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## MATERIALS ENGINEERING | RESEARCH ARTICLE

# Impact assessment of biodiesel production using CaO catalyst obtained from two different sources

A.A. Ayoola<sup>1\*</sup>, O.S.I. Fayomi<sup>2,3</sup>, O.A. Adeeyo<sup>1</sup>, J.O. Omodara<sup>1</sup> and O. Adegbite<sup>1</sup>

**Abstract:** In this research work, the comparative analysis of the production of high yield and environmental friendly biodiesel obtained from the transesterification of waste soybean oil, using technical grade CaO catalyst and CaO catalyst derived from chicken eggshells, was investigated. The results of the transesterification process, SEM (using ME 600T polarising optical microscope) and XRF (using Thermo Scientific ARL OP-TIM'X 166) analysis revealed a similar catalytic performance trend when the two forms of the CaO catalysts were used separately. For technical grade CaO catalyst (using response optimizer), the optimal conditions established for the production of biodiesel were methanol/oil mole ratio of 7.1, catalyst concentration of 5.9 wt/wt% oil and reaction time of 2.1 hours, with 92.6% biodiesel yield. Using CaO catalyst derived from chicken eggshells, the optimal conditions were 7.0 methanol/oil mole ratio, 6.0 wt/wt% catalyst concentration and reaction time of 2.2 hours, with 91.4% biodiesel yield. Impact assessment of the biodiesel production

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### PUBLIC INTEREST STATEMENT

The comparative analysis of the use of the technical grade CaO catalyst and CaO catalyst derived from chicken eggshells for the production of environmental friendly biodiesel from waste soybean oil was investigated. The results obtained (through SEM and XRF analysis) revealed a similar catalytic performance trend when the two forms of the CaO catalysts were used separately. For technical grade CaO catalyst, the optimal conditions established for the production of biodiesel were methanol/oil mole ratio of 7.1, catalyst concentration of 5.9 wt/wt% oil and reaction time of 2.1 hours, with 92.6% biodiesel yield. Using CaO catalyst derived from chicken eggshells, the optimal conditions were 7.0 methanol/oil mole ratio, 6.0 wt/wt% catalyst concentration and reaction time of 2.2 hours, with 91.4% biodiesel yield. The results of impact assessment showed that CaO catalyst derived from chicken eggshells waste has a fairly lesser negative impact on human health and a fairly more pronounced negative effects on ecosystems.

was carried out using ReCiPe Endpoint (E) V1.12/World ReCiPe E/E method (SimaPro 8.0 software) and AAnalyst 200 Perkin Elmer (AAS). The results of the impact assessment showed that technical grade CaO catalyst has more negative impact on human health and a lesser impact on ecosystems. In contrast, CaO catalyst derived from chicken eggshells waste has a fairly lesser negative impact on human health and a fairly more pronounced negative effects on ecosystems.

**Subjects:** Materials Science; Production Engineering; Chemical Engineering

**Keywords:** Biodiesel; CaO catalysts; characterization; damage assessment

## 1. Introduction

Globally, fossil fuels (petroleum oil, gas and coal) are being threatened out of dominance as energy source to other fuels due to instability of the prices of fossil fuels in international market, depletion of the sources resulting from their non-renewable nature, political tensions associated with fossil fuels, the associated negative effects on the environment and the monetary returns on the populations in some countries especially in Africa is not getting to the rural populace, even the generality of the people (Abila, 2010).

As a result of these drawbacks listed amongst other reasons, great efforts are being made by the world leaders, concerned industries and research institutions to promote sustainable and renewable forms of energy (Amanda, Adriana, & Díaz, 2017; Ayoola, Hymore, & Omonhinmin, 2016; Tabatabaei, Karimi, Sárvári, & Kumar, 2015): a step in accordance with the global pursuit of Sustainable Development Goals (SDG) and the *Paris Agreement* on climate change.

Biofuels (energy from biomass) are renewable and sustainable energy, with lesser negative environmental impacts when compared to fossil fuels (Ayoola, Adeniyi, Sanni, Osakwe, & Jato, 2018a). As widely reported in the literature, adoption of biofuels will promote economic growth, sustainable energy and job opportunities, particularly in remote parts of different countries (Abila, 2010; Yunus et al., 2014). However, some countries (especially in Africa) are currently facing the challenge of high production cost of biofuels: an impediment to the commercialization of biofuels in the globe.

Biodiesel, a form of bioenergy obtained from the transesterification process, is one reliable way to overcome the limitation being experienced in the commercialization of bioenergy production. This is because, the varieties of the resources required for its production are abundant, the application of biodiesel in petroleum-diesel engine does not require engine modification, and it is non-toxic, biodegradable, and has insignificant negative environmental impact (Evangelos., 2013).

