

# Waste Cooking Oil Methyl Ester: Transesterification and Evaluation of Corrosion Rates of Aluminium Exposed to Blended Biodiesel and Automotive Gas Oil

Olusegun D. Samuel <sup>1\*</sup>, Taofeek A. Yusuf <sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering,  
Federal University of Petroleum Resources,  
Effurun, Delta State, Nigeria

<sup>2</sup>Department of Mechanical Engineering,  
University of Agriculture,  
Markudi, Benue State, Nigeria

**Abstract:** This study investigated the corrosion of aluminum exposed to biodiesel produced from Waste Cooking Oil (WCO) and Automotive Gas Oil (AGO) blends. Response Surface Methodology (RSM) with three level-three factor central composite design was used in investigating the effects of transesterification variables such as reaction time, catalyst amount and oil/methanol molar ratio on the yield of waste cooking oil methyl ester (WCOME). Reaction time between 40 - 80 min., catalyst amount of 0.5 - 1.5% wt. and methanol to oil molar ratio of 4 - 8 were used in the transesterification experiment. Optimization of process variables was done using RSM. The fuel properties of biodiesel at optimum level in terms of density, kinematic viscosity, flash, pour and cloud points and sulphur content were obtained using standard method as described by ASTM. Blends of WCO biodiesel 0, 10, 20, 40 and 100% of AGO were designated as B0, B10, B20, B40 and B100 respectively. Corrosion characteristics of blends on aluminium (Al) were studied by static immersion test at room temperature. Mechanical properties of the Al were investigated before and after corrosion test. Changes in the morphology of coupons were also investigated. The optimization technique predicted WCOME yield of 97.1% at the optimal level of 78 minutes, 5.99, 1.1% wt. for the reaction time, methanol to oil molar ratio and catalyst amount respectively. The fuel properties at the optimal level were within the

limits specified by ASTM D6751 and EN 14214 standards. The ranges of corrosion rates obtained for the blends were 0-0.2830 mpy. The Brinell hardness ranged for the blends were 105.012, 109.177, 133.717, 155.393, 166.803 N/mm<sup>2</sup> while the tensile strength for the blends were 371.20, 386.12, 484.62, 495.22 and 592.89 MPa for B0, B10, B15, B20, B40 and B100 respectively. As the percentage of biodiesel in the blends increased, crack and pits on the morphology of the coupons become pronounced. The blend B10 was detected to perform close to B0 with respect to the Brinell hardness and tensile strength.

**Key Words:** Biodiesel, Corrosion, Hardness, Tensile Strength, Optimization

## 1. Introduction

Geometrical demand and the escalating price of fossil diesel coupled with environmental degradation have propelled researchers to seek for renewable energy sources that are sustainable and environmental friendly [1, 2]. Owing to the technical advantages associated with biodiesel, it has been preferred to other biofuels such as biogas, solid fuel and bio-ethanol. Biodiesel has gained wider acceptance due to its inherent lubricity, higher cetane, superior flash point, biodegradability, higher cetane number, reduced toxicity and reduced exhaust emissions [3]. However, biodiesel has been linked with degradation of elastomers and corrosion of automotive parts when exposed to renewable fuel [4]. The key parts of vehicular diesel engine such as cylinder head, piston, connecting rod and cylinder sleeves are made of aluminum and they are always in contact with fuel [5]. Sing et al. [5] further stressed that corrosion of aluminum is aggravated either by the impurities in biodiesel or the deterioration of biodiesel. Chew et al. [6] emphasized that the degradation can be attributed to changes in simulated environments such as nature of the fuel, acid content, water and hygroscopic

environments. Corrosion of biodiesels produced from lipid feedstocks such as jatropha oil, palm oil, sunflower oil and rapeseed oil with aluminum and other metals have been investigated by researchers [2, 6-8]. Their results indicated that corrosiveness of the biodiesel is higher than diesel. Reports abound on the corrosion studies of lipid feedstock oils aforementioned in the literature; however, no work has been reported on the corrosion of light alloy automotive parts exposed to optimized biodiesel from waste cooking oil and its blends. In spite of colossal consequence occasioned by metallic interactions with the alternative fuels, information regarding the spectrum of biodiesel-diesel will provide insight information for effective planning and feasibility tendency to reduce the menace of corrosion. The study has not only examined the optimal production condition of methyl ester from waste cooking oil but also investigated the corrosion characteristics of aluminum resulting from the optimal condition and automotive gas oil mixture/diesel blends.

## 2. Materials and Method

### 2.1. Materials and Analysis of Oil

Waste cooking oil (WCO) donated by United African Company,

restaurant in Sango, Lagos State, Nigeria was utilized for the production of biodiesel from the WCO. The chemicals such as methanol, ethanol and KOH were of analytical grade and the fossil diesel employed for blending process was purchased from Jocceco Filling station, Warri, Delta State, Nigeria.

Machining from the bars was coupon of aluminium which is 99% commercially pure (35 mm length x 25 mm breadth x 2 mm thickness) was used as coupon for corrosion assessment.

Analysis of properties of WCO was conducted by determining the physicochemical properties.

**2.1.1. Adoption of response surface method for methyl ester of WCO**

Transesterification of WCO was conducted in a 2 L reactor, equipped with a reflux condenser and a magnetic stirrer. The waste cooking oil methyl ester (WCOME) was produced by an alkaline

transesterification and the transesterification protocol was well expounded in [9]. The WCOME was oven dried at 90 °C and average yield of WCOME was determined.

Presented in Table 1 is the range of reaction time (X<sub>1</sub>), molar ratio (X<sub>2</sub>), and catalyst amount (X<sub>3</sub>) investigated on the yield of WCOME.

The graphical analysis of the interactions of the transesterification variables versus WCOME were studied using Eq. (1)

$$Y = \phi_0 + \phi_1x_1 + \phi_2x_2 + \phi_3x_3 + \phi_{12}x_1x_2 + \phi_{13}x_1x_3 + \phi_{23}x_2x_3 - \phi_{11}x_1^2 + \phi_{22}x_2^2 + \phi_{33}x_3^2$$

where Y is the predicted yield of WCOME (%),  $\phi_0$  is the intercept,  $\phi_1, \phi_2$  and  $\phi_3$  linear coefficients,  $\phi_{12}, \phi_{13}$  and  $\phi_{23}$  are the interactive coefficients,  $\phi_{11}, \phi_{22}$  and  $\phi_{33}$  are the polynomial coefficients and  $x_1, x_2$  and  $x_3$  are the coded variables.

Table 1 Independent parameters and levels employed for the WCOME

Independent variable	Ranges and their levels			
	Symbols	-1 (low)	0 (medium)	1 (high)
Reaction time (min)	X <sub>1</sub>	40	60	80
Oil/methanol molar ratio	X <sub>2</sub>	4.0	6.0	8.0
Catalyst amount (wt.%)	X <sub>3</sub>	0.5	1.0	1.5

**2.1.2 Waste Cooking Oil Methyl Ester Blends**

Detailed properties of WCOME/Automotive Gas Oil blends such as kinematic viscosity, density, sulphur content, boiling point, cetane number cloud point and pour point and acid value of the WCOME synthesized were analyzed following international biodiesel standards.

**2.1.3 Corrosion Testing of Aluminium in Automotive Gas Oil-WCOME blends**

To conduct corrosion testing, aluminium of 35 mm length/25 mm breadth/2 mm thickness were prepared from bar after grinding operation. At the edge of the coupon, a hole of 3.5 mm was drilled. Before immersion, the coupon was dipped in acetone after it had been degreased, polished and weighed. The prepared

coupons were subjected to a static immersion as reported elsewhere [10]. At every 240 hours, the corrosion rate (CR) of the coupon exposed to the fuel types was estimated using the expression stipulated in Eq. (2).

$$CR = \frac{W_L}{\rho_{Al} A_{Al} T_e} \quad 1$$

where  $W_L$ ,  $\rho_{Al}$ ,  $A_{Al}$  and  $T_e$  are weight loss (mg), density of aluminium ( $g/cm^3$ ), total surface area (square inch) and exposure duration (hours).

