

Optimization of Biodiesel Production from *Strychnos Innocua* del. Seed Oil Using Heterogeneous Catalyst

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Abstract- In this study, biodiesel was produced from *strychnos innocua* Del. seed oil through transesterification using heterogeneous catalyst. Optimization of biodiesel production from the seed oil was carried out by Taguchi method and design based on four transesterification variables (methanol/oil ratio, catalyst amount, reaction temperature and reaction time). Optimum biodiesel yield of 85.0% was obtained at reaction conditions of 9:1 methanol to oil ratio, 60°C reaction temperature, 0.2g catalyst amount and 90 minutes reaction time. The significance of the process variables and their combined effects on the transesterification efficiency were established through full quadratic model. GC-MS was used to determine the methyl esters profile of the biodiesel results and indicated the presence of 9-hexadecenoic acid methyl ester with hexadecanoic acid methyl esters as the dominant fatty acid methyl esters. Most of the observed characteristics of the biodiesel produced were in conformity with ASTM standards.

Indexed Terms- *Strychnos Innocua*, Optimization, Biodiesel, Heterogeneous, Catalyst.

I. INTRODUCTION

Energy plays indispensable roles in human life and it is an essential element for human economics development. The rising demand for energy across the world has necessitated the search for alternative sources of fuel from renewable resources and waste materials (Gautam, 2013). Biomass remains very promising in this regard as it has always been a major source of energy for mankind. The need to investigate bio energy for potential of some underutilized plants is very crucial as it enhances economic and environmental sustainability (Kubilay *et al.*, 2014).

Basically, *Strychnos innocua* Del. seed and cowry shell are presently of little economic importance as

they are being treated as waste by people having them. In order to allay this improper deposition, there is need to highlight their potential for biodiesel production. The seed oil of *S. innocua* is a reliable feed-stock for biodiesel production and cowry shell contains calcium based acids which can be used as catalyst for transesterification of *S. innocua* seed oil.

Biodiesel which is environmentally viable seems to be an alternative for diesel fuel as a result of increased demand for fossil fuel across the country. As fossil fuel is fast depleting, there is need to develop an alternative source of economical fuel (biodiesel) that can be made from renewable resources. The main novelty of this research work is that, the seed of *S. innocua* has never been previously evaluated for biodiesel production using heterogeneous and homogeneous catalysts.

II. MATERIALS AND METHODS

• Sample Collection and Treatment

The seed of *S. innocua* Del fruits were collected using a method described by Ayaz *et al.*, (2002) from Zuru in Zuru Local Government Area of Kebbi State, Nigeria. The fresh fruit samples were authenticated at the Herbarium Botany unit (Voucher No: UDUS/ANS) of the Biological Sciences Department of Usmanu Danfodiyo University, Sokoto, Nigeria. The seeds were separated manually from the peel and air dried for 14 days, then mechanically grounded into fine powder using blender.

• Oil Extraction

The powdered *S. innocua* Del seed (30g) was placed in the thimble and n-hexane (300 cm³) was poured into the round bottom flask. The apparatus was heated at a temperature of 60°C for six (6) hours of continuous extraction using Soxhlet apparatus. The experiment was repeated for the same weights of the sample. The solvent was removed from the oil using rotary

evaporator. The percentage oil yield was calculated using equation (1)

$$\% \text{ Oil Yield} = \frac{\text{Weight of extract oil (s)}}{\text{Weight of sample}} \times 100 \quad (1)$$

• Preparation and Characterization of the Catalyst

The catalyst was prepared by hydrothermal treatment of cowry shell. The powdered shell was calcined in a muffle furnace under static air conditions at a temperature of 800°C for three (3) hours and then refluxed in distilled water at 60°C for six (6) hours. The solid particles were filtered and dried in a hot air oven at 105°C overnight. The solid product was recalcined at 800°C for three (3) hours to change the hydroxide formed to oxide (Yoosuk, *et al.*, 2010). The catalyst was characterized using, FT-IR and X-Ray Fluorescence (XRF).

• Design of Experiment

The experiments were designed using Taguchi, a response surface design on MINITAP 17 Statistical Software. In the optimization process, the influence of solvent to oil molar ratio, catalyst concentration, reaction temperature, and reaction time on the yield of *S. innocua Del* seed oil biodiesel were investigated. Solvent to oil molar ratio and catalyst concentration were selected from 6:1 to 12:1, and 1.0 to 2.0 g respectively, while reaction temperature and time were respectively varied from 50°C to 60°C and 30 to 90 minutes. The design generated a total of twenty seven (27) runs (Table 1).