Transesterification process is a chemical process that involves reversible reaction between the triglyceride in vegetable oil (or animal fat) and alcohol (methanol, ethanol, propanol), in the presence of a catalyst (heterogenous or homogenous in nature) to yield fatty acid alkyl ester (biodiesel) and glycerol (Evangelos., 2013; Ayoola, Igho, & Fayomi, 2018bb; Ayoola, Fayomi, & Usoro., 2018cc). To overcome the challenge of high cost of production, concerted efforts are being made to use readily available and low-cost raw materials for its production. For instance, waste cooking oils (WCO) are now preferred feedstocks for biodiesel production. In addition, animal shells (rich in  $\text{CaCO}_3$ ) are the raw materials being processed as CaO catalyst. By so doing, the environmental pollution problems arising from the wrong disposal of the large volume of animal shells and WCO generated are minimized. Moreover, the use of WCO averts food—fuel crisis resulting from the use of fresh cooking oils (Aguieiras, Cavalcanti-Oliveira, & Freire, 2015; Ayoola et al., 2015; Nasrollahzadeh, Sajadi, & Hatamifard, 2016; Shan, Zhao, Lv, Yuan, & Yao, 2016).

CaO has been widely reported as a suitable heterogeneous form of catalyst due to its high reusability, high selectivity and high biodiesel yield (Chen, Shan, Shi, & Yan, 2014; Correia et al.,

2014; El-Gendy & Deriase, 2015). The current trend in the production of biodiesel, using CaO heterogenous catalyst, involves the processing of animal wastes that are rich in  $\text{CaCO}_3$ . These waste materials include periwinkle shells, egg shells, duck shells, fish bones, chicken bones, cow bones, chitosan and snail shell. In addition, the use of CaO catalyst from wastes promotes stable and highly efficient catalytic performance, produces low freezing point biodiesel and enhances high surface area and uniform porosity of the catalysts, as well as excellent water and acid resistant ability (Shan et al., 2016; Srinivas & Satyarathi, 2010).

Case-specific analyses of the feedstocks (WCO), catalytic materials and the production processes are essential to establish the environmental implication, quality of biodiesel produced and benefits associated with the biodiesel as a biofuel (Ayoola et al., 2018d; Liang, Xu, & Zhang, 2013; Ranjan & Premananda, 2003). These analyses can be achieved through the impact assessment of the biodiesel produced. Impact assessment of the biodiesel produced can assist in: the choice of materials that are environmental friendly during biodiesel production, identifying opportunities to improve the production process of biodiesel, and the enforcement of biodiesel production standards (Ali & Tay, 2013; Zahira, Masita, Mohammad, & Zahangir, 2013).

The aim of this research work is to carry out comparative analysis of the production of high yield and environmental friendly biodiesel obtained from the transesterification of waste soybean oil, using technical grade CaO catalyst and CaO catalyst derived from chicken eggshells.

## 2. Materials and methods

### 2.1. Materials, reagents and equipment

Some of the materials and reagents used include waste soybean oil, chicken eggshells, methanol, CaO (93%, Qualikems, India), KOH pellets (98%, Sigma-Aldrich, UK), methanol (99.8%, Romil Ltd UK), hydrochloric acid (97%, Riedel-Dietzen, Germany), tetraoxosulphate (IV) acid (96.5%, Sigma-Aldrich, UK) and benzene (96%, J.T Baker, USA).

Some of the equipment used in this research work include Gas Chromatography Mass Spectroscopy (Agilent Technologies 7890A, GC System/5975C VL MSD, USA, for the identification and determination of percentage composition of fatty acids in oil), Atomic Absorption Spectroscopy (AAAnalyst 200 Perkin Elmer precisely, USA, for the identification and quantification of the heavy metals (potential emissions) from biodiesel), XRF spectroscopy (Thermo Scientific ARL OP-TIM'X 166, to determine the elemental compositions of the catalysts), and Scanning Electronic Microscope (ME 600T polarising optical microscope, to examine the size or morphology of the catalysts).

### 2.2. Pre-treatment of the waste soybean oil (WSO)

WSO contain solid particles such as sand, sticks, fish particles, free fatty acid and water. These particles present were first removed, to prevent low biodiesel yield and soap formation. The specified removal processes involved are sedimentation, filtration, neutralisation and heating processes.

### 2.3. Fatty acid composition of WSO

Analysis of the fatty acid composition of WSO was carried out using GCMS. The result of the analysis is shown in Figure 1 and Table 1.

### 2.4. Design of experiment

Central composite method (Minitab 17 software) was used for the experimental design. The process variables considered are methanol-oil mole ratio, catalyst concentration and reaction time (Table 2).