The hardness of the coupon prior and after exposure was determined by the Brinell hardness testing machine situated in the Mechanical workshop, Petroleum Training Institute, Effurun, Delta State, Nigeria and it was determined according to ASTM E10 [11].

Estimation of the ultimate tensile strength (UTS, MPa) for the aluminium after being exposed to the fuel types were done using the expression highlighted in Eq. (3)

$$UTS = 3.4 BHN \quad 3$$

Before exposing and after immersing the coupon to the fuel types, the morphology of the aluminium was detected by the JCM 100 mini scanning electron microscope (Joel, USA). Moreover, changes in the basic fuel properties such as density, viscosity, total acid number of fuel types before and after being exposure to aluminium were also examined.

### 3. Results and Discussion

#### 3.1 Quality of Waste Cooking Oil

The quality of waste cooking oil (WCO) was detected by analyzing the significant properties of WCO and comparing with those of Vietnam waste cooking oil (VWCO), sunflower waste cooking oil

(SWCO), Moroccan waste frying oil (MWFO), diesel fuel (B0) and international biodiesel standards, as presented in Table 2.

The acid value (AV) of WCO (0.84 mg KOH/g) was found to be moderate compared to those SWCO (1.83 mg KOH/g) [12] and MWFO (0.98 mg KOH/g) [13]. As a result of low AV of WCO, the oil will not be subjected to the acid pre-treatment. Hence, the WCO was subjected to alkaline transesterification since its AV certified the requirement needed for alkaline transesterification [14-15]. The moisture content of the WCO (0.08 %w/w) certified the norms of EN14214 and ASTM D6751 (0.05 %w/w max) standards. Hence, the ester conversion will not be significantly affected [16]

The viscosity of the WCO (33.17  $mm^2/s$  at 40 °C) was found to be extremely high and 9 times higher than that of B0 (3.61  $mm^2/s$  at 40 °C). The viscosity of WCO is comparable to those of VWCO (33.47  $mm^2/s$  at 40 °C) [17], SWCO (36.6  $mm^2/s$  at 40 °C) [12], MWFO (36.3  $mm^2/s$  at 40 °C) [13] but higher than those ASTM (1.9-6.0  $mm^2/s$  at 40 °C) and EU (3.5-5.0  $mm^2/s$  at 40 °C) standards. The higher viscosity of WCO had been reported to limit mixing of oil during transesterification [18].

The density of WCO (931  $kg/m^3$ ) is comparable with those of SWCO (921.9  $kg/m^3$ ), MWFO (962  $kg/m^3$ ) and VWCO (920  $kg/m^3$ ), as hinted by EL-Gendy et al. [12], Nachid et al. [13] and Phan and Phan [17], respectively but lower than that of B0 (850  $kg/m^3$ ) and certified the range of EU14214 standard (860-900  $kg/m^3$ ).

The lower calorific value of WCO (36.20 MJ/kg) was lower than that of B0 (43.79). The higher calorific value of WCO (38.40 MJ/kg) was lower than those of B0 (46.77 MJ/kg) and waste frying oil (45.34

MJ/kg) reported by Al-Hamamre and Yamin [18]. The presence of oxygen content has been attributed to the lower heating values in biodiesel [19].

Table 2 Physicochemical properties of waste cooking oil

Properties	WCO <sup>a</sup>	VWCO <sup>b</sup>	SWCO <sup>c</sup>	MWFO <sup>d</sup>	BO <sup>a</sup>	ASTM D6751-02	EU 14214
Acid value (mgKOH/g)	0.84	3.64	1.85	0.98	NA	0.50 max	0.50 max
Moisture content wt.%	0.08	-	-	ND	0.02	0.05	500 max
Kinematic viscosity (mm <sup>2</sup> /s)	33.17	33.47	36.6	36.3	3.61	1.9-6.0	3.5-5.0
Density (kg/m <sup>3</sup> )	931	920	921.9	96.2	850	NS	860-900
Lower calorific value (MJ/kg)	36.20	ND	ND	ND	43.79	NS	NS
Higher calorific value (MJ/kg)	38.40	ND	ND	ND	46.77	NS	NS

a, Present study; b, Phan and Phan [17]; c, EL-Gendy et al. [12]; d, Nachid et al. [13]; ND, Not determined; NS, Not specified.

**3.2. Transesterification Process**

Highlighted in Table 3 is the experimental and predicted value for WCOME yield at the design points and all the three parameters in coded form. The response polynomial obtained to compute the yield of WCOME including all experimental variables is represented by Eq. (4) in terms of coded experimental variables and Eq. (5) in terms of actual experimental variables.

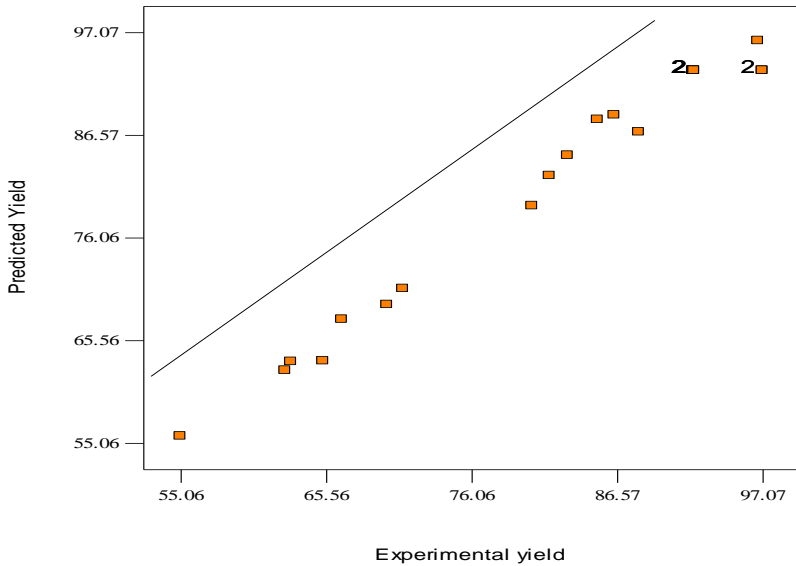
$$Y = 93.18 + 3.80x_1 + 0.63x_2 + 7.35x_3 - 0.77x_1^2 - 5.67x_2^2 - 18.12x_3^2 - 1.70x_1x_2 + 2.14x_1x_3 - 1.51x_2x_3 \tag{4}$$

$$Y = -76.81 + 0.46X_1 + 21.39X_2 + 155.94X_3 - 0.001922X_1^2 - 1.42X_2^2 - 72.50X_3^2 - 0.043X_1X_2 + 0.21X_1X_3 - 1.51X_2X_3 \tag{5}$$

where Y is the yield of waste cooking methyl ester, x<sub>1</sub>, x<sub>2</sub> and x<sub>3</sub> are coded experimental values for reaction time (X<sub>1</sub>), oil/methanol molar ratio (X<sub>2</sub>) and catalyst amount (X<sub>3</sub>), respectively.

The graph between the predicted and actual ester yield (%) is presented in Fig. 1. The closeness of the predicted value to the experimental implies that model developed can be employed to correlate the

transesterification variables and the WCOME yield.



**Fig. 2** Plot of predicted yield versus experimental yield of waste cooking oil methyl ester

**Table 3** Design matrix for the three-factor three level face centered central composite design in coded variables

Run	Coded factors			Biodiesel Yield (%)		
	Reaction time (min)	Methanol to oil molar ratio	Catalyst amount (% w/w)	Experimental	Predicted	Residual
1	-1	-1	-1	55.06	55.76	-0.70
2	1	-1	-1	62.63	62.49	0.14
3	-1	1	-1	65.36	63.46	1.90
4	1	1	-1	63.04	63.38	-0.34
5	-1	-1	1	69.97	69.21	0.76
6	1	-1	1	83.01	84.48	-1.47
7	-1	1	1	71.13	70.85	0.28
8	1	1	1	80.45	79.32	1.13
9	-1	0	0	86.38	88.61	-2.23
10	1	0	0	96.75	96.21	0.54
11	0	-1	0	88.15	86.88	1.27
12	0	1	0	85.18	88.15	-2.97
13	0	0	-1	66.71	67.71	-1.00
14	0	0	1	81.71	82.40	-0.69

15	0	0	0	97.07	93.18	3.89
16	0	0	0	92.04	93.18	-1.14
17	0	0	0	92.04	93.18	-1.14
18	0	0	0	97.07	93.18	3.89
19	0	0	0	92.13	93.18	-1.05
20	0	0	0	92.13	93.18	-1.05

### 3.3 Optimization of Waste Cooking Oil Methyl Ester

The yield of WCOME and the process variables are presented in Fig. 2. It was noticed that WCOME yield increased with an increase in the reaction temperature. Similar

observation was also reported by Dwivedi and Sharma [20]. WCOME yield is noticed to increase with the methanol to oil molar ratio beyond stoichiometric ratio (3:1 molar ratio) but decreased beyond molar ratio of 6:1 M.

