AIMS Energy, 8(4): 527–537.
DOI: 10.3934/energy.2020.3.527
Received: 15 November 2019
Accepted: 05 April 2020
Published: 24 June 2020

http://www.aimspress.com/journal/energy

Research article

Biodiesel production from used vegetable oil and CaO catalyst impregnated with KNO_3 and $NaNO_3$

A.A. Ayoola[1,*], F.K. Hymore[1,2], C.A. Omonhinmin[3], O. Agboola[1], E.E. Alagbe[1], D. Oyekunle[1] and M.O. Bello[1]

[1] Chemical Engineering Department, Covenant University, Ota, Ogun State, Nigeria
[2] Regent University College of Science and Technology, Accra, Ghana
[3] Biological Sciences Department, Covenant University, Ota, Ogun State, Nigeria

* **Correspondence:** Email: ayodeji.ayoola@covenantuniversity.edu.ng.

Abstract: The rise in global energy demand has encouraged exploring into other innovative methods of generating renewable fuels from different forms of waste. Due to its accessibility, culinary used vegetable oil is regarded as a potential source for profitable production of biodiesel. In the present study, the viability of producing biodiesel from used vegetable oil (UVO) by utilizing CaO catalyst (derived from the calcination of chicken eggshell and impregnated with KNO_3 and $NaNO_3$) was studied. Higher yield of biodiesel was obtained at methanol/oil mole ratio of (9–10) and CaO catalyst concentration of (2.0–3.0) wt/wt% Oil, for the three forms of catalyst used. Also, higher yield of biodiesel was obtained when CaO with impregnated KNO_3 was used, followed by the operation involving CaO with impregnated $NaNO_3$. At optimum conditions of methanol/oil mole ratio of 9 and catalyst concentration of 2.4 wt/wt% Oil, the yields of biodiesel obtained were 90% (for unimpregnated catalyst), 92% (using CaO impregnated with $NaNO_3$) and 95% (using CaO impregnated with KNO_3). The higher biodiesel yield obtained for CaO impregnated with KNO_3 (compared to the yield from CaO impregnated with $NaNO_3$) could be traced to a more reactive nature of potassium and arrangement of electrons of both potassium and sodium. The results of the tests and analysis on biodiesel properties reveal that quality biodiesel were produced from the three forms of catalyst used. This is because, each of the values of the properties considered falls within the ASTM standard.

Keywords: biodiesel; calcination; CaO; eggshells; impregnation; KNO_3; $NaNO_3$; waste vegetable oil

1. Introduction

Energy is the key driver of modern civilization and technological advancement. Galloping energy demand has inspired new innovations in the field of renewable energy. In line with the United Nations' Sustainable Development Goals (SDGs), specifically Goal 7 (Affordable and Clean Energy) and Goal 13 (Climate Action), adoption of cleaner and renewable fuel alternatives to petroleum-based fuels demands combined global efforts from governments, industries and research institutes [1]. Biodiesel (renewable energy that can be produced from the triglycerides of plant oils or animal fats) is one the promising alternative energy sources. Biodiesel is composed of long-chain alkyl esters and can be utilized directly in the petroleum diesel engine with little or no modifications [2,3].

Another benefits of the use of biodiesel as fuel is that it requires little or no engine modification when introduced into petroleum diesel engine. Biodiesel can be blended directly with petroleum diesel, at any desired proportion by using a specific notation. The notation B20, B50 and B75 implies that 20%, 50% and 75% of biodiesel are blended with petroleum diesel in diesel engine respectively [2,3].

However, one major setback in the commercialisation of biodiesel is the high cost of production. But the reuse and recycling of waste materials for biodiesel production is a good option in addressing this economic challenge [4]. Production of biodiesel involving used vegetable oil (UVO) will not only serve as a cost-effective feedstock but also alleviate pollution problems arising from improper disposal of such used oils [4–6]. This is because, improper disposal of UVO is life threatening for both terrestrial and aquatic lifeforms that come in contact with land and water polluted with such oil [5]. Also, UVO disposed via kitchen sinks can clog drains on solidification and results in corrosion of metallic pipes and fittings, reducing metal life span with resultant increase in expenditure cost [5].