### 2.5. Catalyst preparation

The raw chicken eggshells obtained from a Covenant University Cafeteria were carefully washed in pure water and then dried in an oven for 45 minutes at  $110^\circ\text{C}$  to remove water present. The dried

Figure 1. Fatty acid composition of WSO.

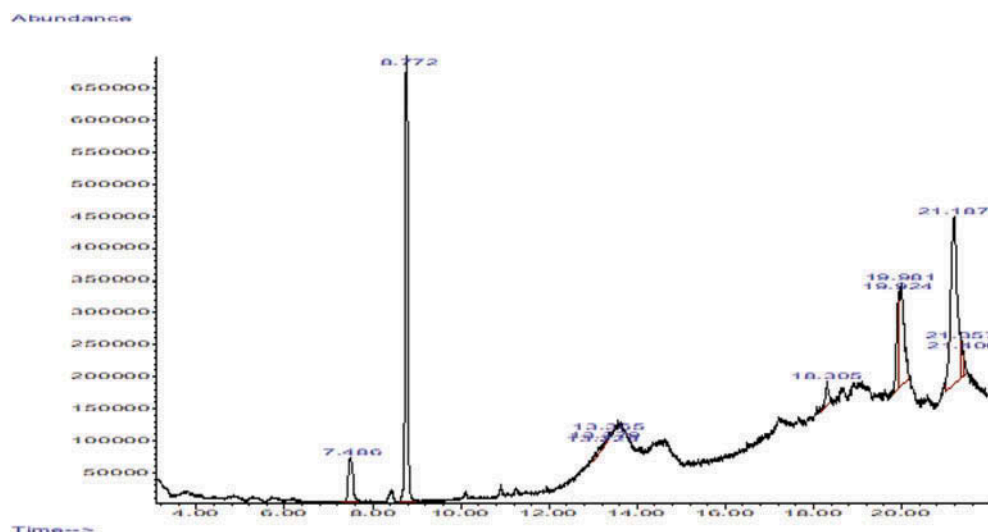


Table 1. Fatty acid composition of WSO

Peak Number	Retention Time (min)	Component	Formula	Structure	Composition (%)
1	7.486	stearic	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	5.819
2	8.772	linoleic	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	36.351
3	13.223	arachidic	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	20:0	0.903
4	13.279	myristoleic	C <sub>14</sub> H <sub>26</sub> O <sub>2</sub>	14:1	0.151
5	13.365	palmitoleic	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	16:1	0.158
6	18.305	gadoleic	C <sub>20</sub> H <sub>36</sub> O <sub>2</sub>	20:2	2.058
7	19.924	linolenic	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	18:3	7.264
8	19.981	palmitic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	13.081
9	21.187	oleic	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	31.677
10	21.357	gondoic	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	20:1	1.424
11	21.400	behenic	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	22:0	1.113

Table 2. Experimental design (central composite method) showing variables and their levels

Process variables	Levels	-1	0	+1
Methanol/Oil Mole Ratio	9	12	15	
CaO Catalyst Concentration	(% w/w Oil)	2	5	8
Reaction Time	(hours)	1	2	3

eggshells were then crushed in a mechanical grinder to fine particulate size then sieved on an automated sieve to obtain <75 µm particle sizes. The fine powdered was then dried in the oven for 30 minutes at 110°C.

Calcination of the fine powdered was carried out in a Muffle furnace (Carbolite HTF 1700) at 850° C for 3 hours. The chicken eggshells CaO catalyst obtained was then stored in an air tight container to prevent the CaO catalyst poison by reacting with air the environment. The physiochemical characteristics of both the technical grade CaO catalyst and CaO catalyst derived from chicken eggshells were carried out through SEM and XRF analysis.

### 2.6. Transesterification process

As described in the previous work (Ayoola et al., 2018c, 2018b), treated waste soybean oil was reacted with methanol (in the presence of CaO catalyst) in a laboratory scale reactor (considering the specified process variables), to produce biodiesel.

### 2.7. Elemental analysis on biodiesel

Potential emissions from both the biodiesel samples were identified and quantified using AAS (AAAnalyst 200 Perkin Elmer precisely, USA). The data obtained were needed in the assessment of the impact of the potential emissions from the biodiesel.

Biodiesel samples were first digested (using a solution containing HCl and HNO<sub>3</sub>) and then aspirated into the nebulizer compact of AAS where the sample mixed with air and acetone to form a mixture. Flame burned and atomized the sample to the excited state. At excited state, absorption occurred and monochromator selected the wavelength in agreement with the atom. Moreover, the atom detected (by the detector) was then transferred as quantitative concentration reading to the reader.

### 2.8. Potential impact assessment of the biodiesel production

Impact assessment of the biodiesel production was carried out using ReCiPe Endpoint (E) V1.12/ World ReCiPe E/E method (SimaPro 8.0 software). The potential emissions from the biodiesel produced were characterized, and their potential damage assessment to human health and ecosystem was determined.

