosion rate of copper in all the samples was more severe than those of aluminum and stainless steel. The results obtained show that the corrosion rate of copper is 0.0002319 mm/year for biodiesel from rapeseed oil, 0.0003155 mm/year for biodiesel from soapnut seed oil, and 0.0000835 mm/year for petroleum diesel, the corrosion rate of aluminium is 0.0000773 mm/year for biodiesel from rapeseed oil, 0.0000869 mm/year for biodiesel from soapnut seed oil, and 0.0000386 mm/year for petroleum diesel, while the corrosion rate of stainless steel is 0.0000147 mm/year for biodiesel from rapeseed oil, 0.0000147 mm/year for biodiesel from soapnut seed oil, and 0.0000074 mm/year for petroleum diesel, respectively at room temperature. The results also show that biodiesel from soapnut seed oil has a higher corrosion potential than biodiesel from rapeseed oil, while petroleum diesel has the lowest corrosion potential when compared to the produced biodiesel samples. The results collectively show that there is good promise in the use of biodiesel for running engines.

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