DESIGN-EXPERT Plot

Yield

Actual Factors  
 A: Time = 60.00  
 B: M:O ratio = 6.00  
 C: KOH concentration = 1.00

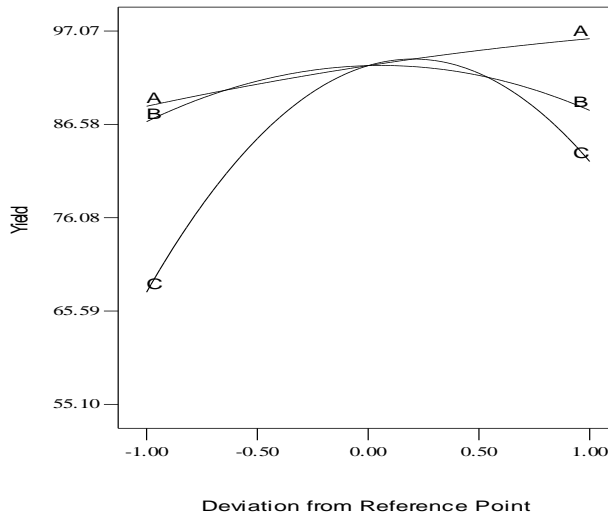


Fig. 2 Effect of reaction time, molar ratio and catalyst amount on yield of WCOME

### 3.4. Influence of Transesterification Variables and Optimization of Waste Cooking Oil Methyl Esters

The contour plots and response surface for conversion yield of waste cooking oil methyl ester depending on methanol/oil molar ratio and reaction time (Fig.3a), reaction time and catalyst amount (Fig. 3b) and methanol/oil molar ratio and catalyst amount (Fig.3c), while the third

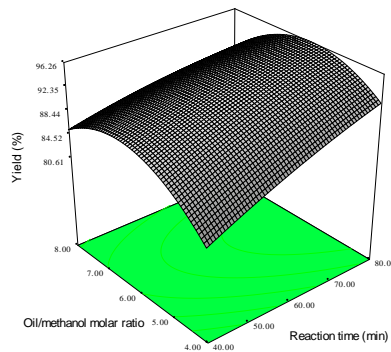
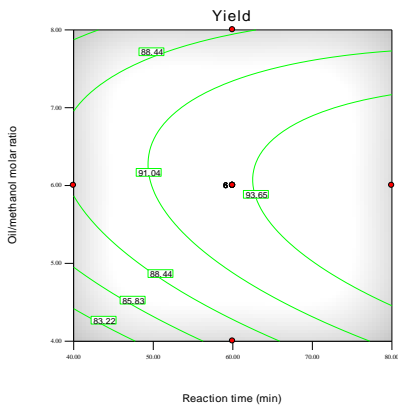
parameter is kept constant at the optimum value are depicted in Fig. 3. The 3D response curve and contour plot of ester yield versus methanol molar ratio and reaction time are shown in Fig. 3a. The WCOME yield of 83.22-93.65% was obtained within the range of 4:1-8:1 M for WCOME as the reaction time was varied from 40 to 80 °C. The optimum WCOME yield (93.65%) was obtained at 6:1 M methanol/oil molar ratio with 60

min reaction time. However, the ester conversion was observed to reduce with a further increased in molar ratio.

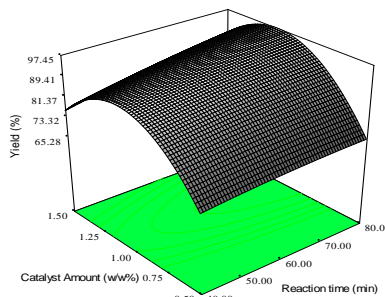
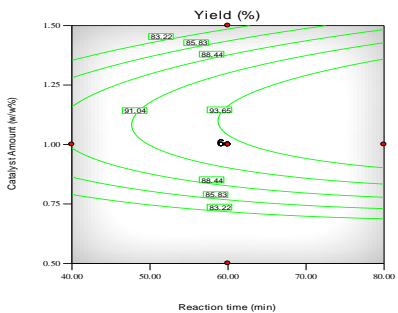
As can be observed in Fig. 3b, ester conversion is moderate when the catalyst amount was 0.75 wt.% with the reaction time. There is a decline in WCOME yield when the catalyst amount is increased beyond 1.0 w/w%. The reduction in ester conversion has been linked to the formation of emulsion and gel

formation [21]. The highest WCOME yield (93.65%) was attained at a catalyst amount of 1.0 wt.% and reaction time of 60 min.

It was noticed from Fig. 3c that catalyst amount in the range of 0.50-1.50 wt.% and methanol/oil molar ratio of 4:1-8:1 had an ester yield of 83.22-93.65%. In this study, the optimum condition was achieved at 6:1 methanol/oil molar ratio with 1 wt.% of KOH amount.

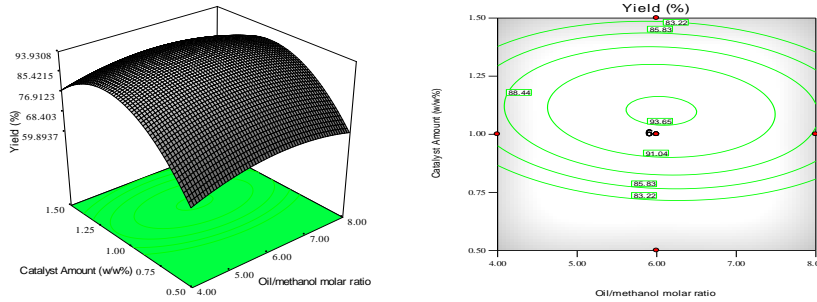


(a)



(b)





(c)

**Fig. 3** Contour plots and response surface of conversion yield of waste cooking oil methyl ester as a function of (a) methanol/oil molar ratio and reaction time, (b) reaction time and catalyst amount and (c) methanol/oil molar ratio and catalyst amount

### 3.5. Optimization of response parameters

The sets of optimized solutions for optimal production of the WCOME are detailed in Table 4. The reaction time (77.6 minutes), methanol to oil molar ratio (5.99) and catalyst

amount (1.11% w/w) with a predicted yield of 97.1% was chosen as the optimized parameters points. After validation, average between the predicted and actual values was found to be 0.03%.

**Table 4** Optimization summary for modified yield response model

Solution Number	Reaction Time (X <sub>1</sub> ) (min)	Methanol to Oil Molar Ratio (X <sub>2</sub> )	Catalyst Amount (X <sub>3</sub> ) (% w/w)	Estimated Yield of Waste Cooking Oil Methyl Ester (%)
1	77.60	5.99	1.10	97.07*
2	77.62	5.81	1.11	97.16
3	77.54	5.82	1.11	97.12
4	77.64	6.00	1.11	97.08
5	77.64	5.69	1.15	97.15
6	78.01	5.67	1.13	97.22
7	79.34	5.62	1.15	97.40
8	79.69	6.15	1.15	97.23
9	77.35	5.81	1.13	97.13
10	79.75	6.05	1.12	97.37

\* Optimal value selected

Summarized in Table 5 are the properties of produced waste cooking oil methyl ester (WCOME) and its comparison with those Vietnam waste cooking oil methyl Ester (VWCOME), ASTM D6751 and EN

14214 biodiesel standard specifications. The properties of WCOME concurred with those of VCOME and standard specifications. The boiling point (BP) of WCOME (310 °C) was higher than that of

diesel (290 °C) but was not specified by the ASTM D6751 and EN 14214 standards. This indicates that WCOME will not evaporate at low temperature. The high BP of the WCOME has been associated with the absence of volatile compound [22]. The sulphur content of B0

(0.2905 mg) was found to be higher than that of WCOME (0.0071 mg). The finding is in agreement with the report of Bamgboye and Oniya [23]. Fuel of low SC has been associated with a reduction in the environmental pollution during combustion process [24].