Conversion of UVO to any valuable substance or material is of global interest. This presents a great opportunity in the conversion of UVO to biodiesel through transesterification process. Transesterification is a reversible process that involves chemical reaction between the triglycerides of lipids (oils or fats) and short chained alcohol (preferably methanol or ethanol) in the presence of a suitable catalyst (basic, alkaline, acidic, or enzymatic in nature) to form biodiesel and glycerol [7–9]. It is the commonly adopted technique for biodiesel production process due to its ease of operation and efficiency [10].

The choice of catalyst for the production process is a function of both the composition and nature of the feedstock [11,12]. The high content of free fatty acids (FFA) in UVO is responsible for the pre-treatment of such oil with heterogenous catalyst, like CaO. To further reduce biodiesel production cost, waste materials that are rich in $CaCO_3$ can be processed into CaO, through calcination process [13–15]. Also, the use of CaO (and other heterogenous catalysts) helps to eliminate the soap formation resulting from the side reaction of homogenous catalysts which can hamper the yield of biodiesel produced [16,17].

The current trend in the use of heterogenous catalysts involves the impregnation of the catalyst with certain compounds that will promote more stable and highly efficient catalytic performance, low freezing point biodiesel, high surface area and uniform porosity of the catalysts, as well as excellent water and acid resistant ability [18]. Wet impregnation (in which an excess amount of solution is introduced) is the common practice. Examples of the catalysts with this form of combination include K_2CO_3/Al-O-Si aerogel, KF/CaO, K_2CO_3/SiO_2 [19]. The results of [18] revealed that the catalytic performance of CaO can be enhanced through its impregnation using KF

or any other salt of Potassium. It is a general belief that Potassium and Sodium perform in a similar manner, in term of chemical reactions. Hence, in this study, biodiesel production from waste vegetable oil using Calcium oxide (derived from calcined chicken eggshells and then impregnated with KNO_3 and $NaNO_3$) will be investigated. The novelty of this work is the explorative investigation of the viability of both $NaNO_3$ and KNO_3 for CaO catalyst impregnation.

2. Materials and methods

2.1. Materials, reagents and equipment

Chicken eggshells and used vegetable oil were obtained from Cafeteria 2, Covenant University, Ota, Ogun State, Nigeria. The reagents used include methanol (99.8%, Romil Ltd UK), hydrochloric acid (96.5%, Sigma-Aldrich, UK), potassium hydroxide (97.9%, J.T Baker, USA), benzene (99.8%, Sigma-Aldrich, UK). And the equipment used include X-ray diffractometer (X'Pert Pro model diffractometer), GC-MS (GC System/5975C, Agilent, USA) and muffle furnace.

2.2. Catalyst preparation and characterisation

Eggshells were carefully and thoroughly washed in warm water before being dried in oven at 110 ℃ for 2 hours. The samples were then soaked in 0.05M HCl and stirred continuously for 2 hours to remove the cuticle layer so as to reduce the Phosphorus content. The eggshells were then dried in oven at 110 ℃ for 1 hour and then crushed to 80 nm (nano-sized particles). The powdered eggshell was calcinated in an electric furnace at 700 ℃ for 4 hours. The catalyst was then divided into three portions, a portion was impregnated with KNO_3, another portion was impregnated with $NaNO_3$, no impregnation material was added to the third portion of CaO catalyst.

Simple steps were involved in the impregnation of CaO catalyst. 40 mL of 0.05 M KNO_3 (or $NaNO_3$) solution was doped into every10 g of the calcined CaO. To ensure homogeneity, the mixture was stirred for 15 minutes and then dried in an oven at constant temperature of 120 ℃ for 2 hours. The dried sample was then calcined in muffle furnace at 300 ℃ for 2 hours. The three different forms of the catalysts were kept in airtight container before subsequent use to prevent any contact with air or moisture. XRF and XRD analyses were carried out on the three forms of the catalyst samples to determine their elemental compositions.

2.3. Pretreatment and esterification of UVO

Impurities (such as small stones, sticks, fish) were first removed from the used vegetable oil through sedimentation and filtration. The oil composition was determined through GCMS analysis. The acid values of UVO (before and after FFA removal) were determined through acid esterification process which involves titration (ASTM D664 procedure), this procedure reduced the acid value to < 1%. The acid esterified oil sample was then heated to 105 ℃ for 30 minutes and continuously stirred at 2500 rpm, in order to completely remove the moisture content present [5].

