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Assessment and Optimization of Conversion of *L. siceraria* Seed Oil into Biodiesel using CaO on Kaolin as Heterogeneous Catalyst

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ABSTRACT

Central composite response surface design was used to investigate and optimize the reaction conditions for conversion of *L. siceraria* seed oil into biodiesel with calcium oxide supported on kaolin as catalyst, whose concentration was held constant. The results (biodiesel yield) were fitted into a full quadratic model. Methanol to oil molar ratio and reaction time followed by temperature were found to be variably effective on the yield. The optimum and most economical condition for transesterification of *L. siceraria* oil to biodiesel was when the temperature, reaction time and methanol to oil molar ratio are held at 70.5°C, 60 min and 6.83, respectively. The model obtained has good predictive power. The catalyst was observed to be more effective in catalyzing the transesterification than either neat CaO or neat kaolin. The oil produced from the conversion process was found to meet most of the standard specifications set EU and ASTM.

Key words: Kaolin, calcium oxide, heterogeneous catalysis, biodiesel, *Lageneria siceraria*

INTRODUCTION

Depletion of fossil fuel reserves coupled with their negative environmental impact have been impetus to increasing search for alternative renewable fuels, to complement or replace petrofuels (Agarwal *et al.*, 2015; Atabani *et al.*, 2012). Biodiesel, fatty acid methyl esters of seed oils and fats, has been found suitable for use as fuel in diesel engine (Atabani *et al.*, 2012; Hoekman *et al.*, 2012). It is renewable and produces much fewer harmful emissions than conventional petrodiesel (Dwivedi *et al.*, 2011; Issariyakul *et al.*, 2008). Thus, its significant utilization instead of petrodiesel would lead to a decrease of the carbon dioxide, sulfur dioxide, unburned hydrocarbon and particulate matter emissions (Antolin *et al.*, 2002).

However, in spite of these favorable attributes, the economic aspect of biodiesel production is the major barrier to its worldwide commercialization. The cost of biodiesel production is highly dependent on the cost of feedstock, which accounts for 60-80% of the cost of the finished product (Gui *et al.*, 2008; Haas, 2005b; Singh and Singh, 2010). Partially or fully refined edible vegetable oils, such as soybean, rapeseed-and sunflower oils, are the predominant feedstock for biodiesel production (Haas, 2005a), which obviously results in the high price of biodiesel. Therefore, exploring ways to reduce the cost of the raw material is of great interest. Consequently, inedible oils are now being sought, from algae (Galadima and Muraza, 2014) as well as other crops and sources (Ashraful *et al.*, 2014; Koh and Ghazi, 2011; Zhang *et al.*, 2014), to help reduce the cost of biodiesel thereby making it competitive to petrodiesel (Haas, 2005b). In particular,

Lagenaria siceraria species (including Calabash) are among the cultivated crops in the north-western region of Nigeria that have no established large scale application. It has relatively short maturity time of about 3-4 months and produces large amount seeds with up to 50% inedible oil content and thus with stable price that may not subject to distortion by food prices.

Currently, the main process for the synthesis of biodiesel is the transesterification of vegetable oils using a strong base as homogeneous catalyst. However, this process presents some disadvantages, as it requires the use of relatively large amount of unrecoverable catalyst with consequent generation of waste/liquor which has to be treated (Daud *et al.*, 2015) and the purification of glycerine. These aspects also play important roles in the economy of the process (Ramos *et al.*, 2008), hence the growing interest on heterogeneous catalysts (Boon-anuwat *et al.*, 2015; Borges and Diaz, 2012), which have generally found to be environmentally benign process and significantly reduce production cost of biodiesel (Kim *et al.*, 2004; Sharma *et al.*, 2011).