**Table 5** Fuel properties of WCOME in comparison with those of VWCOME and European and American Standards

Property	Unit	Waste Cooking Oil Methyl Ester <sup>a</sup>	ASTM Standard D6751-02	EU Standard EN14214	VWCOME <sup>b</sup>	B0
Density; 15 °C	kg/m <sup>3</sup>	883.34	NS	860 – 900	880	850
Kinematic viscosity; 40 °C	mm <sup>2</sup> /s	4.31	1.9 - 6.0	3.5 - 5.0	4.89	3.61
Flash point	°C	155	130 min	120 min	120	75
Acid value	mg KOH/g	0.40	0.5 max	0.50 max	0.43	-
Cloud Point	°C	2	Report	-	3	-8 <sup>a</sup>
Pour Point	°C	-12	<0	<0	0	-18
Mid-Boiling point	°C	310			-	290 <sup>a</sup>
Sulphur Content	mg	0.0071	<15.0	<10.0	-	0.2905
Higher Heating value	MJ/kg	40.07	-	-	-	46.77
Cetane number		61	47	51 min	-	48 <sup>a</sup>

a, Present study; b, Phan and Phan [17]; NS, Not specified.

#### 4.5. Characterization of WCOME and its Automotive Gas Oil/Conventional Fuel

Depicted in Figs. 4a-e is the influence of WCOME content on the respective thermophysical properties such as density, kinematic viscosity, flash point, cloud and pour point and sulphur content. Significant improvement in density, kinematic viscosity and flash point (FP) were noticed. Conversely, sulphur content value reduced while cloud point (CP) and pour point (PP) became worsened as the fraction of WCOME advanced in the blends. The higher density of WCOME resulted in more fuel being injected. Fuel of higher viscosity has been remarked to generate good spray across the

combustion chamber [18]. In addition, fuel types having higher flash point has been preferred to that of lower FP as it can be properly stored, transported and powered diesel engine without fire hazard [25].

Fuel having lower sulphur content has been remarked to reduce sulphur (VI) oxide if a diesel engine is powered with WCOME [22]. However, WCOME of high CP and PP has been limited for wider utilization in cold and arctic regions as they can result in fuel line clogging [26]. In order to reduce the limitation, cold flow improvers have been suggested by researchers [27-31]