Table 1: Independent Parameters and Their Levels

Factors	Low Levels	High Levels
Reaction Temperature (°C)	50	60
Reaction Time (Minutes)	30	90
Solvent to Oil Ratio	6	12
Catalyst Amount (g)	1.0	2.0

• Transesterification of the Seed Oil

Oil sample of 30cm³ was measured into a beaker of 100cm³ and placed on a hot magnetic plate and heated at 100°C to remove any water present, then cooled to 60°C. The catalyst (0.3g) was weighed and mixed with methanol (6 cm³) into a beaker (100cm³). The mixture

of methanol and CaO was covered and preheated at a temperature of 50°C for two (2) minutes. The mixture was added to the oil and heated in a water bath at a temperature of 60°C for three (3) hours with constant stirring. After the reaction time, the mixture was allowed to settle under gravity for twenty four (24) hours in a separating funnel. Two layers were formed; the upper layer consisted of methyl ester and residual catalyst while the lower layer consisted of glycerol and excess catalyst. After separation, the methyl ester layer was centrifuged to remove residual catalyst (Nurhayati, *et al.*, 2017). The same method was adopted for the transesterification of each run based on the design of the experiment (Table 1). The percentage biodiesel yield was calculated using equation. 2:

$$\% \text{ Biodiesel Yield} = \frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}} \times 100 \quad (2)$$

• Analysis of the FAME

Fuel properties such as Specific Gravity, Kinematic Viscosity, Moisture Content, Sphated Ash, Flash Point, Pour Point, Cetane Number and Copper Strip Corrosion were analyzed using standard test methods and compared with ASTM standards. The biodiesels were characterized using a method reported by Muhammad *et al.* (2021). 0.5 cm³ of the sample was transferred into a 15 cm³ plastic centrifuge tube and to it, n-hexane (1,0%) was added and then vortex mixed for 10 rminutes. The mixture was centrifuged at 3500 rpm for 10 minutes. The supernatant (1,0 uL) was injected into GC. The oven temperature was initially set at 80°C, hold time (0 min.) with an equilibration time of 0.5 minutes and maximum temperature of 325°C.

III. RESULTS AND DISCUSSION

• Characterization of Catalysts.

The percentage oxide compositions of the calcined cowry shell are presented in Table 2, with CaO as dominant metallic oxide.

Table 2: Chemical Composition by XRF of Calcined Cowry Shell.

Oxides	Concentration (% wt)
SiO ₂	1.225
V ₂ O ₅	0.019
MnO	0.015

Fe ₂ O ₃	0.340
CoO ₄	0.055
NiO	0.019
CuO	0.068
Nb ₂ O ₃	0.007
SO ₃	0.291
CaO	83.321
MgO	8.908
K ₂ O	0.062
BaO	0.070
Al ₂ O ₃	4.064
Ta ₂ O ₅	0.056
TiO ₂	0.092
ZnO	0.018
Cl	0.351
ZrO ₂	0.004
SnO ₂	0.738
SrO	0.279

• XRF Analysis

Variability in the fatty acid composition of the oils, as reported by the different investigation, may be due to the age of the tissue analyzed, genetic history, climate, nutrition, temperature and oxygen tension, any of which can profoundly alter the composition of endogenous lipid of a plant.

The chemical composition of the calcined cowry shell shows that calcium oxide was found to be the major component in the material as shown in Table 2. The calcium oxide content was found to be 83.321 (% wt). However, other oxides identified in the material included Al₂O₃, SnO₂, Fe₂O₃, SiO₂, V₂O₅, MnO, CoO₄, NiO, CuO, Nb₂O₃, SO₃, K₂O, BaO, Ta₂O₅, TiO₂, ZnO, ZrO₂ and SrO. Chlorine (cl) was also found present with 0.351% wt. Heterogeneous catalyst

and less sensitive to the presence of free fatty acid and water can be regenerated and separated easily. CaO is one of the well-researched heterogeneous catalysts and has many advantages like higher reactivity, non-corrosive nature, being inexpensive and environmentally friendly (Natarajan *et al*, 2013). CaO derived from cowry shell could therefore be used in biodiesel production.