## 3. Results and discussions

### 3.1. Analysis on catalyst

The results of XRF analysis of the two catalysts used during the transesterification process are as shown in Table 3. High percentage of CaO was observed in the two samples. The calcination of chicken eggshells powder at 850°C for 3 hours greatly enhanced the conversion of CaCO<sub>3</sub> (main component of the shell) to CaO. Moreover, the minute quantities of all other compounds (including 7.07% of P<sub>2</sub>O<sub>5</sub>) showed that these unwanted compounds could not pose any significant hindrance against the catalytic performance of the two forms of CaO.

Table 3. XRF analysis of the two catalysts used

Compound	Technical Grade CaO	CaO from Chicken Eggshells
CaO	98.89	90.07
P <sub>2</sub> O <sub>5</sub>	0.35	7.07
Na <sub>2</sub> O	0.02	0.11
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.34
K <sub>2</sub> O	0.29	0.07
MgO	0.01	0.91
Mn <sub>2</sub> O <sub>3</sub>	0.01	0.10
Cr <sub>2</sub> O <sub>3</sub>	0.23	0.06
Al <sub>2</sub> O <sub>3</sub>	0.07	1.27
TiO <sub>2</sub>	0.09	0.00

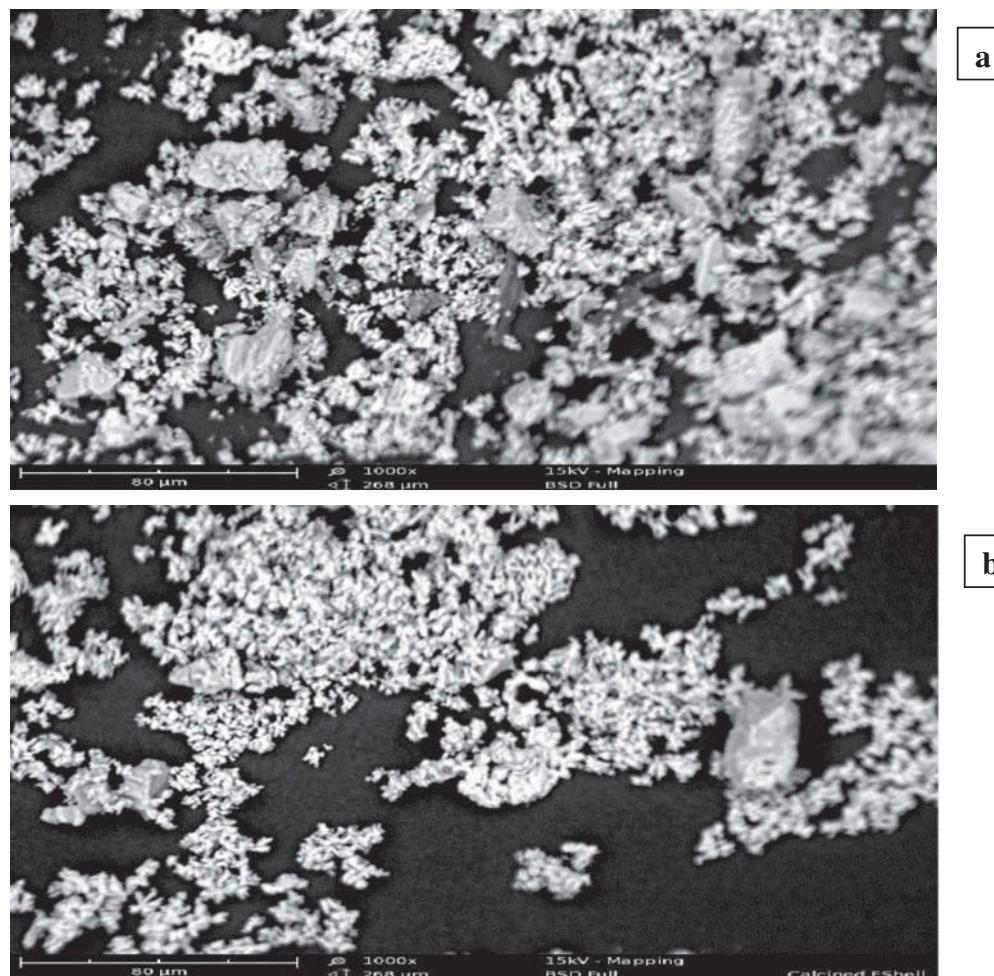
SEM of the technical grade CaO catalyst and CaO catalyst from chicken eggshells, with magnification X1000, are shown in Figure 2. Both the technical grade CaO catalyst and CaO catalyst from chicken eggshells have similar morphological structures. This is an indication that the two forms of catalyst contain mainly same compound (CaO), as justified by the XRF analysis.