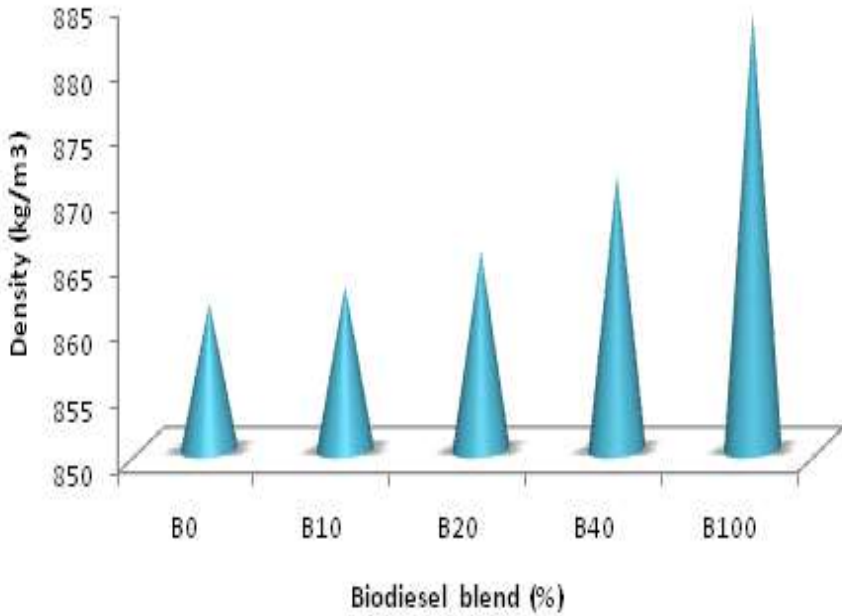


Fig. 4a Variation of density with biodiesel percentage

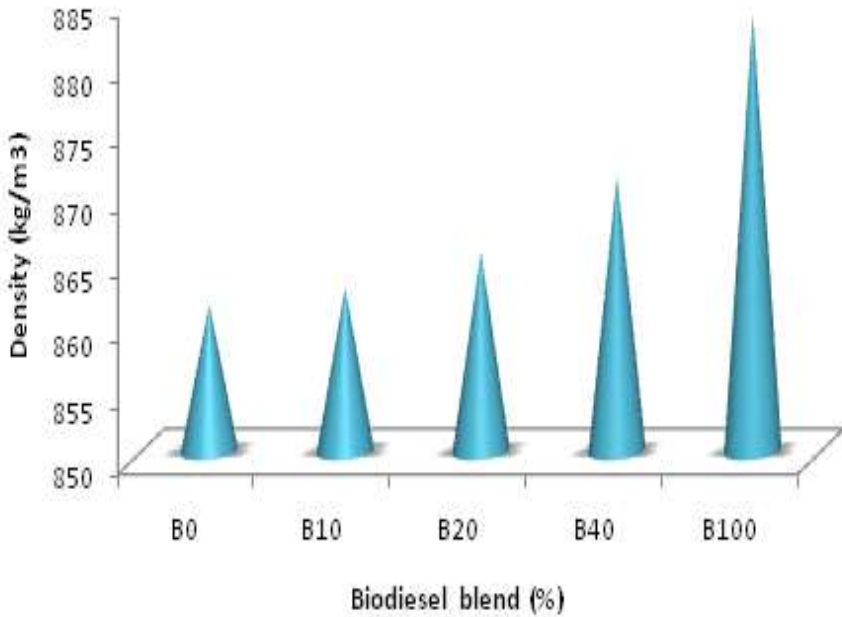


Fig. 4b. Variation of kinematic viscosity with biodiesel percentage

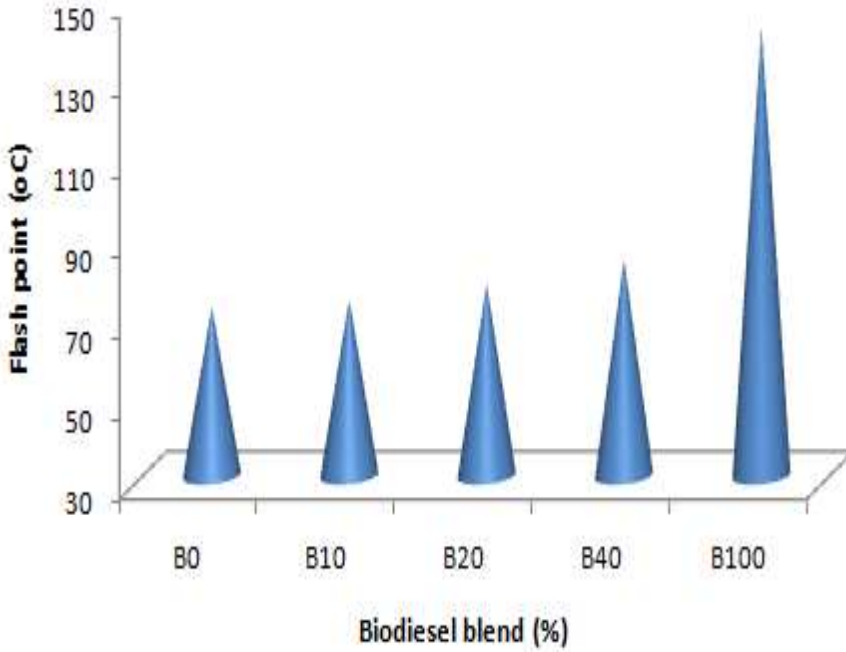


Fig. 4c Variation of flash point with biodiesel percentage

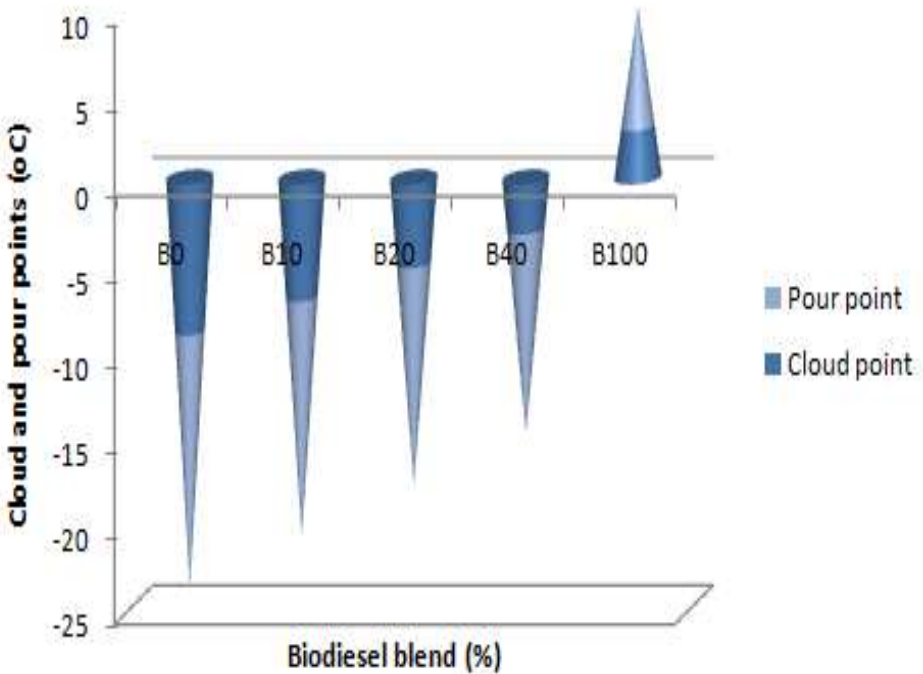


Fig. 4d Variation of cloud point and pour point with biodiesel percentage

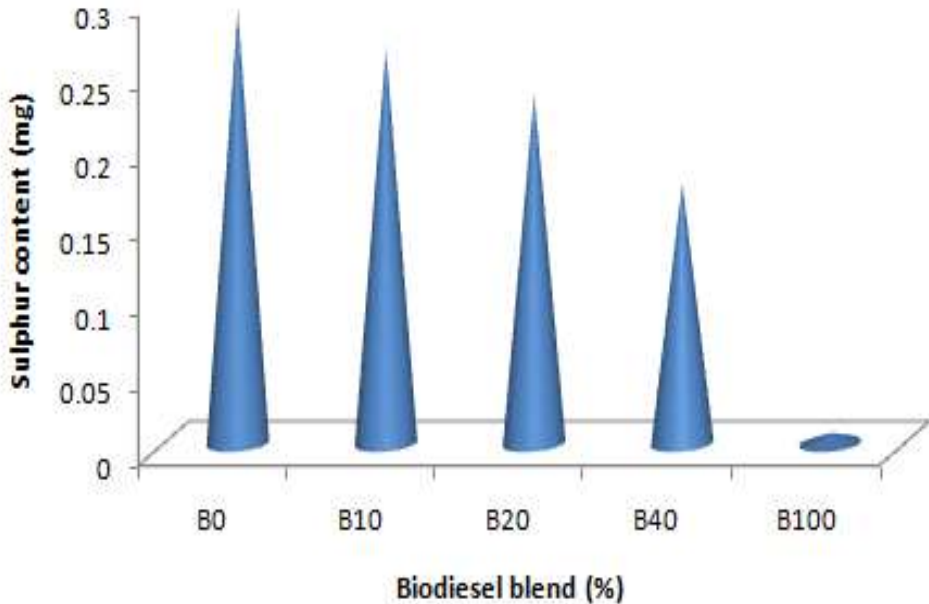


Fig. 4e. Variation of sulphur content with biodiesel percentage

#### 4.6. Mathematical Relationship Resulted from WCOME-Automotive Gas Oil/Diesel Blends

Mathematical correlations were developed for the prediction of density, kinematic viscosity, flash point, cloud point, pour point and sulphur content of the fuel types and biodiesel fraction (Table 6). A second-degree equation was found suitable to correlate the variation of densities and WCOME–diesel fuel blends. The coefficient of determinant ( $R^2$ ) from the density regression model shows that over 99.6% of the experimental density is captured in the empirical equation. The second-degree model equation was found adequate to correlate the variation of kinematic viscosity (KV) and WCOME–diesel fuel blends. The high  $R^2$  (0.978) indicates that over 97.8% of the actual KV is captured in the empirical equation.

A third-degree polynomial equation was found suitable to correlate the variation of flash point (FP) with biodiesel content at any blend. The  $R^2$  of 0.999 reveal that over 99.9 % of the measured FP was captured.

Polynomial regression equation and third-degree equation were found suitable for the respective cloud point and pour point variation with biodiesel percentage. The high  $R^2$  (0.999) and  $R^2$  (0.995) resulting from the pour point regression model and cloud point polynomial, respectively indicate that not less than 99 % of the experiment data were captured for the cloud and pour points measured.. The second degree model equation was found adequate to correlate the variation of sulphur content and WCOME–diesel fuel blends. The high  $R^2$  (0.9999) indicates that 99.9 % of the experiment was captured by the sulphur content model equation.

**Table 6** Model for predicting fuel properties for WCOME-diesel fuel blends

Fuel properties	Regression Model	R <sup>2</sup>
Density (Kg/m <sup>3</sup> )	$Y = -0.000x^2 + 0.260x + 860.6$	0.996
Kinematic viscosity (mm <sup>2</sup> /s)	$Y = -0.00009x^2 + 0.013x + 4.691$	0.978
Flash point (°C)	$Y = 0.00007x^2 - 0.002x + 0.309 + 71.77$	0.999
Cloud point (°C)	$Y = -0.000x^2 + 0.176x - 8.766$	0.995
Pour point (°C)	$Y = 0.00004x^3 - 0.003x^2 + 0.149x - 15.04$	0.999
Sulphur content (m/m %)	$Y = 0.000001x^2 - 0.003x + 0.292$	0.999

Y= Fuel property; x= Percentage of WCOME in the blend

#### 4.7 Degradation of Aluminium Coupon and Deterioration of Fuel Types

The corrosion rate of aluminium upon exposure to diesel and WCOME blends is depicted in Fig. 5 while the variation of the corrosion rates for the fuel types with the regression model is detailed in Table 7. The degradation of aluminium exposed to the fuel types for 960 hours were assessed by investigating changes in hardness and tensile strength and showed in Figs. 6 and 7, respectively. Before the commencement and after the exposure of the coupon to the fuel types, the density, viscosity and total acid number (TAN) were determined and presented in Figs. 8-10. The morphological structure of the aluminium prior exposure to the fuel types are presented in Plate 1a while those of coupons after being exposed are depicted in Plates 1b-f. The corrosion rate slightly increased with advancement in biodiesel content in the blends and exposure duration as

shown in Fig. 5. As presented in Table 7, corrosion rates variation with 480 and 720 hour duration of exposure are correlated using 2<sup>nd</sup> empirical equation while those of 240 hour and 960 hour are fitted with 4<sup>th</sup> degree model equation and 3<sup>rd</sup> degree regression equation, respectively. The experimental corrosion rates ranges covered by the corrosion rates regression models for aluminium coupon ranged from 86.1 to 99.6%. With the increasing in biodiesel percentage in the blends, there is an increase in hardness and tensile strength (TS) of aluminium, as depicted in Figs. 6-7, respectively. The change in hardness of aluminium in WCOME (62.89%) was higher than those of B100 (62.89%), B40 (44.37%), B20 (31.71%) and B10 (11.0%). Similarly, the change in TS of aluminium coupon exposed to WCOME (62.90%) was higher than those of the conventional diesel (2.65%) and blended diesel and WCOME.