Recently, several studies on the transesterification of triglycerides have been conducted using heterogeneous catalysts, such as supported CaO (Kouzu and Hidaka, 2012; Yan *et al.*, 2008), $(\text{CH}_3\text{CH}_2\text{O})_2\text{Ca}$ (Li and Rudolph, 2007), MgO-functionalized mesoporous catalyst (Li and Rudolph, 2007), MgO loaded KOH (Ilgen and Akin, 2009) and zeolites (Brito *et al.*, 2007) among many others (Chouhan and Sarma, 2011; Gurunathan and Ravi, 2015; Konwar *et al.*, 2014; Sani *et al.*, 2014; Zabeti *et al.*, 2009). In this paper we report the performance of CaO/kaolin as heterogeneous catalyst in the transesterification of inedible *L. siceraria* seed oils.

MATERIALS AND METHODS

Sampling and sample preparation: *Lagenaria siceraria* (calabash) seeds were collected from Gummi in Gummi Local Government area of Zamfara State, Nigeria and were identified at the Botany Unit, Department of Biological Sciences, Usmanu Danfodiyo University, Sokoto. The seeds were dried and powdered for oil extraction. Kaolin, on the other hand, was obtained from a kaolin quarry at Kankara in Kankara Local Government area of Katsina State, Nigeria. The kaolin grounded into powder using mortar and pestle.

Extraction of oils: Oil from the powdered seeds was extracted using Soxhlet extraction methods (60°C, 8 h) with n-hexane as a solvent after which the solvent was removed using a rotary evaporator (35°C, 30 mmHg). The percentage crude lipid yield was calculated from Eq. 1. The oil was stored at 20°C until required for experiments.

$$\text{Crude lipid (\%)} = \frac{\text{Weight of the extracted oil}}{\text{Weight of the sample}} \times 100 \quad (1)$$

Catalysts preparation: Three different catalysts were used in this research and they were prepared as described below.

Kaolin preparation: Kaolin (~1000.0 g) was calcined (1000°C, 5 h) in a muffle furnace. After cooling, the kaolin was extracted with n-hexane using Soxhlet method (60°C, 8 h), to remove soluble organic matter and dried (100°C, 5 h). The resulting kaolin was labeled CK.

Preparation of CaO on kaolin: CK (40.0 g) was added to Na_2CO_3 solution (1 M, 100 cm^3) in a beaker. The mixture was stirred for 30 min and CaCl_2 solution (1 M, 100 cm^3) was added slowly

while stirring. The mixture was filtered and the residue (CaCO₃ on kaolin) washed severally with distilled water, dried (110°C, 5 h) and then calcined (780°C, 8 h). This was labeled LK.

Preparation of CaO: The CaCl₂ solution (1 M, 100 cm³) was added slowly Na₂CO₃ solution (1 M, 100 cm³) in a beaker while stirring. The mixture was stirred for 30 min and then filtered through Whatman No. 1 filter paper. The residue (CaCO₃) was washed severally with distilled water, dried (110°C, 5 h) and then calcined (780°C, 8 h). The final residue left (CaO) was stored in a glass bottle until required.

Experimental design: Response surface (Box-Behnken) statistical experimental design was employed in designing the experiments for determination of the optimal conditions for conversion of *L. siceraria* oil into biodiesel using calcium oxide on kaolin (LK) as catalyst. Three independent variables including reaction time, methanol to oil molar ratio and temperature, selected based preliminary experimental study, were investigated and optimized. Table 1 shows the levels of the factors employed in the design.

Each run was set in triplicate and all the runs were completely randomized to obtain a total of 45 runs (Table 2). The design and analysis, as well as optimization, of the results were done on MINITAB 15 statistical software platform.

Description of experimental run: The CK (0.5 g) catalyst was added to a known amount of methanol mixed with *L. siceraria* oil (100 g) in a flat bottom flask. The amount of methanol was chosen to get the desired molar methanol/oil ratio (Table 2). The mixture was refluxed at constant stirring speed and at a temperature and for a period of time as specified in the design matrix (Table 2). At the end of the reaction time, the biodiesel (yellowish upper layer) was recovered using a separating funnel after complete separation overnight under gravity. The spent catalyst was recovered from the bottom layer by centrifugation (4500 rpm, 10 min). The crude biodiesel in an evaporating dish, was heated on a water bath (90°C, 30 min) to remove the residual methanol. It was further purified by neutralization with dilute phosphoric acid (pH 4.0), washed with hot distilled water until the washed water has a pH of 7.0 and the residual water was removed by drying at 100°C over anhydrous Na₂SO₄. The biodiesel yield was calculated from Eq. 2 as follows:

$$\text{Biodiesel yield (\%)} = \frac{\text{Weight of the biodiesel}}{\text{Weight of the oil}} \times 100 \quad (2)$$

