Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
Garba & al. / Mor. J. Chem. 9 N°1 (2021) 132-141

OPTIMIZATION AND EVALUATION OF BIODIESEL QUALITY PRODUCED FROM CATTLE FAT USING CaO/Al_2O_3 AS CATALYST

***Abdulrashid Abubakar Garba* [a] *and Bishir Usman** [*] [b]

[a]*Department of chemistry, Faculty of Science Sokoto State University Sokoto. Sokoto, Nigeria*

[b]*Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, College Natural and Phamaceutical Sciences Bayero University Kano, Kano, Nigeria*

** Corresponding author:*
busman.chm@buk.edu.ng

Received 28 Aug 2019, Revised 19 Dec 2020, Accepted 12 Jan 2021.

Abstract

Biodiesel was produced from cattle fat, In transesterification method usingCaO and Al_2O_3 ascatalyst. The catalyst was also characterized by XRD pattern, SEM and FTIR analysis. Response Surface Methodology using Central Composite Design (CCD) was used to determine the optimum operating conditions for the biodiesel yield. The result showed that catalyst CaO/Al_2O_3 give maximum biodiesel yield of 99.37% with methanol to oil ratio, catalyst dosage and reaction temperature of (10.5:1), (3.5) and (50^0C) respectively. The fuel parameters of the biodiesel produced and its blend are close to commercially available petrol diesel, indicating that the two could be blended together in order to minimize the environmental effects of the petroleum diesel. The fatty acid methyl ester (FAME) composition of the biodiesels was determined using Gas Chromatography coupled with Mass Spectrophotometer (GC-MS). The fatty acid methyl esters (FAMEs) profile indicates that the dominants compounds in biodiesel are ester compounds. The thermodynamic and kinetics of the biodiesel produced was investigated to check the feasibility, order of the biodiesel. It was found to be non-spontaneous and endergonic. The biodiesel and its blend quality were asses using and it was found out to be low in B_{100} but high in B_{20} indicating that the biodiesel produced from waste cattle fat have high quality and can be used for engines.

Keywords: *Biodiesel, CaO/Al_2O_3, RSM and FAMES*

1. Introduction

Recently, there has been a dramatic increase in the amount of greenhouse gases in the atmosphere which increase the risk of global warming (Al-Hamamre and Yamin, 2014). The most abundant greenhouse gases in the atmosphere include: Carbon Dioxide (CO_2), Methane, (CH_4) and water vapour (H_2O). Oxides of Nitrogen, Ozone and Chlorofluorocarbons (CFC) are also readily available in the atmosphere. However, the concentration of carbon dioxide is the highest among the greenhouse gases. This is due the burning of fossil fuels (Jazie *et al.,* 2013).Biodiesel has been considered as a promising potential substitute for conventional diesel-based petroleum. Biodiesel is the mixture of mono alkyl esters that can be continuously derived from vegetable oils or animal fats and therefore it is terms as renewable energy (Atadashi *et al.,* 2011).CaO is a solid basic catalyst that shows a promising result in transesterification process with oil conversion of more than 95 % (*Liu et al*., 2008). Although good performance in transesterification with CaO tends to leach out into the reaction medium and thus reduces its reusability. CaO is a basic heterogenic catalysts which is most widely used for transesterification reaction because it is highly basic, and has a low solubility in methanol (Nautiyal*et al*., 2009; Slama*et al*., 2011).Optimization study for biodiesel production is crucial to assist researchers to develop a more efficient and cost-effective system in biodiesel industry. Generally, the reaction parameters such as reaction time, reaction temperature, catalysts loading and methanol to oil molar ratio, are being manipulated to optimize the biodiesel yield.

2. Material and method

Cattle fat was purchased from abattoir in Kano state and was pre-treated and melted at 60-50^{0}C before transesterification process. Methanol (99.8%, Sigma Aldrich) calcium oxide (99.9% aldrich) were obtained from Chemistry Department Laboratory of Bayero University, Kano.