### 3.2. Biodiesel production

Table 4 shows the material balance for the production of 1 kg of biodiesel using technical grade CaO catalyst and CaO catalyst from chicken eggshells. The result revealed that the production of 1 kg biodiesel (using same quantity of CaO catalyst) would require lesser quantity of both the methanol and soybean oil in the case of using technical grade CaO catalyst. This is due to the slight difference observed in the percentage of CaO in the two forms of catalyst used (Table 3).

The result of the transesterification process, as shown in Table 5, revealed a similar trend when technical grade of CaO catalyst and CaO catalyst obtained from chicken eggshells were used separately. The yield of biodiesel was slightly higher using technical grade of CaO catalyst. The slight difference could be attributed to the percentage level of CaO in the two forms of catalysts, as revealed by the XRF analysis (Table 3). An indication that production process of CaO from chicken eggshells requires minor modification for the enhancement of the functionalisation of the CaO obtained (Shan et al., 2016).

Figure 2. SEM of the (a) technical grade CaO catalyst and (b) CaO catalyst from chicken eggshells.



**Table 4. Material balance on 1 kg of biodiesel produced**

ITEM		CaO (EggShell)	CaO (EggShell)
<b>Feed</b>			
Methanol Used	kg	0.4748	0.4743
Oil Consumed	kg	1.0070	1.0060
Catalyst Used	kg	0.0318	0.0318
Total	kg	1.5136	1.5121
<b>Products</b>			
Biodiesel	kg	1.0000	1.0000
Crude Glycerol	kg	0.4818	0.4803
Catalyst Used	kg	0.0318	0.0318
Total	kg	1.5136	1.5121

**Table 5. Biodiesel yield using eggshells and tech. grade Cao catalyst**

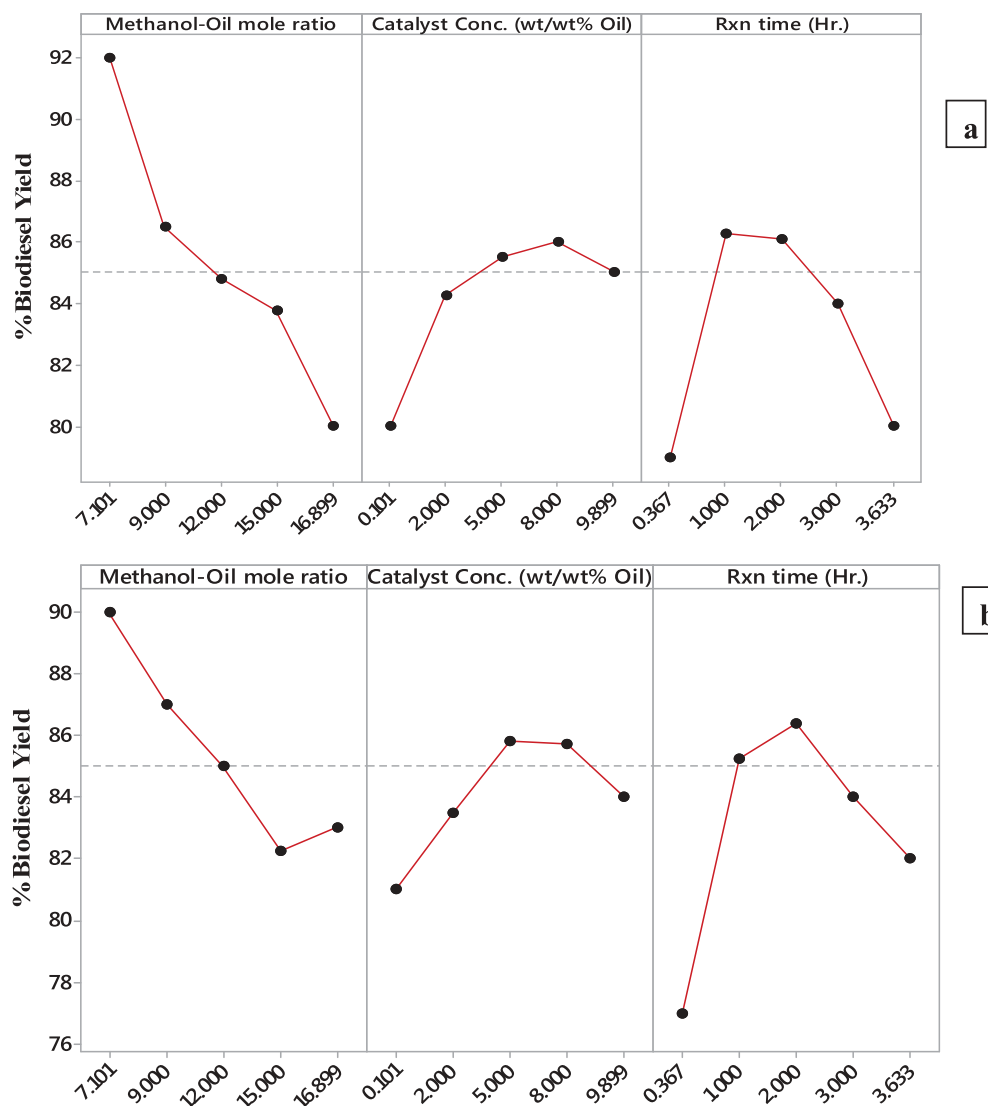
Methanol–Oil (mole ratio)	Catalyst Conc. (wt/wt% Oil)	Rxn time (Hr.)	Yield (%) using Eggshells	Yield (%) using Tech. Grade
9.000	2.000	3.000	85	86
12.000	5.000	2.000	89	89
9.000	8.000	3.000	92	91
15.000	2.000	3.000	81	82
9.000	8.000	1.000	83	85
15.000	8.000	1.000	90	89
9.000	2.000	1.000	88	88
15.000	8.000	3.000	78	81
12.000	5.000	2.000	84	85
12.000	5.000	2.000	93	94
15.000	2.000	1.000	80	83
12.000	5.000	2.000	86	88
12.000	5.000	3.633	82	80
12.000	9.899	2.000	84	85
7.101	5.000	2.000	90	92
12.000	0.101	2.000	81	80
16.899	5.000	2.000	83	80
12.000	5.000	2.000	89	90
12.000	5.000	0.367	77	79
12.000	5.000	2.000	85	87