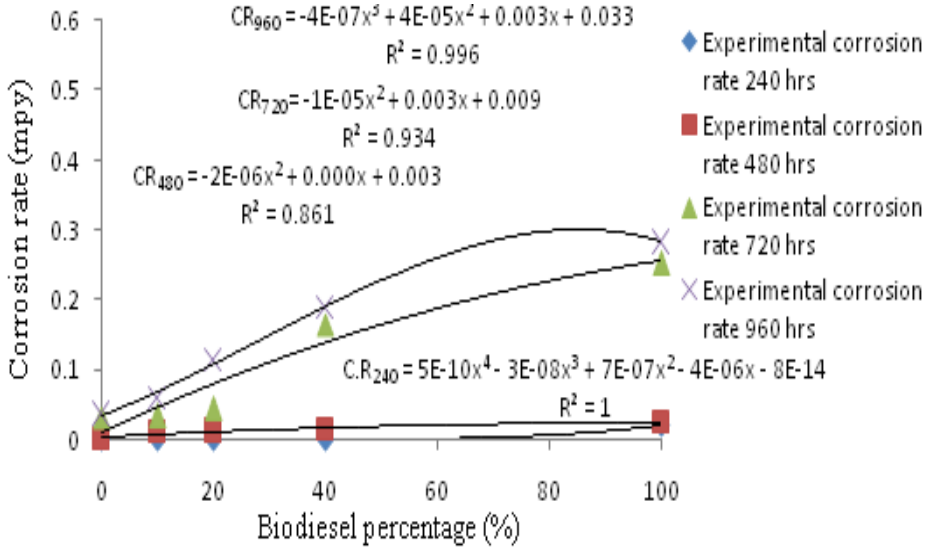


Fig. 6 Variation of corrosion rates of aluminium in waste cooking oil biodiesel -diesel blends

**Table 7** Regression models for corrosion rates of aluminium in blending ratios of waste cooking oil biodiesel

Exposed period (hours)	Regression Models	R <sup>2</sup>
240	$CR = 0.0000000005x^4 - 0.00000003x^3 + 0.00000007x^2 - 0.000004x - 0.00000000000000000008$	1
480	$CR = -0.000002x^2 + 0.000x + 0.003$	0.861
720	$CR = -0.00005x^2 + 0.003x + 0.0009$	0.934
960	$CR = 0.0000004x^3 - 0.00004x^2 + 0.003x + 0.033$	0.996

CR= corrosion rate (mil/yr); x = percentage of waste cooking oil biodiesel in the blend.

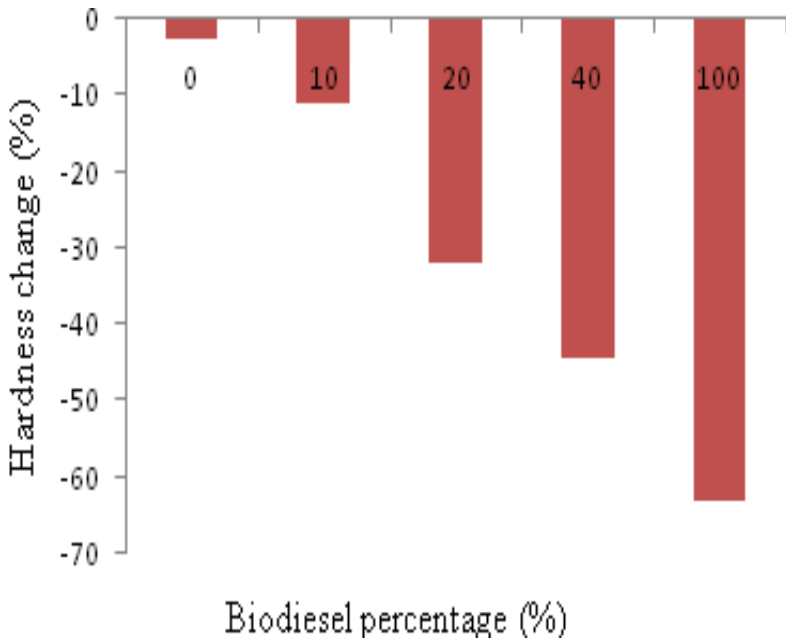


Fig. 6. Variation of hardness change and fuel types after static immersion test for 960 hours

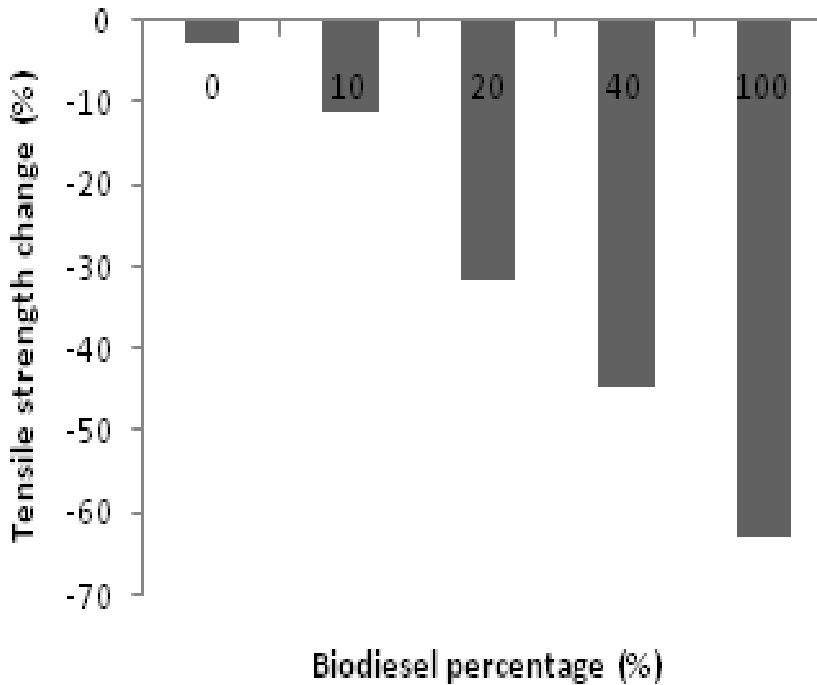


Fig. 7. Variation of tensile strength change and fuel types after static immersion test for 960 hours

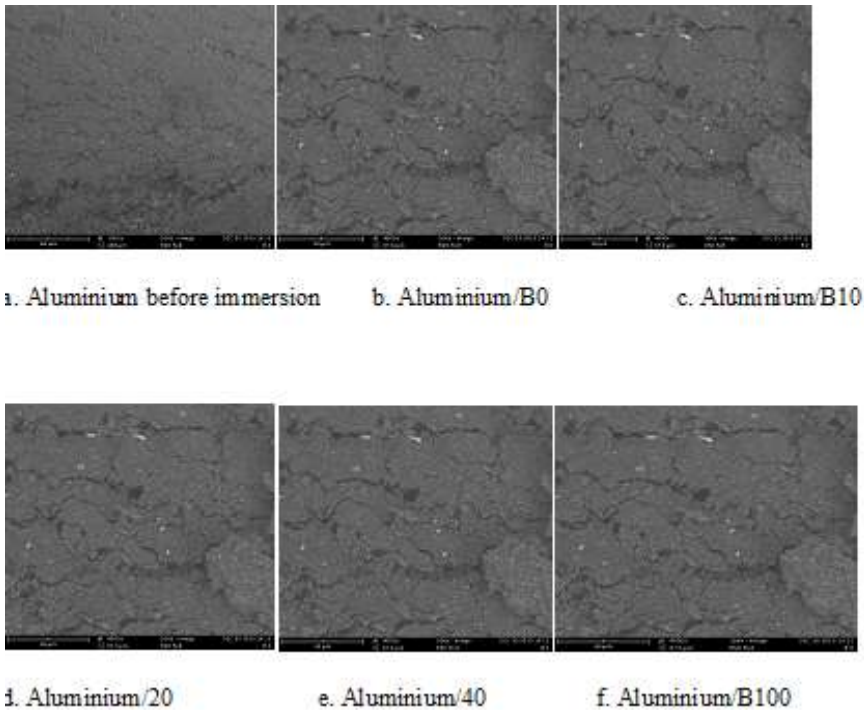
The coupon's surface morphology of the fossil diesel (plate 1b) has less

strike than those of WCOME and its blends (Plates 1c-f). The changes in



the appearance of the coupon exposed to WCOME and its blends are caused by the oxidation product which enters into the fuel, leading to fatty acid salts on the aluminium coupon. This implies that the WCOME and its blends are prone to corrosion attack than that of diesel [2]. Moreover, the micrographs show that there were slight damages to aluminium coupon exposed to

biodiesel and its blends than diesel. The extents of damage are revealed by the pits on the coupon surfaces. This was further proven by deterioration of basic fuel properties such as density, viscosity and total acid number (see Figs. 8-10). This observation is in agreement with the published reports of other researchers [32-35].