2.1 Preparation of Calcium Oxide /Alumina (CaO /Al_2O_3)

80g of aluminium oxide were accurately weighed and dissolved in 100cm^3 of distilled water in a 500cm^3 beaker. Then 20g of calcium nitrate powder were weighed and added to the same solution. The mixture was then placed on a hot plate magnetic stirrer and heated at a temperature of 50^{o}C for 2hours.It was then transferred to the crucibles and taken to the oven and dried at a temperature of 105oC for 2hrs. It was later removed from the oven and taken to the muffle furnace and calcined at 600^{o}C for 2hrs. (Asri *et.al*, 2012).

2.2 FTIR Analysis

The Fourier transform infrared spectroscope of the Al_2O_3catalyst was carryout using FT-IR Cary 630 (Agilent Technology) at frequency range of 4000-650 cm^{-1}.

2.3 X-ray Diffraction Analysis

The CaO/Al_2O_3 catalyst sample was analyzed using an X'Pert Pro (Philips) diffractometer with Cu-Kα radiation (λ = 0.15406 nm) and a proportional counter as a detector. A divergent slit of 1/32^0 on the primary optics and an anti-scatter slit of 1/16◦ on the secondary optics were used to measure the data in the low-angle region. The XRD patterns were measured in the 2θ range of 20^o to 120^o at a scan rate of 1 and 4^o/min.

2.4 Scanning Electron Microscope (SEM)

SEM of the Al_2O_3catalyst sample was recorded using a SEM Leica 440 instrument at accelerating voltage 10kV and magnification 500x. The sample was coated on the sample holder and subjected into the machine. Result was observed.

2.5 Design of Experiments

Response surface methodology (RSM) with central composite design (CCD) was applied to different variables to optimize the biodiesel production from cattle fat oil. In this study, three independent parameters were evaluated which were reaction time, catalysts loading and methanol to oil molar ratio while the dependent variable was fatty acid methyl esters (FAME) yield or biodiesel yield. The range and levels of the independent variables for transesterification process was shown in Table 2.Each response obtained from the transesterification process was used to develop a mathematical model that correlates the biodiesel yield to the independent reaction variables via second-order polynomial equation as given equation 1.

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (1)$$

Where *Y* is the predicted FAME yield, b_o is the constant coefficient, b_i is the linear coefficients, b_{ij} is the interaction coefficients, b_{ii} is the quadratic coefficients and x_i, x_j are the coded values of the experimental variables in Table 1

Table 1: Variables, Coded value, unit and Levels for Transesterification process

Levels			-α	-1	0	1	α
Variables	coded value	units					
Reaction temp.	A	k	45	50	55	60	65
Catalyst loading	B	wt. %	1	2	3	4	5
Methanol/oil ratio	C	mol/mol	6	9	12	15	18

2.5 Biodiesel Production

Ten gram (10g) of cattle fat oil were weighed and poured into conical flask (250ml). Proper proportion of methanol to oil ratio and catalyst were added to the oil, the mixture was then placed in a water bath and heated at various parameters selected for optimization process as stipulated in the design matrix (Table 2).. The fatty acid methyl ester was analyzed using GC-MS to identify the formation of (FAME) (Rutto and Enweremadu, 2013).

Coupons Preparation

The mild steel were prepared according to ASTM, A29M-05 as described by (Usman, 2015), and corrosion standard at (2cm × 2cm). The coupons were ground and polish with enmery paper of 240-800 grade, degreased with methanol, water dry in acetone and warm air, stored in desiccator before used

2.6 Weight loss and Corrosion Rate of the Biodiesel Produced

The weight loss corrosion rate measurements were carried out according to the method reported by (Usman, 2015). Weight loss is a practical and reliable method experiment that is use to carry out weight loss and corrosion rate. Weight loss was taken to be the differences between the weights of coupons at a given time (200, 400 hours) and its initial weight. From the initial and final weight of mild steel coupons, the weight loss (gh^{-1}), corrosion rate ($gh^{-1}\ cm^{-2}$) were calculated using equation 7. (Eddy *et al.*, 2010)

$$CR\ (gh^{-1}\ cm^{-2}) = \frac{DW}{At} \quad (2)$$

Where ΔW is the change in weight, CR is the corrosion rate, A is the area of the coupons and

3. RESULT AND DISCUSSION

The cattle fat oil was found to have acid value, free fatty acid and saponification value after treatment with organic base (ammonium hydroxide) of 2.402 mg KOH/g, 1.34% and 194 mg KOH/g Oil respectively (Table 2).