### 3.3. Main effects of the process variables on the yields of biodiesel

The main effects of each of the three process variables (methanol–oil mole ratio, catalyst concentration and reaction time) on the yields of biodiesel are shown in Figure 3. In Figure 3(a), an increase in methanol–oil mole ratio resulted in decrease in biodiesel yields. Similar result was noticed in Figure 3(b). Transesterification process is a reversible one. Hence, the excess methanol used increased the polarity of the reaction mixture, thereby increased the solubility of glycerol and favoured the reversible reaction between glycerol and biodiesel, thereby resulted into lower yields of biodiesel (Ayoola et al., 2016). Figure 3 showed that excellent catalytic performance of the two



**Figure 3. Main effects of the three process variables on the yields of biodiesel: (a) technical grade CaO, (b) CaO from chicken eggshells.**



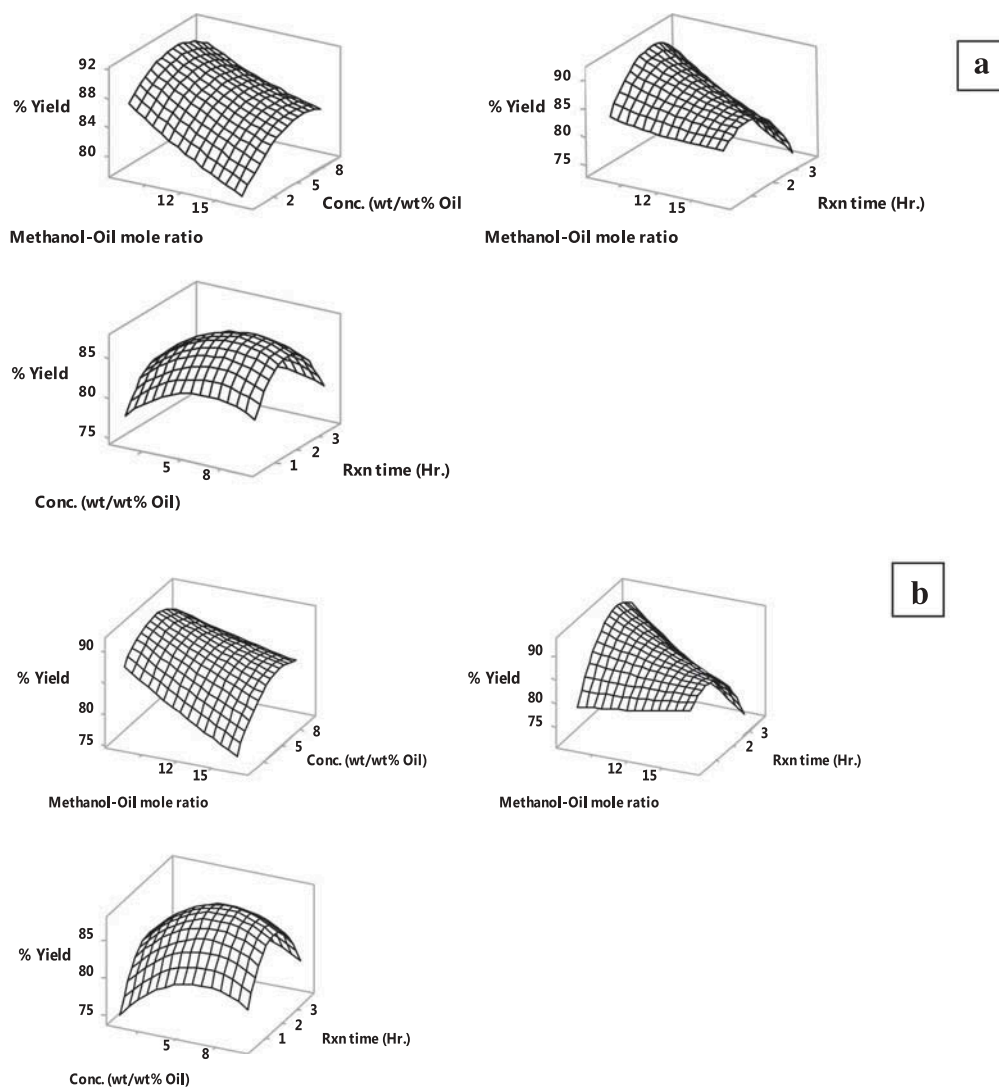
forms of CaO was achieved within the catalyst concentration of 5–8 wt/wt% oil. Beyond this range, the excess solid nature of CaO hindered transesterification reaction, thereby reducing the yields of biodiesel (Ayoola et al., 2018b). Reaction time of 1–2 hours favoured forward reaction of biodiesel production. Beyond this time range, backward reaction of biodiesel consumption was favoured, thereby resulting in lower yields of biodiesel.