Characterization of the catalysts: The X-Ray Fluorescence (XRF) analysis was conducted on glass bits prepared from kaolin, fresh CK and spent CK catalysts. The sample of the catalyst, in the platinum crucibles, was calcined (950°C, 30 min) in a muffle furnace. Then the calcined sample (1.2 g) was mixed with a mixture Lithium borate and lithium bromide (8.4 g) as flux. The mixture was fed in Claisse machine to obtain a glass bit, which was then analysed on an X-ray fluorescence analyzer to obtain the percentage elemental composition of the samples.

Table 1: Levels of the transesterification condition variables used in the experimental design

Variables	Coding	Lower	Upper
Temperature (°C)	T	60	120
Time (min)	t	60	120
Molar M/O ratio	r	6	9

Table 2: Experimental design matrix and results (biodiesel yield) from the experimental runs

Run order	Pt type	Blocks	Temp (T)	Time (t)	M/O (r)	Yield (%)
1	2	1	60	90	9.0	69.6
2	2	1	60	90	9.0	68.0
3	2	1	120	90	6.0	82.1
4	2	1	60	90	6.0	73.9
5	2	1	90	60	9.0	79.0
6	2	1	120	120	7.5	81.6
7	0	1	90	90	7.5	81.3
8	2	1	60	120	7.5	83.1
9	2	1	60	90	9.0	77.7
10	2	1	120	120	7.5	79.1
11	0	1	90	90	7.5	84.1
12	2	1	90	120	9.0	85.9
13	2	1	120	90	9.0	82.8
14	2	1	90	60	6.0	82.6
15	2	1	90	120	6.0	84.5
16	2	1	120	60	7.5	85.0
17	0	1	90	90	7.5	82.7
18	2	1	90	60	9.0	80.7
19	2	1	90	120	6.0	86.9
20	2	1	120	90	9.0	80.7
21	2	1	60	120	7.5	89.1
22	2	1	120	60	7.5	83.3
23	2	1	60	60	7.5	89.4
24	2	1	60	60	7.5	88.7
25	2	1	120	60	7.5	84.4
26	2	1	90	120	6.0	84.5
27	0	1	90	90	7.5	83.6
28	0	1	90	90	7.5	83.6
29	2	1	90	60	6.0	82.8
30	0	1	90	90	7.5	84.5
31	2	1	120	90	9.0	81.2
32	2	1	60	60	7.5	83.5
33	2	1	60	90	6.0	86.9
34	0	1	90	90	7.5	82.7
35	2	1	120	120	7.5	80.4
36	2	1	60	120	7.5	81.1
37	2	1	60	90	6.0	75.1
38	2	1	90	60	6.0	82.7
39	2	1	90	120	9.0	81.1
40	2	1	120	90	6.0	83.1
41	2	1	90	60	9.0	80.3
42	2	1	90	120	9.0	84.0
43	0	1	90	90	7.5	83.6
44	0	1	90	90	7.5	82.9
45	2	1	120	90	6.0	82.7

RESULTS AND DISCUSSION

The results of biodiesel yield obtained from experimental runs conducted are presented in Table 2. The results show that the yield obtained within the condition investigated vary within a fairly narrow range of $\pm 4.22\%$ with minimum and maximum yields of 68.0 and 89.0%, respectively and the average yield of 82.14%.