Table 2. Properties of cattle fat oil

Properties	Unit	Before treatment	After treatment
Acid value	mg KOH/g oil	19.33	2.402
FFA	%	9.66	1.344
Saponification value	mg KOH/g oil	207.57	194
pH	-	4.30	4.97

Table 3: Design Matrix

Run	A: Temperature Degree	B:catalyst dosage Wt%	C:Methal to oil ratio Mol:Mol
1	50	50	10.5
2	65	1	15
3	50	2.5	10.5
4	75	2.5	10.5
5	24	2.5	10.5
6	65	4.1	15
7	50	2.5	2.93
8	65	4	6
9	50	2.5	18.07
10	35	4.1	6
11	50	2.5	15
12	50	3.5	10.5
13	50	5	10.5
14	65	1.5	6
15	50	2.5	10.5
16	50	2.5	10.5
17	35	1	15
18	50	2.5	10.5
19	35	1	6
20	35	2	10.5

a

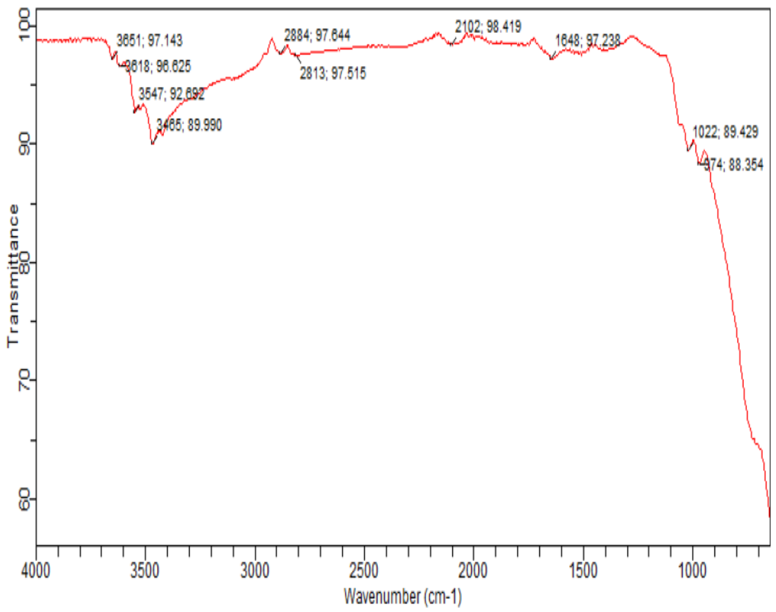

Fig. 1: FT-IR SPECTRUM FOR Al_2O_3

The absorption peak at 3420cm^{-1} is attributable to O-H bending vibration of adsorbed water molecules. Peaks observed at 2117cm^{-1} is attributable to Al-O bond as observed in figure 1 above indicate the present of Al_2O_3. Temperature, catalyst dosage and methanol to oil ratio were optimized for biodiesel production from Cattale Fat using Respond Surface Methodology (RSM) with Central Composite Design (CCD) in which temperature ranges from 45^{0}C to 70^{0}C, catalyst loading 1 4wt% and methanol to oil ratio of 3 to 15 were used The peaks at 3640cm^{-1} correspond to Ca-O bond. Peaks at 1417cm^{-1} and 877cm^{-1} due to stretching vibration of Ca-O bond indicate the presence of CaO in the prepared catalyst as shown in figure 2 above.