### 3.4. Interactive effects of the process variables on the yields of biodiesel

The results of the interactive effects of the three process variables on the yields of biodiesel are shown in Figure 4. These results are the same with the results observed in the main effects, but with the exception that specific conditions for high biodiesel yields were clearly specified under interactive effects. For instance, Figure 4(a,b) shows that high biodiesel yields would be obtained at catalyst concentration of 6 wt/wt% oil and reaction time of 2 hours.

Using Response Optimizer, the optimal conditions established for the production of biodiesel are tabulated in Table 6

**Figure 4. Interactive effects of the process variables on the yields of biodiesel (a) technical grade CaO, (b) CaO from chicken eggshells.**



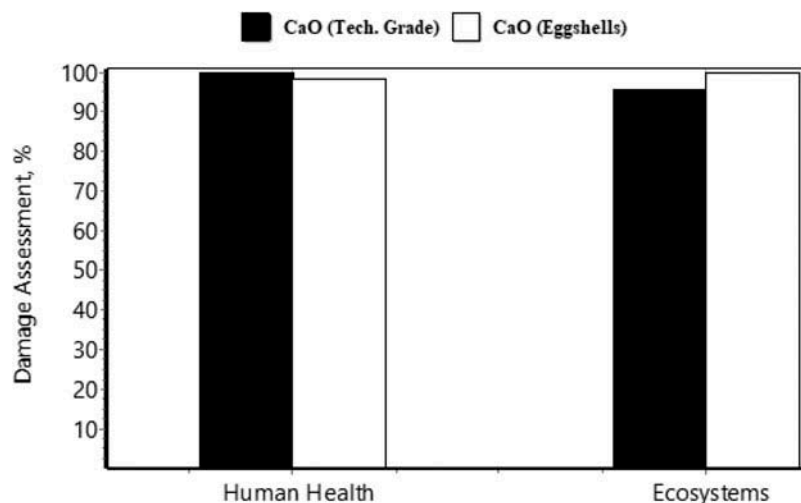
**Table 6. Optimal conditions established for the production of biodiesel**

Catalyst Type	Methanol/Oil Mole ratio	Catalyst Concentration (wt/wt% oil)	Rxn time (Hours)	Biodiesel Yield (%)
CaO (technical grade)	7.1	5.9	2.1	92.6
CaO (chicken eggshells)	7.0	6.0	2.2	91.4

### 3.5. Damage assessment of the biodiesel production

Figure 5 and Table 7 show the results of the comparative analysis of the potential damage assessment involved in the production of 1 kg of biodiesel, using CaO from two different sources. The damage assessment was carried out in terms of the *damage to Human health* and *damage to Ecosystems*. Table 7 presents the quantification of each of the pollutants, as expressed in DALY (Disability Adjusted Life Year) and *species.yr*. According to WHO, “DALY” means the year lost by man due to ill-health or disability while “species.yr” implies number of species (excluding human)