The FTIR spectra was recorded for the calcined cowry shell powder to determine the absorption bands of the materials present as shown in figure I below:

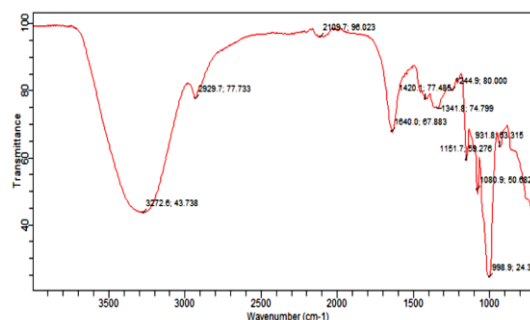


Figure 1: FTIR Spectrum of Calcined Cowry Shell

The calcination of cowry shell produced a sharp absorption band at 998.9cm⁻¹ which represents the out-phase Si –O planar stretching which is in agreement with 997cm⁻¹ (Sempeho *et al.*, 2015). Appearance of weak absorption band at 1341.8 cm⁻¹ and 1420.1 cm⁻¹ could be due to amount of traces of CO₃²⁻ ion in the shell. A sharp absorption bond at 1640.0cm⁻¹ was attributed to observation of broad peak at 3272.6 cm⁻¹ in the calcine shell spectrum which could be attributed to formation of Ca(OH)₂ due to airing of the CaO (Ikbal *et al.*, 2018).

Table 3: Optimization of Biodiesel Production Process

Std Order	Run Order	Temperature (°C)	Time (hrs)	MeOH/Oil ratio	Catalyst (g)	Yield (%)
1	1	45	1.0	3	0.2	52.6
2	2	45	1.5	6	0.4	63.0
3	3	45	2.0	9	0.6	64.1
4	4	45	2.5	12	0.8	53.0
5	5	50	1.0	6	0.6	66.0
6	6	50	1.5	3	0.8	63.4

7	7	50	2.0	12	0.2	59.9
8	8	50	2.5	9	0.4	67.4
9	9	55	1.0	9	0.8	68.6
10	10	55	1.5	12	0.6	65.5
11	11	55	2.0	3	0.4	75.7
12	12	55	2.5	6	0.2	81.4
13	13	60	1.0	12	0.4	55.0
14	14	60	1.5	9	0.2	84.0
15	15	60	2.0	6	0.8	72.9
16	16	60	2.5	3	0.6	60.6

Figure 1 to 5 give the summaries of the biodiesel yield obtained from the 16 runs concluded at different levels of the four process variables investigated as shown in Table 3. The biodiesel yields varied from a minimum of 52.6% to 84.0% for transesterification.

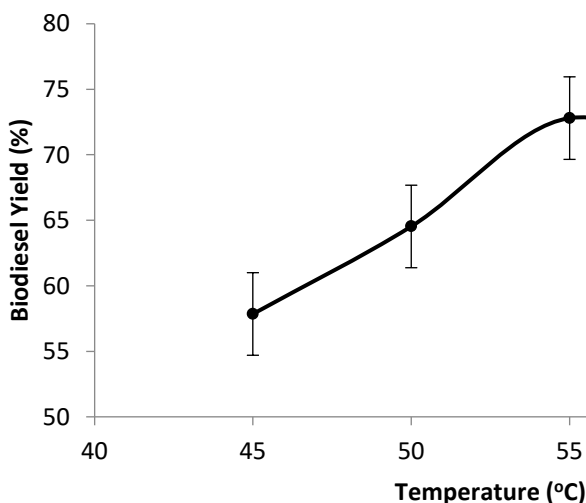


Figure 2. Effect of Temperature (°C) on Biodiesel Yield.

The product yield increased as the temperature increased from 45°C to 55°C. A maximum yield of 72.8 % was achieved at 55°C after which the yield decreased as the temperature increased beyond this value. High temperatures reduce the molecular interaction time between methanol, oil and catalyst causing thermal degradation and reduction of biodiesel yield (Modiba *et al.*, 2014).