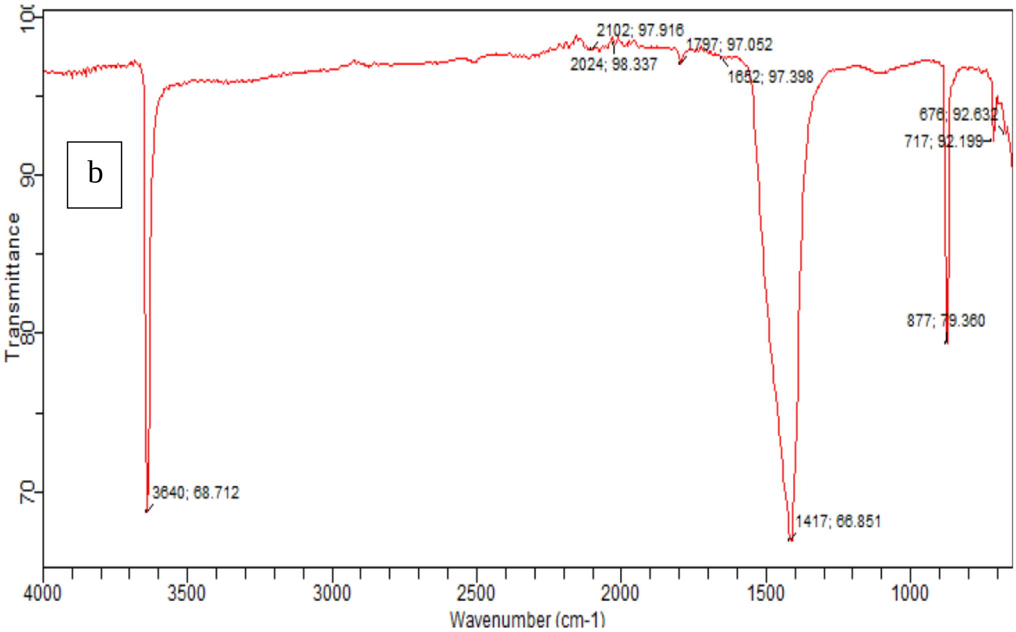

Figure 2: FT-IR Spectrum for CaO

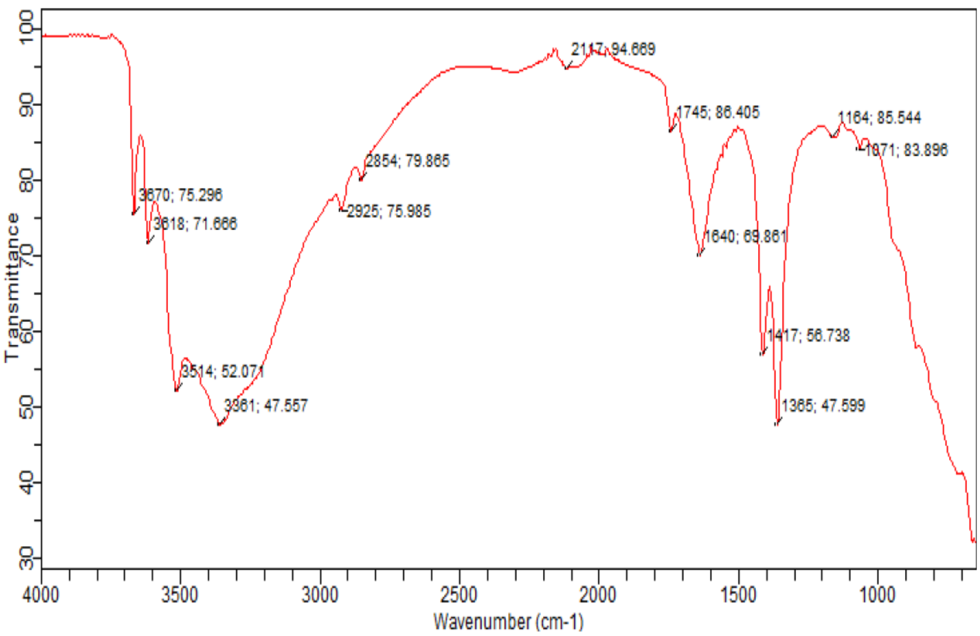

Fig.3: FT-IR SPECTRUM FOR CaO/Al_2O_3

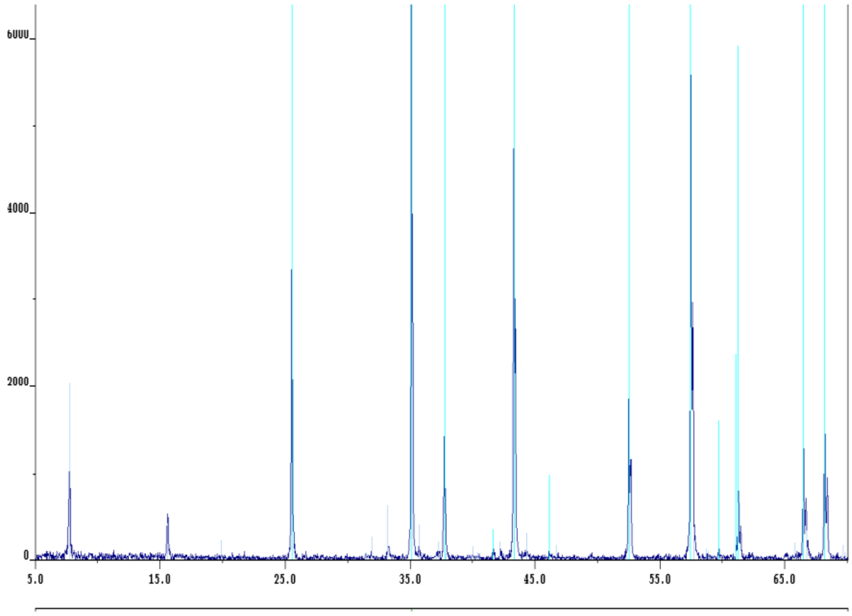

Figure 4: XRD spectrum of CaO/Al_2O_3

Fig.3 above indicate the presence of CaO/Al_2O_3 as a mixed oxide. The X-ray diffractogram for the CaO/Al_2O_3 catalyst is shown in (Figure 4.4). The diffraction peaks at the 2θ position of 34.08^0, 47.123^0, 34.351^0 and 62.613^0 correspond (111), (200), (220) and (311). Which are in agreement with the standard JCPDS file (JCPDS 82-1698) for CaO. The peaks 43.5^0 and 54.23^0 are attributable to Al_2O_3 component of the catalyst.

Table 4: Actual and Predicted Values of the Response Variables

Run	A: Temperature Degree	B:catalyst dosage Wt%	C:Methal to oil ratio Mol:Mol	Actual yield %	Predicted yield %
1	50	50	10.5	62.12	65.33
2	65	1	15	92.19	90.19
3	50	2.5	10.5	94.79	91.47
4	75	2.5	10.5	64.14	70.15
5	24	2.5	10.5	34.4	29.33
6	65	4.1	15	84.2	87.30
7	50	2.5	2.93	60.27	66.24
8	65	4	6	96.7	93.67
9	50	2.5	18.07	81.31	85.89
10	35	4.1	6	48.4	51.50
11	50	2.5	15	63.73	61.34
12	50	3.5	10.5	99.37	97.96
13	50	5	10.5	91.57	94.57
14	65	1.5	6	81.4	85.30
15	50	2.5	10.5	94.68	90.01
16	50	2.5	10.5	94.52	89.98