Effect of the variables on the conversion process: Four main factors are known to affect biodiesel yield namely methanol/oil molar ration, temperature, reaction time and catalyst concentration (Freedman *et al.*, 1984; Leung and Guo, 2006; Leung *et al.*, 2010). The statistical effects of these variables in transesterification of *L. siceraria* seed oil with CaO/kaolin as catalyst are summarized in Table 3. The yield was fitted into a model consisting of linear, square and interaction terms. Table 3 shows that all the interaction and linear terms are statistically not significant ($p > 0.05$) while two (t^2 and r^2) out of the three square terms are significant with $p < 0.05$.

Table 3: Results from analysis of variance for yield (%)

Sources	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	308.738	308.738	34.304	2.53	0.024
Linear	3	73.648	111.311	37.104	2.74	0.058
Temp (T)	1	17.170	3.626	3.626	0.27	0.608
Time (t)	1	0.050	41.081	41.081	3.03	0.091
M/O (r)	1	56.427	45.319	45.320	3.34	0.076
Square	3	208.100	208.100	69.367	5.12	0.005
Temp*Temp (T ²)	1	32.119	32.590	32.590	2.40	0.130
Time*Time (t ²)	1	85.569	72.106	72.106	5.32	0.027
M/O*M/O (r ²)	1	90.411	90.411	90.411	6.67	0.014
Interaction	3	26.991	26.991	8.997	0.66	0.580
Temp*Time (T t)	1	0.907	0.908	0.908	0.07	0.797
Temp*M/O (T r)	1	25.230	25.230	25.230	1.86	0.181
Time*M/O (t r)	1	0.853	0.853	0.853	0.06	0.803
Residual Error	35	474.613	474.613	13.560		
Lack-of-Fit	3	230.024	230.024	76.675	10.03	0.000
Pure error	32	244.589	244.589	7.643		
Total	44	783.351				

Table 4: Estimated regression coefficients for yield (%)

Terms	Coef	SE coef	T	P
Constant	47.8653	40.3053	1.188	0.243
Temp (T)	0.1571	0.3038	0.517	0.608
Time (t)	-0.5287	0.3038	-1.741	0.091
M/O (r)	14.5907	7.9812	1.828	0.076
Temp*Temp (T ²)	-0.0019	0.0012	-1.550	0.130
Time*Time (t ²)	0.0028	0.0012	2.306	0.027
M/O*M/O (r ²)	-1.2698	0.4917	-2.582	0.014
Temp*Time (T t)	-0.0003	0.0012	-0.259	0.797
Temp*M/O (T r)	0.0322	0.0236	1.364	0.181
Time*M/O (t r)	0.0059	0.0236	0.251	0.803

The statistical insignificance of some of the terms investigated is due to the significantly large experimental error involved compared to the effect of the factors under investigation (Table 3). The effects of the variables are relatively small within the levels of the variable investigated. Nevertheless, the practical effects of the variables can be observed from the contour plots.

Table 4 shows the estimated coefficients of the respective terms of the fitted model. As observed from the ANOVA results (Table 3) only coefficients of two quadratic terms, namely t² and r², are statistically significant (p<0.05). It should however be noted that, with coefficient of regression (R²) of only 0.394, only about 40% of the data is described by the model hence the statistically significant lack-of-fit (p<0.005). Furthermore, although eliminating the statistically insignificant terms from the model, makes the model less cumbersome (Eq. 3) and the lack-of-fit statistically insignificant (p = 0.114), the coefficient of regression (R²) is reduced to 0.29.

$$\text{Yield} = 45.995 - 0.5382t + 17.144r + 0.003t^2 - 1.211r^2 \quad (3)$$

Figure 1 contains contour plots showing how any two of the three factors investigated affect biodiesel yield while the third is held constant at the mid-value. High yields (>85%) are obtained at temperatures higher than 75°C when the reaction time is either 60-66 min or greater than 115 min (Fig. 1). A similar pattern is also displayed by r (M/O) against t (reaction time). Biodiesel yields above 85% are obtained at M/O values of about 6.2-7.8, when the reaction time is either below 66 or above 215 min, when the reaction time is between 66-115 min, lower yields are obtained irrespective of the levels of the reaction temperature and M/O. This is further confirmed by Fig. 1c: with the reaction time held at 90 min, the highest yield obtainable is 80.0-82.5%. It is