u

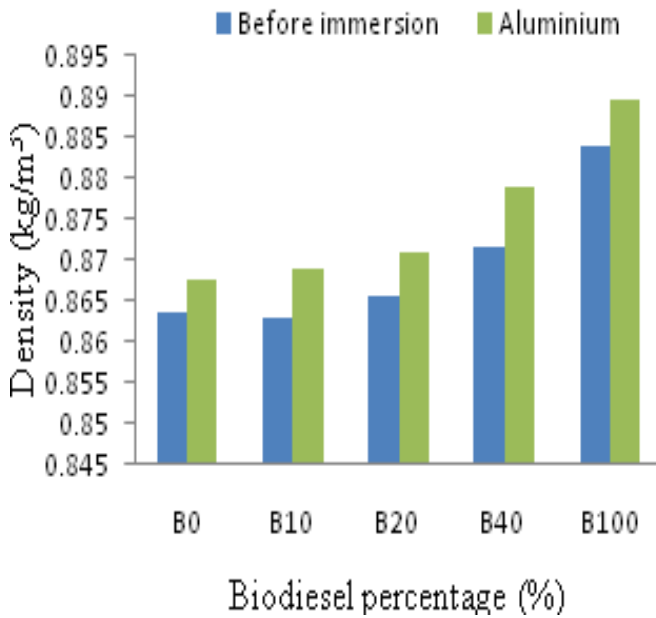
Plate 2: SEM micrographs of aluminium (Al) surface before and after exposure to diesel (B0), B10, B20, B40 and B100 at room temperature for 960 h.

The investigated density, kinematic viscosity (KV) and total acid number (TAN) before and after exposure to different fuel types are depicted in Figs. 8-10, respectively. The density, KV and TAN were observed to increase with biodiesel content in the

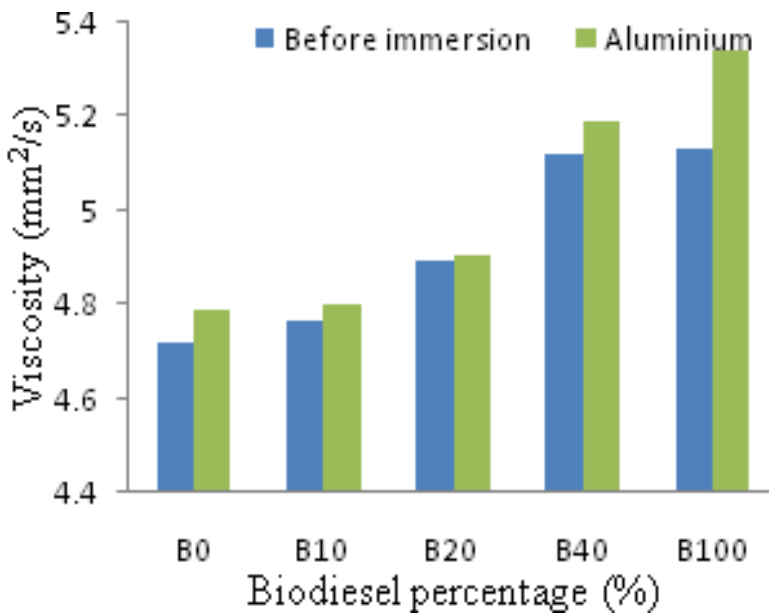
blends after being exposed. However, the density and KV are within the standards of density and viscosity of European Union (EN 14214) ASTM D671 specifications. Degradation of metallic component

and compositional variation has been

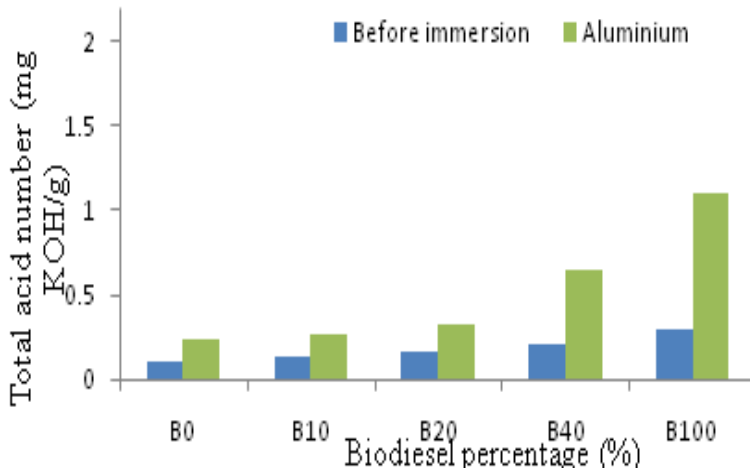
indicated for the changes [36-39].



**Fig. 8** Variation of density with biodiesel fraction, before and after 960 h of exposure to coupons



**Fig. 9** Variation of kinematic viscosity with biodiesel fraction, before and after 960 h of exposure to coupons



**Fig. 10** Variation of TAN with biodiesel fraction, before and after 960 h of exposure to coupons

## 5. Conclusions

Based on the corrosion study of aluminium coupons exposed to optimized waste cooking oil methyl ester (WCOME) and automotive gas oil blends, the following conclusion can be deduced:

- Maximum 97.1% WCOME yield was obtained with 1.1 wt.% KOH and 5.99 oil/methanol molar ratio at 60 oC for 78 min.
- Basic properties of WCOME met the specification of the ASTM D6751 and EN14214 standards.
- Sulphur content decreased while those of other key properties increased with the increased in the content of the blend of WCOME.
- Corrosion rates of aluminium increased with biodiesel fraction and duration of exposure

- Hardness and tensile strength of aluminium increased with biodiesel fraction
- Results showed that high blending ratios can degrade aluminium coupon in comparison with that of B0. It was observed that the 10% WCOME (B10) as a blend ratio operated close to B0 with respect to Brillness hardness and tensile strength, and the reductions in cold flow properties which make B10 a viable substitute to fossil diesel in cold and arctic regions.

## Acknowledgment

The financial assistance received from the Tertiary Educational Trust Fund for the project and assistance rendered by Pastor Akinola Omotayo in the production of biodiesel from waste cooking oil are gratefully appreciated by the authors.

## References

- [1] Verma, P., Sharma, M.P., "Comparative analysis of effect of methanol and ethanol on Karanja biodiesel production

and its optimisation, *Fuel*, 180, pp. 164-174, (2016).