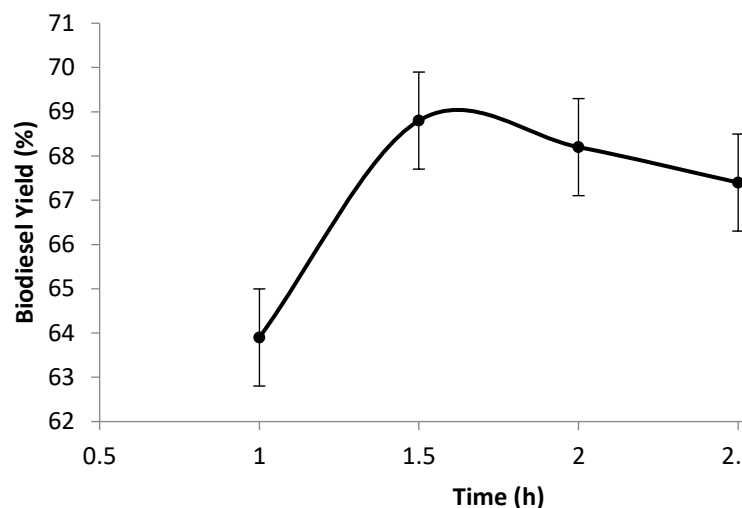


Figure 3. Showing Time (h).

As shown in figure 3, high yield of methyl ester was obtained at 1.5 h reaction. As the reaction time increased the biodiesel yield increased to a maximum at 1.5 h; thereafter there was a slight decrease in biodiesel yield. Reversible reaction might have led to reduction in the biodiesel yield at high reaction time (Yun *et al.*, 2011)

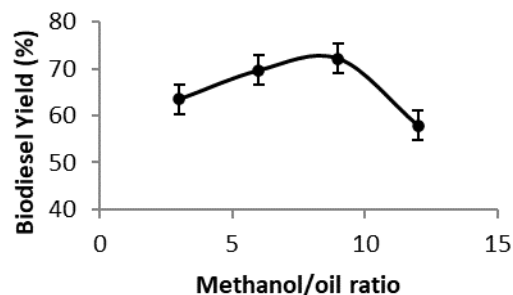


Figure 4. Showing Methanol/oil Ratio

Increases in methanol to oil ratio led to corresponding increase in methyl ester yield; an optimum yield of 72.2 % was obtained at methanol to oil ratio of 9:1. Further increases in the ratio caused a fall in the esters yield. This could be due to solubility of glycerine in the reaction mixture causing a reverse glycerolysis reaction when the quantity of methanol was increased (Leung & Guo, 2006).

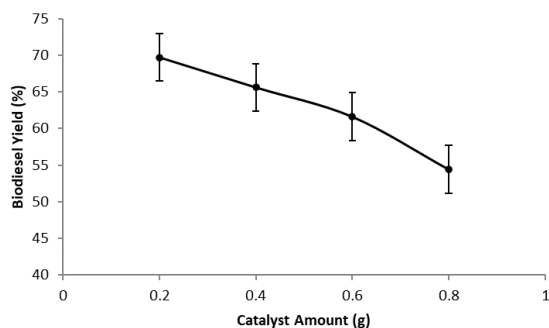


Figure 5. Showing Catalyst Amount (g)

Figure 5 shows that high a catalyst amount resulted in reduction of biodiesel yield. The maximum yield of 69.7 % was obtained at catalyst content of 0.2g. Further increase in catalyst content led to decrease in catalytic activity during the transesterification process causing reduction in biodiesel yield due to leaching of the catalyst in the reaction mixture (Baroutian *et al.*, 2010)

- Analysis of Variance (ANOVA).

The Taguchi design array as generated by Minitab 17 software and the experimental data obtained in the

transesterification of *Strychnos innocuadel* seed oil with methanol in the presence of catalyst are shown in Table 3.1. For statistical analysis of the experimental data, the generated matrix was defined using Box-Behkhen design. A second-order model equation relating biodiesel yield to the studied parameters is given by:

$$\text{Biodiesel Yield (\%)} = -2527 + 99.55A + 25.10B + 47.63C - 532.3D - 0.9546A^2 - 10.985 B^2 - 1.7454 C^2 + 260.9 D^2 + 0.036 AB - 0.0097 AC - 2.057 AD - 12.372 BC + 212.0 BD$$

The biodiesel yield from the seed oil ranged from 53.6 to 84.0 %. From Table 2, it was observed that the most controlling factors for biodiesel yield were temperature and catalyst amount due their levels of significance. The quadratic terms explain the interaction with itself with respect to biodiesel yield and all these terms were observed to be statistically significant on the yield of esters.