**Figure 5. Comparative analysis of the potential damage assessment.**



**Table 7. Comparative analysis of the potential damage assessment**

Substance	CaO (Tech. Grade)	CaO (Eggshells)		
<b>Human Health</b>				
Arsenic	Air	DALY	$3.096 \times 10^{-10}$	$3.483 \times 10^{-10}$
Arsenic	Water	DALY	$2.150 \times 10^{-9}$	$2.050 \times 10^{-9}$
Cadmium	Air	DALY	$9.658 \times 10^{-11}$	$1.053 \times 10^{-10}$
Cadmium	Water	DALY	$4.632 \times 10^{-13}$	$5.018 \times 10^{-13}$
Chromium Air	DALY	$3.570 \times 10^{-16}$	$1.428 \times 10^{-16}$	
Cobalt	Air	DALY $5.738 \times 10^{-12}$	$5.436 \times 10^{-12}$	
Cobalt	Water	DALY	$4.160 \times 10^{-31}$	$4.000 \times 10^{-31}$
Lead	Air	DALY	$4.860 \times 10^{-12}$	$6.48 \times 10^{-12}$
Lead	Water	DALY	$3.430 \times 10^{-13}$	$3.430 \times 10^{-13}$
Nickel	Air	DALY	$8.109 \times 10^{-13}$	$8.586 \times 10^{-13}$
Nickel	Water	DALY	$2.527 \times 10^{-13}$	$3.325 \times 10^{-13}$
		<b>Total DALY</b>	<b><math>2.568 \times 10^{-9}</math></b>	<b><math>2.517 \times 10^{-9}</math></b>
<b>Ecosystems</b>				
Arsenic	Air	species.yr	$4.495 \times 10^{-15}$	$3.996 \times 10^{-15}$
Arsenic	Water	species.yr	$2.006 \times 10^{-14}$	$1.913 \times 10^{-14}$
Cadmium	Air	species.yr	$1.575 \times 10^{-14}$	$1.718 \times 10^{-14}$
Cadmium	Water	species.yr	$3.249 \times 10^{-16}$	$3.520 \times 10^{-16}$
Chromium Air	species.yr	$2.208 \times 10^{-15}$	$8.833 \times 10^{-16}$	
Cobalt	Air	species.yr	$2.911 \times 10^{-14}$	$2.757 \times 10^{-14}$
Cobalt	Water	species.yr	$5.994 \times 10^{-14}$	$5.764 \times 10^{-14}$
Lead	Air	species.yr	$4.115 \times 10^{-16}$	$5.487 \times 10^{-16}$
Lead	Water	species.yr	$4.523 \times 10^{-18}$	$4.523 \times 10^{-18}$
Nickel	Air	species.yr	$5.920 \times 10^{-14}$	$6.269 \times 10^{-14}$
Nickel	Water	species.yr	$3.436 \times 10^{-14}$	$4.521 \times 10^{-14}$
		<b>Total</b>	<b><math>2.250 \times 10^{-13}</math></b>	<b><math>2.360 \times 10^{-13}</math></b>

in the ecosystem that suffer from ill-health, disability or death in a year. Damage to Ecosystems connotes the degradation in quality of water, soil and air; this may impose varied degree of hazard to plants and animals found in the ecosystem.

Considering *damage to Human health*, a total of  $2.5,686,482 \times 10^{-9}$  DALY (100%) potential harmful substances were involved when CaO technical grade was used during biodiesel production. Moreover,  $2.517,612 \times 10^{-9}$  DALY (98%) potential harmful substances were involved, using CaO from chicken eggshells. The result of *Ecosystem damage* shows  $2.25 \times 10^{-13}$  species.yr (96%) using CaO technical grade and  $2.36 \times 10^{-13}$  (100%) species.yr (using CaO from chicken eggshells).

These values appear insignificant, but the results indicated that the use of CaO technical grade (during biodiesel production) would cause a more pronounced negative impact on human health. That is, the higher level of harmful substances from the use of CaO technical grade, when utilised/ consumed by man (through water or air), would cause more harm to the body systems. On the contrary, release from the use of CaO technical grade (during biodiesel production) appeared to be more environmentally eco-friendly, compared to the release resulted from the use of chicken eggshells CaO. This is due to the fact that the threshold level of some of these substances are higher in plants and animals compared to human (Ranjan & Premananda, 2003).

#### 4. Conclusion

The results of this research work reveal that CaO catalyst derived from chicken eggshells waste is a good replacement to the costly technical grade CaO, for high-yield biodiesel production. CaO catalyst (technical grade) has more negative impact on human health and a lesser impact on ecosystems, while CaO catalyst derived from chicken eggshells waste has a fairly lesser negative impact on human health and a fairly more pronounced negative effects on ecosystems.

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