- [2] Cursaru, D.L., Brănoiu, G., Ramadan, I., Miculescu, F., "Degradation of automotive materials upon exposure to

- sunflower biodiesel”, *Industrial Crops and Products*, (54), pp. 149-158, (2014).
- [3] Moser, B.R., “ Biodiesel production, properties, and feedstocks”, *In vitro Cell Biol. Plant*, 45, pp. 229-266, (2009).
- [4] Zuleta, E.C., Baena, L., Rios, L.A., Calderón, J.A., “The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: a review”, *Journal of the Brazilian Chemical Society*, 23(12), pp. 2159-2175, (2012).
- [5] Singh, B., Korstad, J., Sharma, Y.C., “A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition”, *Renewable and Sustainable Energy Reviews*, 16(5), pp. 3401-3408, (2012).
- [6] Chew, K.V., Haseeb, A.S.M.A., Masjuki, H.H., Fazal, M.A., Gupta, M., “Corrosion of magnesium and aluminum in palm biodiesel: A comparative evaluation”, *Energy*, 57, pp. 478-483, (2013).
- [7] Akhabue, C.E., Aisien, F.A., Ojo, C.O., “The effect of Jatropha oil biodiesel on the corrosion rates of aluminium and mild carbon steel”, *Biofuels*, 5(5), pp.545-550, (2014).
- [8] Norouzi, S., Eslami, F., Wyszynski, M. L., Tsolakis, A., “Corrosion effects of RME in blends with ULSD on aluminium and copper”, *Fuel processing technology*, 104, pp. 204-210, (2012)
- [9] Samuel, O.D., *Characteriation and performance evaluation of waste cooking oil biodiesel-diesel fuel blends in diesel engines*, Ph.D. Thesis, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria , (2016).
- [10] Chuckwumenogor, O., *Characterization and corrosion behaviour of copper, aluminium and brass exposed to waste cooking oil biodiesel*, B.Eng. Project, Federal University of Petroleum Resources, Effurun, Nigeria, (2016).
- [11] Robert, C., *Introduction to manufacturing processes and materials*, New York
- [12] El-Gendy, N.S., Deriase, S.F., Hamdy, A., “The optimization of biodiesel production from waste frying corn oil using snails shells as a catalyst” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 36(6), pp.623-637, (2014).
- [13] Nachid, M., Ouanji, F., Kacimi, M., Liotta, L.F., Ziyad, M., “Biodiesel from moroccan waste frying oil: the optimization of transesterification parameters impact of biodiesel on the petrodiesel lubricity and combustion”, *International Journal of Green Energy*, 12(8), pp.865-872, (2015).
- [14] Zhang, Y., Dube, M.A., McLean, D.D.L., Kates, M., “Biodiesel production from waste cooking oil: 1. Process design and technological assessment”, *Bioresource*

- Technology, 89(1), pp.1-16, (2003).
- [15] Freedman, B., Pryde, E.H., "Fatty esters from vegetable oils for use as a diesel fuel", In: Vegetable oils fuels", *proc. of the int. conf. on plant and vegetable oils as fuels*, St. Joseph, Mich., ASAE; pp. 117-22, (1982).
- [16] Atadashi, I.M., Aroua, M.K., Aziz, A.A., Sulaiman, N.M.N., "The effects of water on biodiesel production and refining technologies: A review", *Renewable and Sustainable Energy Reviews*, 16(5), pp.3456-3470, (2012).
- [17] Phan, A.N., Phan, T.M., "Biodiesel production from waste cooking oils", *Fuel*, 87(17), pp.3490-3496, (2008).
- [18] Al-Hammare, Z, Yamin J., "Parametric study of the alkali catalyzed transesterification of waste frying oil for biodiesel production", *Energy Conversion and Management*, 79, pp. 246-54, (2014).
- [19] Gopal, K. N., Karupparaj, R. T., "Effect of pongamia biodiesel on emission and combustion characteristics of DI compression ignition engine", *Ain Shams Engineering Journal*, 6(1), pp. 297-305, (2015).
- [20] Dwivedi,G., Sharma, M.P., "Application of Box- Behnken design in optimization of biodiesel yield from Pongamia oil and its stability analysis", *Fuel*, 145, 256-262, (2015).
- [21] Ong, H.C., Masjuki, H.H., Mahlia, T.M.I, Silitonga, A.S., Chong W.T., Leong, K.Y., "Optimization of biodiesel production and engine performance from high free fatty acid Calophyllum inophyllum oil in CI diesel engine", *Energy Conversion and Management*, pp.30-40, (2014).
- [22] Bora, D. K., Polly, M., Sanduja, V., "Performance evaluation and emission characteristics of a diesel engine using mahua oil methyl ester (MOME), *SAE Technical paper*, No. 2004-28-0034, (2004).
- [23] Bamgboye, A.I., Oniya, O.O., "Fuel properties of loofah (*Luffa cylindrica* L.) biofuel blended with diesel", *African Journal of Environmental Science and Technology*, 6(9), pp.346-352, (2012).
- [24] Taravus, S., Temur, H., Yartasi, A., "Alkali-catalyzed biodiesel production from mixtures of sunflower oil and beef tallow", *Energy and Fuels*, 23, pp. 4112-4115, (2009).
- [25] Agarwal, A.K., Das, L.M., "Biodiesel development and characterization for use as fuel in compression ignition engines", *Journal of Engineering for Gas Turbines and Power*, 123, pp. 440-447, (2001).
- [26] Rasimoglu, N., Temur, H., "Cold flow properties of biodiesel obtained from corn oil", *Energy*, 68, pp.57-60, (2014).
- [27] Islam, M.M., Hassan, M.H., Kalam, M.A., Habibullah, M. and Hossain, M.M., "Improvement of cold flow properties of *Cocos nucifera*

- and Calophyllum inophyllum biodiesel blends using polymethyl acrylate additive, *Journal of Cleaner Production*, 137, pp.322-329, (2016).
- [28] Verma, P., Sharma, M.P., Dwivedi, G., "Evaluation and enhancement of cold flow properties of palm oil and its biodiesel", *Energy Reports*, 2, pp.8-13, (2016).
- [29] Altaie, M.A.H., Janius, R.B., Rashid, U., Yap, Y.H.T., Yunus, R., Zakaria, R., "Cold flow and fuel properties of methyl oleate and palm-oil methyl ester blends", *Fuel*, 160, pp. 238–244, (2015).
- [30] Anon, "Determination of ester and linolenic acid methyl ester contents", *English version of DIN EN 14103*, (2003).
- [31] Bhale, P.V., Deshpande, N.V., Thombre, S.B., "Improving the low temperature properties of biodiesel fuel", *Renew. Energy*, 34 (3), pp.794–800, (2009).
- [32] Fazal, M.A., Haseeb, A.S.M.A., Masjuki, H.H., "Degradation of automotive materials in palm biodiesel", *Energy*, 40(1), pp.76-83, (2012).
- [33] Hu, E., Xu, Y., Hu, X., Pan, L., Jiang, S., "Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol", *Renewable Energy*, 37(1), pp.371-378, (2012).
- [34] Samuel, O.D., Ashiedu, F.I., Oreko, B.U., "Analysis of coconut ethyl ester (biodiesel) and fossil diesel blending: properties and corrosion characteristics", *Nigerian Journal of Technology*, 35(1), pp.107-113, (2016).
- [35] Meenakshi, H. N., Shyamala, R. , "Effect of Flow and Dissolved Oxygen on the Compatibility of Pongamia pinnata Biodiesel with Common Construction Materials Used in Storage and Transportation", *International Journal of Chemical Engineering (1687806X)*, (2015)
- [36] Fazal, M.A., Haseeb, A.S.M.A., Masjuki, H.H., "Effect of temperature on the corrosion behavior of mild steel upon exposure to palm biodiesel", *Energy*, 36(5), pp.3328-3334, (2011).
- [37] Thangavelu, S.K., Chelladorai, P., Ani, F.N., "Corrosion Behaviour of Carbon Steel in Biodiesel-Diesel-Ethanol (BDE) Fuel Blend", In *MATEC Web of Conferences* (Vol. 27). EDP Sciences, (2015).
- [38] Haseeb, A.S.M.A., Masjuki, H.H., Ann, L.J., Fazal, M.A., "Corrosion characteristics of copper and leaded bronze in palm biodiesel", *Fuel Processing Technology*, 91(3), pp.329-334, (2010).
- [39] Fernandes, D.M., Montes, R.H., Almeida, E.S., Nascimento, A.N., Oliveira, P.V., Richter, E.M., Muñoz, R.A., "Storage stability and corrosive character of stabilised biodiesel exposed to carbon and galvanised steels", *Fuel*, 107, pp.609-614, (2013).