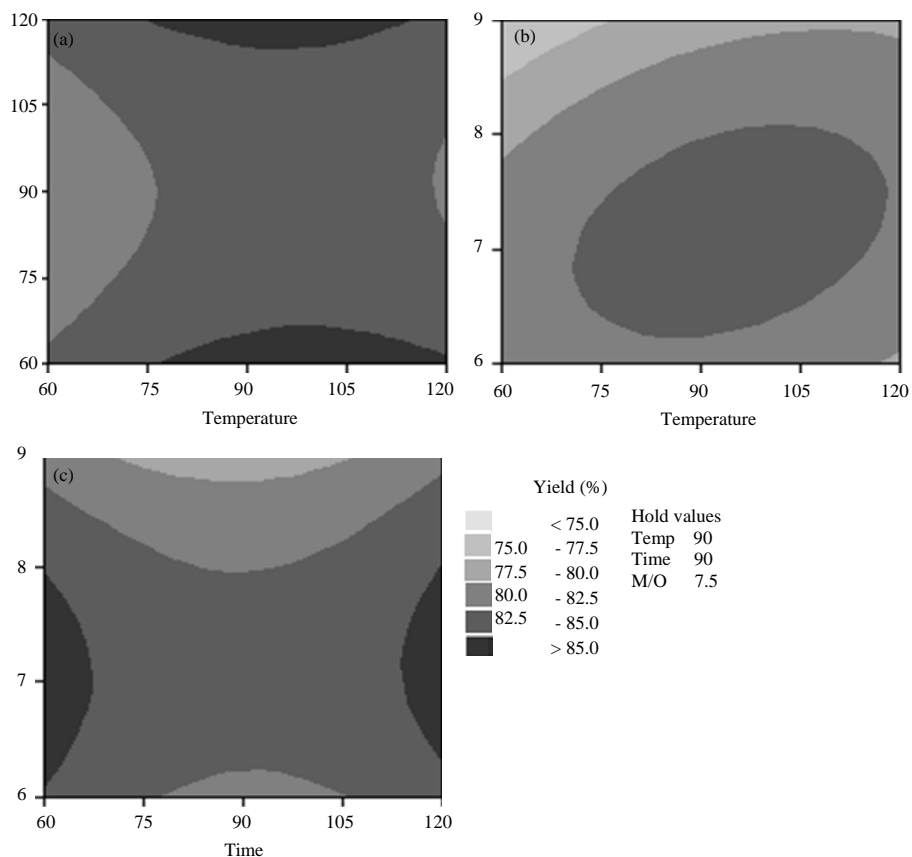


Fig. 1(a-c): Contour plots showing the effect of pairs of the factors on biodiesel yield when the third factor held constant, (a) Time*Temp, (b) M/O*Temp and (c) M/O*Time

also interesting to note that from both Fig. 1b and c, high (or <6.2) M/O results in relatively low yields irrespective of the levels of the reaction time and temperature. Although, interesting, it not clear, why the biodiesel yield decreases between 66 and 115 min after the reaction started.

To further gauge the effect of temperature and M/O, the reaction time is held at its lowest possible level of 60 min (Fig. 2). From the figure, higher yields ($>86\%$) are obtained at temperatures between $88-108^{\circ}\text{C}$, when the M/O ratio is about 7.