The model summary is presented in Table 3. The coefficient of determination (R^2) measures the degree of fitness of the model. Greater value of R^2 (very close to 1) indicates good model fitness (Akintunde *et al.*, 2015). The R^2 value of 0.9995 entails that 99.95 % of the variation in the data is explained by the model. The value implies that the model equation describes the relationship between biodiesel yield and the fators studied.

Table 4: Analysis of Variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	13	1267.49	97.499	340.82	0.003
Linear	4	94.07	23.517	82.21	0.012
Temp (A)	1	28.94	28.938	101.16	0.01
Time (B)	1	3.84	3.837	13.41	0.067
MeOH/oil ratio (C)	1	22.89	22.893	80.02	0.012
Catalyst Amount (D)	1	25.92	25.922	90.61	0.011
Square	4	419.21	104.803	366.36	0.003
A ²	1	93.95	93.954	328.43	0.003
B ²	1	120.67	120.67	421.82	0.002
C ²	1	157.93	157.929	552.07	0.002

D ²	1	79.23	79.23	276.96	0.004
2-Way Interaction	5	164.64	32.929	115.11	0.009
A*B	1	0.03	0.031	0.11	0.773
A*C	1	0.1	0.103	0.36	0.61
A*D	1	44.17	44.172	154.41	0.006
B*C	1	65.6	65.596	229.3	0.004
B*C	1	74.91	74.907	261.85	0.004
Error	2	0.57	0.286		
Total	15	1268.06			

S = 0.534854 R² = 99.95% R² (adj) = 99.66%
 R² (pred) = 89.24%

Table 5: Physicochemical Properties of Biodiesel Produced From *S. innocua* Seed Oil

Property	Units	Obtained Value	ASTM Value
Methyl Ester Yield	%		
Moisture Content	% wt	0.031 ± 0.021	0.050max
Specific Gravity		0.861 ± 0.069	0.88 to 0.90
Acid Value	Mg/KOH/g	0.65 ± 0.057	0.50 to 0.80
Cloud Point	°C	8.63 ± 0.191	-3 to 12
Pour Point	°C	5.25 ± 0.247	-5 to 10
Flash point	°C	142.67 ± 0.772	100 to 170
Kinematic Viscosity	Cst	4.88 ± 0.191	1.9 to 6.0
Cetane Number		54.07 ± 0.075	48 to 65
Sulphur Content	Wt%	0.06 ± 0.058	0.015 to 0.05
Copper Corrosion		1b	
High Heating Value	MJ/Kj	42.56 ± 0.075	

Kinematic viscosity is an important fuel property which affects atomization of fuel upon injection into a

combustion chamber and which may led to the formation of soot and engine deposit (Calisor *et al.*, 2005). Kinematic viscosity of the biodiesel produced was found to be 4.88 Cst which is higher than 3.93 Cst for biodiesel from snake gourd seed oil (Adeniyi & Esiaka, 2013) and 3.7Cst for biodiesel from rubber seed oil as reported by Umar *et al.*, (2013). The value obtained was found to be slightly higher than 4.5 Cst for *Jatropha curcas* (Abadi & Omar, 2015). The value obtained is within the ASTM standard (1.9 to 6.0). This implies that the corcas (Abadi & Omar, 2015). The biodiesel produced sustained high quality which clearly indicates that bio-diesel samples could operate efficiently as an important parameter in diesel engines.

• Cetane Number

Cetane number measures how promptly ignition occurs upon injection of fuel into combustion chamber and the smoothness of combustion (Garpen *et al.*, 2004). The cetane number of the biodiesel produced in this work was 54.07±0.075, this was within ASTM specification of 48 to 65. Fuels with low cetane number give a good ignition performance (Da-Silva, 2013). This implies that the biodiesels produced will have good ignition performance when used or blended with conventional diesel.

• Sulphur Content

The value of sulphur content was 0.06±0.058; the percentage sulphated ash in the sample agreed with specification limits of ASTM standard (0.05%). Sulphated ash is a measure of ash formed from inorganic compounds after burning biodiesel. Sulphated ash causes saturation of filters and production of wears on various parts of the engine and may be present in the form of abrasive solids, soluble metals, soaps and catalyst residues.