17	35	1	15	96.34	96.05
18	50	2.5	10.5	94.79	94.13
19	35	1	6	33.5	33.00
20	35	2	10.5	63.86	64.56

Table 4. Shows the experimental and the predicted values of the percentage conversion (yied) of biodiesel obtained as responses at the design of different operating conditions. The yield of biodiesel varied from 33.5 to 99.37. the minimum biodiesel yield 33.50% was obtained at 6:1 methanol to oil molar ratio, 1% catalyst dosage, 35ºc reaction temperature, whereas the maximum biodiesel yield 99.37% was obtained at 10.5:1 methanol to oil ratio, 3.5 catalyst dosage and 50ºc reaction temperature.

Table 5: ANOVA for Quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	6785.28	9	753.920	4.1900	0.0178	Significant
A-Temperature	1781.74	1	1781.74	9.9000	0.0104	
B-Catalyst Dosage	16.4200	1	16.4200	0.0912	0.0688	
C-Methanol to Oil ratio	947.900	1	947.900	5.2700	0.0446	
AB	100.450	1	100.450	0.5580	0.4722	
AC	766.840	1	766.840	4.2600	0.0659	
BC	613.070	1	613.070	3.4100	0.0947	
A^2	2143.62	1	2143.62	11.910	0.0062	
B^2	105.660	1	105.660	0.5870	0.4613	
C^2	340.180	1	340.180	1.8900	0.1992	
Residual	1799.99	10	180.000			
Lack of Fit	253.130	4	63.2800	0.2455	0.9024	not significant
Pure Error	1546.85	6	257.810			
Cor Total	8585.27	19				