Optimization of biodiesel yield: Optimization of the results using Minitab Response Optimizer facility gives six local solutions and one global solution (Table 5). All the solutions have M/O levels vary within relatively narrow range of 7.26 ± 0.36 in agreement with observations from contour plots (Fig. 2). Reaction temperature and time however show significant variations amongst the solutions. As observed from Fig. 1, high yields are obtained at either low (60 min) or high (120 min) reaction times and temperatures above 70°C . However, taking process economics into consideration, solutions that require high temperatures and /or long reaction time are impractical. This eliminates solution 1 to solution 5 as economically more viable process conditions. Furthermore, global solution has the highest desirability (23.5%) and thus, gives highest yield (86.2%) compared to solution 6 (0.4 and 85.0%, respectively), the later operates at significantly

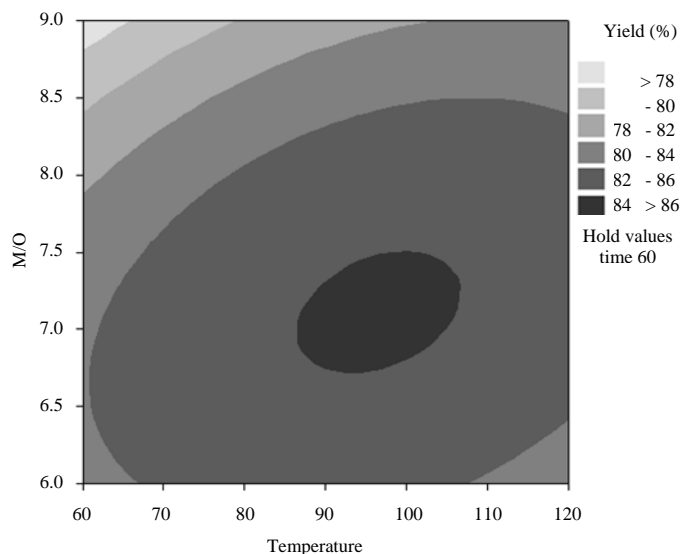


Fig. 2: Contour plot of M/O versus reaction temperature with the reaction time held at 60 min

Table 5: Results of optimization of biodiesel yield

Solutions	T (°C)	t (min)	r	Yield (%)	Desirability (%)
Local solution 1	96.36	60	7.12	86.2	23.5
Local solution 2	119.98	60	7.64	85.2	3.4
Local solution 3	114.02	120	7.49	85.1	1.7
Local solution 4	114.25	120	7.59	85.1	1.0
Local solution 5	69.96	120	6.89	85.0	0.4
Local solution 6	70.49	60	6.83	85.0	0.4
Global solution	96.36	60	7.12	86.2	23.5

T: Temperature, t: Time and e: M/O ratio

Table 6: Relative biodiesel yields of from heterogeneous transesterification of *Lageneria siceraria* seed oil using different catalysts

Catalysts	T (°C)	t (min)	r	Experimental field (%)	Predicted yield (%)
CaO, KO	60	60	7	65.40±0.12	-
Kaolin, CK	60	60	7	71.80±0.12	-
CaO/Kaolin, LK	60	60	7	83.90±0.10	85.17

T: Temperature, t: Time and e: M/O ratio

lower temperature. The global solution requires an increase in temperature by up to 36.7% relative to solution 6, with added advantage of increased biodiesel yield of only about 1.4%. It may therefore be more economical to operate at conditions provided by solution 6 than at those provided by the global solution.

Table 6 compares the biodiesel yields obtained from transesterification of *L. siceraria* seed oil under the same condition but using different catalysts namely CaO, kaolin and CaO/kaolin. ANOVA reveals that the three yields are statistically different from each other. It is evident from the table that loading CaO on kaolin appears to significantly improve the catalytic activity of the CaO in agreement with previous observation that Al₂O₃ and SiO₂ supported CaO exhibit more catalytic activity than neat CaO (Albuquerque *et al.*, 2008; Umdu *et al.*, 2009). This may partly due to increased basic site density and strength (Albuquerque *et al.*, 2008) possibly associated with increased surface area and more importantly due to the intrinsic catalytic activity of the kaolin which appears to be even more catalytically active than the neat CaO (Table 6).