- Acid value

Acid value in diesel determines the level of free fatty acid or processing acid that may be present in biodiesel and is an indicator of biodiesel quality. The acid value obtained for the biodiesel produced was 0.65 ± 0.057 mg/KOH which is higher than 0.36Mg/KOH for crude palm oil (Nurhayati *et al.*, 2017) and $0.59 \text{ mg/KOHg}^{-1}$ reported by Ogunkunle *et al.*, 2017 for milk bush. High biodiesel with high acid value has been reported to increase fueling system deposit and increases the likelihood of corrosion (NRE, 2009). The results obtained are within the ASTM maximum limit (maximum of 0.8mg/KOH/g). This indicates that they have less tendency of causing wear of fuel systems and storage tanks.

- Copper Corrosion

Corrosivity of copper due to sulphur compounds as well as due to free fatty acid can lead to problems of corrosion in storage tanks and same parts of engines. The maximum acceptable value is degree 1 for both ASTM and EN standards. The copper strip corrosion of the biodiesel produced as presented in Table 4 is degree 1b which is found to be in agreement with the value reported by Tint and Mya (2009) for *jatropha curcas*.

- Moisture Content

The results of moisture content of biodiesel produced was 0.03 ± 0.021 which is higher than $0.020 + 0.009\%$ reported by Dominic *et al.*, (2016) for biodiesel produced from castor seed oil. Moisture content promotes biological growth, sludge and slime formation in diesel engines which may cause blockage of fuel filters of fuel lines. Moreover, high moisture content is also associated with hydrolysis reactions, partly converting biodiesel to free fatty acids. This indicates that the biodiesel produced is clean and is not likely to form free acids due to hydrolysis and may have minimal microbial growth during storage (Garpen *et al.*, 2004).

- Flash Point

Flash point is the lowest temperature at which a volatile product gives off sufficient flammable vapour to ignite. The flash point is often used as descriptive characteristic of liquid fuel and also helps to characterize the five hazards of the liquids. The flash

point of the biodiesel obtained was found to be 142.67 ± 0.772 . The value obtained conforms to ASTM standards. The results imply that biodiesel produced is of a non-hazardous category and therefore, safe to handle during storage or transportation as compared to conventional diesel.

- Pour Point

The temperature at which fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow is referred to as pour points. The value of pour point obtained was 5.25 ± 0.247 . The result obtained is therefore within the ASTM standards (-15 to 10). The results suggest that, the biodiesel produced may be used as fuel at low temperature as it met ASTM specification for pour point.

The percentage composition of calcined cowry shell is presented in Table 2. The predominant oxide recorded was CaO having 83.321% and other traces of oxide were detected.

Table 6: Fatty Acid Methyl Ester Composition of Biodiesel Produced

Methyl Ester	Relative Percentage (%)
Hexadecanoic Acid Methyl Ester	18.40
Tetradecanoic Acid Methyl Ester	1.40
Methyl Stearates	8.20
7,10 –octadecadienoic Acid Methyl Ester	0.56
9- Hexadecenoic Acid Methyl Ester	47.50
9- Octadecenoic Acid Methyl Ester	6.40
11- Octadecenoic Acid Methyl Ester	4.50
Ecosenoic acid Methyl Ester	2.34
1.80 Saturated	30.9
Unsaturated	60.20
Total	91.1

Fatty acid methyl ester profile is one of the key factors that determines the suitability or otherwise of a feedstock for use in biodiesel fuel production (Knoth,

2009). The results of transesterified oil revealed that the abundant esters are not highly unsaturated as they contain only one double bond in the structure. Higher degree of unsaturation in fatty acid methyl ester limits its suitability for use as fuel due to high polymerization tendency like peroxidation (Gaby & Peter, 1997). At high temperatures, commonly experienced in combusting engines, peroxidation can be accelerated and the engine can quickly become gummed with polymerized fatty acid methyl esters (Mohible *et al.*, 2005). Feedstock with high percentage of polyunsaturated acid is therefore not a valuable material for use as biodiesel. Table 6 shows the fatty acid methyl esters composition of biodiesel produced as the predominant methyl ester as 9-hexadecenoic acid methyl ester of 47.50%.

CONCLUSION

This study has shown that, *S. innocua* Del. seed oil can be converted to biodiesel using calcined cowry shell. The experimental results have shown that the reaction variables have significant effects on biodiesel yield. The optimum conditions for biodiesel production are; 9:1 methanol/oil ratio, 0.2g catalyst amount, 90 minutes reaction time and 60°C reaction temperature, achieving maximum yield of 85.0%. The fuel characteristics of the esters produced show good agreement with specified range of ASTM standards. This study has therefore shown that *S. innocua* Del. seed oil can be used as potential feedstock for biodiesel production.

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