Final Equation in Terms of Coded Factors

Yield =+9.25+0.7538 **A** +0.0461 **B** +0.5308 **C** +0.1655 **AB** -0.6355 **AC** -0.5439 **BC** 0.7527 **BC** -0.7527 **A^2** +0.2063+0.2063 **B^2** -0.2677 **C^2**

Where A, B and C are reaction temperature, catalyst dosage and methanol to oil ratio respectively. The result of analysis of variance (ANOVA) for fitting the second –order response surface model by least square method are given in Table 5. The higher value for the model (F_{model}= 4.19) with very low probability value for the model (p<0.0178) indicates the high significance of the fitted model. The high value of R^2 (0.7903) in table 6. Indicate that the fitted model can be used for prediction with reasonable precision. Similarly the normal probability plot shows different dot at scattered position in the straight line confirming the same pattern of distribution as indicated by high degree similarities for experimental and predicted values showing in the figure 4.

Table 6: Fit Statistics

Std. Dev.	13.42	R^2	0.7903
Mean5	76.61	Adjusted R^2	0.6016
C.V.%	17.51	Predicted R^2	0.4297
		Adeq Precision	7.0697

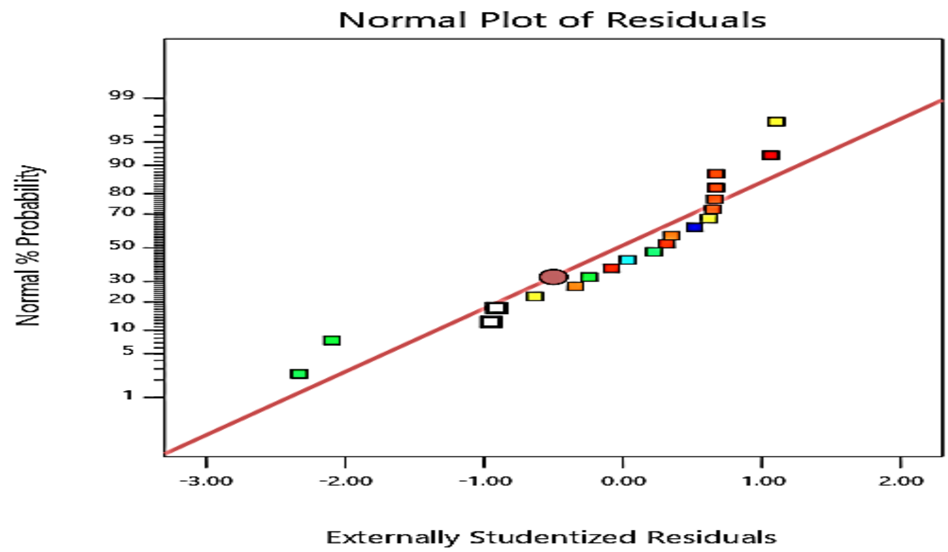

Figure 4: Normal Plot of Residual

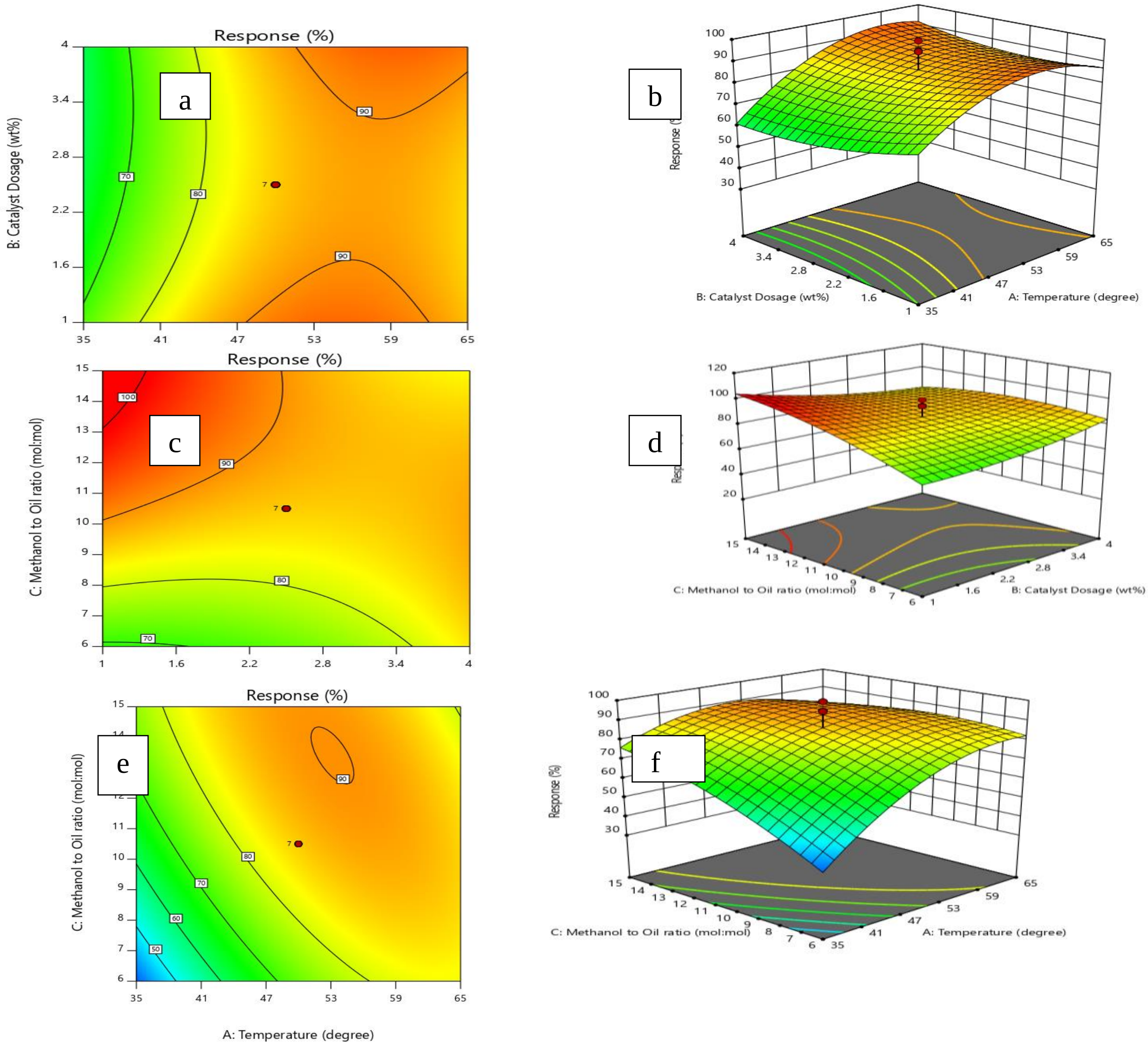

Fig.5: Contour plot and response plot for (a) catalyst dosage against temperature (b) catalyst dosage against Temperature (c) Methanol to Oil Ratio against catalyst dosage (d) methanol to oil ratio against catalyst dosage (e) methanol to oil ratio against temperature (f) methanol to oil ratio against temperature.