The relatively low activity of neat CaO compared to findings by other workers (Granados *et al.*, 2007; Kouzu *et al.*, 2008, 2009; Liu *et al.*, 2008) might be due low methanol/oil molar ratio

employed. For example biodiesel yield of up to 93% was obtained from transesterification of sunflower oil using neat CaO catalyst at 60°C but using oil/methanol molar ratio of 1:13 (Granados *et al.*, 2007). Kaolin, being an aluminosilicate like zeolites (Brito *et al.*, 2007; Sharma *et al.*, 2011; Suppes *et al.*, 2004; Xie *et al.*, 2007), has Lewis acid site, due to the vacant orbital on aluminum and could so serve as acid catalyst in the esterification process while CaO serves as base catalyst.

Table 7 gives the fuel properties of the biodiesel produced using CaO/Kaolin as based-acid catalyst. With the exception of Acid value and Cetane number, the other properties are within the standards of American Society for Testing and Materials (ASTM) and European Standard (ES) for biodiesel (Boey *et al.*, 2011; Leung *et al.*, 2010; Ramachandran *et al.*, 2013). However, both acid value and Cetane number are important fuel properties to be neglected. Acid value indicates the level of free fatty acids in the biodiesel. High values are associated with corrosion of metallic engine part and could so significantly decrease the life span of the engine at the long run. Cetane number, on the other hand, determines the ignition delay of the fuel in Compression Ignition (CI) engines. The higher the Cetane number, the shorter the ignition delay and thus the more easily the fuel combust because of more complete combustion the fuel and less intense shock resulting in smooth and quiet running of the engine. Thus, the biodiesel here obtained from *L. siceraria* seeds may require additives such as 3-ethylhexyl nitrate and di-tert-butyl peroxide to enhance the CN.

Composition and mineralogy of the catalyst: The results of XRF analyses of CK, LK and spent LK show that the catalysts consist mainly of SiO₂ and Al₂O₃, with other oxide such CaO, Fe₂O₃, K₂O, TiO₂ occurring as minor components. Loading CaO on kaolin increased the CaO content from 1.42-3.62%. This resulted in increased biodiesel yield of about 16.9%. CaO appears to be lost during reaction hence the relatively lower CaO content in the spent LK (Table 8).

Table 7: Fuel properties of the biodiesel produced from *Lageneria siceraria* seed oil

Values	Values
Specific gravity at 25°C (g cm ⁻³)	0.887
API gravity	22
Sulfur content (%)	0.012±0.01
Cloud point (°C)	-3
Pour point (°C)	-6
Kinematic viscosity at (40°C cSt)	4.4
Aniline point (°C)	42.2
Diesel index	24
Acid value (mg KOH/g)	1.9±0.12
Flash point (°C)	90
Iodine value (g/100 g)	7.3±0.02
Cetane number	27

Table 8: Results of XRF analysis of calcined kaolin, fresh CaO/kaolin and spent LK

Components (%)	CK	LK	Spent LK
SiO ₂	49.80±0.09	46.52±0.09	33.36±0.12
Al ₂ O ₃	45.77±0.16	43.12±0.19	30.36±0.12
CaO	1.42±0.00	3.62±0.00	2.95±0.00
Fe ₂ O ₃	0.44±0.00	0.46±0.00	0.33±0.00
K ₂ O	0.36±0.00	0.46±0.00	0.32±0.00
Mn ₂ O ₃	0.16±0.00	0.11±0.00	0.12±0.00
TiO ₂	0.12±0.00	0.11±0.00	0.08±0.00
SO ₃	0.00±0.00	0.07±0.00	0.01±0.00

CK: Calcined kaolin, LK: fresh CaO/kaolin

CONCLUSION

Calcium oxide supported on kaolin was used as heterogeneous catalyst to produce biodiesel from inedible oil from *Lageneria siceraria* seeds. The optimal and most economical process condition was discovered to be 70.5°C, 60 min and 6.83 for temperature, reaction time and methanol/oil molar ratio, respectively. Both neat CaO and kaolin were observed to catalyze the transesterification process, respectively. However, CaO supported on kaolin was observed to be more effective under the same conditions. The biodiesel produced using the catalyst was found to meet most of the EU and US specifications for biodiesel. In general, CaO/kaolin has been found to be a promising catalyst for heterogeneous catalysis of transesterification of vegetable oils into biodiesel.

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