Figure 5a-5e shows contour plot and three-dimensional surface, respectively for the effect of two variables on the yield of biodiesel. The contour plots were made by taking two variables at the same time while keeping the other constant. The contour plot in figure 5a, c and e indicate the mutual interaction between the catalyst dosage with temperature, methanol to oil ratio with catalyst dosage and the methanol to oil ratio with temperature respectively. On the other hand the surface plot in figure 5b, d and f indicate the mutual interaction between the catalyst dosage with temperature, methanol to oil ratio with catalyst dosage and the methanol to oil ratio with temperature.

Table 7: GC-MS showing composition of the biodiesel produced

Peak No.	Retention Time	Area Ratio	Identified Compounds	Quality (%)
1	47.182	0.06	Tetradecanoic Acid methyl ester	95
2	54.875	3.37	Hexadecanoic acid methyl ester	99
3	60.810	3.58	(E)-9-octadecanoic Acid methyl ester	99
4	61.433	0.29	Octadecanoic acid methyl ester	99
5	70.371	0.39	9,17-octadecadienal methyl ester	90
6	73.302	0.26	Hexadecanoic acid methyl ester	90
7	86.674	38.65	Dodecanoic Acid 1,2,3-propanetriy ester	76
8	92.059	53.27	Dodecanoic Acid 1,2,3-propanetriy ester	76

GC analysis in Table 7 indicated that the Fatty Acid Methyl Ester (FAME) consisted predominantly of the methyl esters of of six ester compounds: 95% Tetradecanoic Acid methyl ester, 99% Hexadecanoic acid methyl ester, 99% (E)-9-octadecanoic Acid methyl ester, 99% Octadecanoic acid methyl ester, 90% 9,17-octadecadienal methyl ester. The GC analysis indicated that the biodiesel produced under the optimized set of experiments was within the ASTM D 6751 specification for free glycerol.

Table 8: Weight loss for coupons immersed in biodiesel and its blend (B_{20} and B_{100})

Time (Hour)	Blend	W_1 (g)	W_2 (g)	DW (g)
200	B_{100}	7.03	6.93	0.10
400	B_{100}	7.28	7.06	0.22
200	B_{20}	7.92	6.95	0.97
400	7.28	6.02	1.26	7.88

Table 9: Corrosion rate of biodiesel and its Blend at different time

Time (Hour)	Blend	DW(g)	CR ($gh^{-1}cm^{-2} \times 10^{-5}$
200	B_{100}	0.10	1.25
400	B_{100}	0.22	1.38
200	B_{20}	0.97	1.21
400	B_{20}	1.26	788

3.1 Weight Loss

As can be seen from Table 8 the weight of the metal is decreasing with time i.e weight loss increases with increase in time

3.2 Corrosion Rate

The corrosion rate of the biodiesel produced from synthesized CaO/Al_2O_3 as catalyst was investigated to evaluate the quality of its blend at different time. Table 9 shows that the higher the change in weight the more the corrosion rate and this clearly indicate that B_{20} has the highest corrosion rate while B_{100} have less corrosion rate which indicate the quality of waste cattle fat biodiesel produced in this study.

4 CONCLUSION

The cattle fat oil methyl ester production through transesterification process using CaO/Al_2O_3 catalysts has been investigated in this research work. The influence of reaction parameters such as catalyst loading, reaction temperature, methanol to oil molar ratio on biodiesel yield were studied. At optimal reaction condition (catalyst dosage 3.5w% and methanol to oil ratio 10.5:1) the biodiesel yield was found to be 99.37%. This work indicate the feasibility of cattle fat oil as feedstock for biodiesel production with a promising potential to be used as a blend to petroleum diesel.The corrosion rate of biodiesel and its blend was studied and the quality of $B_{100}$is higher than in B_{20} due to less corrosion rate.

References

1. Al-Hamamre,Z.andYamin,J. (2014). Parametric study of the alkalicatalyzed transesterification Of waste frying oil for biodiesel production. *Fuel*, 79: 246-254.

2. Atadashi, I.M.,Aroua, M.K.,AbdulAziz,A.R. &Sulaiman, N.M.N. (2011).Refining technologies for purification of crude biodiesel. *Applied Energy*, 88: 4239-4251.

3. Jazie A., Pramanik, H. and Sinha, S.S.K. 2013. Eggshell as Eco-Friendly Catalyst for transesterification of Rapeseed Oil: Optimization for Biodiesel Production. *International Journal of Sustainable Development and Green Economics* 2: 2315-4721

4. Liu, X., He, H., Wang, Y., Zhu, S. and Ziao, X., (2008). Transesterification of soybean oil to Biodiesel using CaO as a solid base catalyst. *Fuel* 87: 216-221

5. Nautiyal, P., Subramanian, K.A. and Dastidar, M.G. (2014).Kinetic and thermodynamic

6. N. Hassan, A. Shahat, A. El-Didamony, M. El-Desouky, A.A. El-Bindary DOI:https://doi.org/10.48317/IMIST.PRSM/morjchem-v6i3.11110

7. *N. Badri, Y. Chhiti, F. Bentiss, M. Bensitel* DOI: https://doi.org/10.48317/IMIST.PRSM/morjchem-v6i4.14350

8. Slama A., Taufiq-Yap Y.H., Chua C., Chanc E., Ravindraa P. 2013. Studies on design of

9. *N. Badri, Y. Chhiti, F. Bentiss, M. Bensitel* DOI: https://doi.org/10.48317/IMIST.PRSM/morjchem-v8i3.20134

10. Usman Bishir (2015). Prediction of corrosion inhibition efficiency of thiophine derivatives Quantitative structure activity relationship method, unpublished PhD thesis.