2.4. Design of experiment

Taguchi method (Minitab 17 software) was adopted in the experimental design of biodiesel production, the process variables considered were methanol/oil mole ratio and catalyst concentration (Table 1).

Table 1. Design of experiment using Taguchi method.

Symbol	Process variables	Units	Low	High
X_1	Methanol-oil mole ratio	mol/mol	9	12
X_2	Catalyst concentration	wt/wt % Oil	2	4

2.5. Transesterification of the esterified oil

100 g of the acid esterified oil used was used for each of the experiment runs. A mixture of the required quantities of methanol and catalyst was added to the esterified oil, for transesterification reaction to take place at the specified reaction time. At the end of the reaction, catalyst, glycerol, unreacted methanol and biodiesel were carefully separated [20]. Constant reaction temperature of 60 ℃ and reaction time of 60 minutes were considered in each of the four experimental runs.

3. Results and discussion

3.1. Catalyst characterization

The characterisation of the three forms of catalysts used was carried out using XRF analysis. The analysis is very important in order to determine the elemental composition of the catalysts used.

Table 2. X-Ray Fluorescence spectrometry of catalysts used.

Oxide	Impregnated with $NaNO_3$	Impregnated with KNO_3	Unimpregnated
Fe_2O_3	0.00	0.04	0.03
TiO_2	0.66	0.00	0.00
CaO	96.87	97.09	92.70
Al_2O_3	0.00	0.00	0.56
MgO	0.00	0.00	3.22
SiO_2	2.46	2.36	2.99

The results of XRF analysis of the three forms of catalysts used were tabulated in Table 2. CaO catalyst impregnated with KNO_3 had the highest CaO concentration of 97.09 wt% and catalyst impregnated with $NaNO_3$ had 96.87 wt% of CaO while the unimpregnated CaO had 92.70 wt% of CaO concentration. The high level of CaO content confirms the success of the conversion of eggshells to calcination process. Also, the impregnation process enhanced the yield of CaO by facilitating the easy removal of unwanted elemental present in the CaO catalyst.

Furthermore, the results of the XRF (Table 2) showed that the impregnation of KNO_3 and $NaNO_3$ on CaO aids in the removal and/or reduction of the catalyst poisons (impurities such as Al_2O_3,

MgO, SiO_2), an act that favours the catalytic activity of the calcined CaO [9]. The XRD pattern of CaO impregnated with KNO_3 show peaks within the range 2Θ of $(5.20 – 31.20)^0$ with sharp peaks at 2Θ = $(7.0 – 9.0)^0$, 12.0^0 and 25.0^0. While the pattern for CaO impregnated with $NaNO_3$ show peaks within the range 2Θ of $(5.20 – 41.60)^0$ with sharp peaks at 2Θ = 7.0^0, 9.0^0, 20.0^0, 22.0^0, 32.0^0 and 37.0^0. These values were reported in the literatures [18].

3.2. Oil characterization

GCMS analysis of the treated oil showed that the fatty acid compositions of the oil are all unsaturated. The analysis revealed that C18 (n = 3) has 7.04%, C17 (n = 1) has 8.34%, C21 (n = 1) has 4.57%, C18 (n = 2) has 14.38%, C19 (n = 1) with 1.85%, C19 (n = 2) with 25.704%, C19 (n = 3) has 23.70%, C17 (n = 1) has 8.35%, C18 (n = 1) has 5.10% and C16 (n = 1) has 0.90%. This is an indication of high level of reactivity of the treated oil resulting in high yield of biodiesel. It is important to mention that C implies the number of carbon while n connotes the number of double bonds of the fatty acids.

3.3. Biodiesel yields

The results of biodiesel yields obtained are as shown in Table 3, Figures 1 and 2. The results revealed the main and interactive effects of the two process variables on biodiesel yields (Figure 1 and 2). Table 3 and Figure 1 showed that the higher yield of biodiesel was obtained at methanol/oil mole ratio of 9 and CaO catalyst concentration of 2.0 wt/wt% Oil, for the three forms of catalyst used. Figure 2 revealed that the combine (interactive) effects of methanol/oil mole ratio and catalyst concentration on biodiesel yield generated the higher biodiesel yields at methanol/oil mole ratio of (9–10) and CaO catalyst concentration of (2.0–3.0) wt/wt% Oil, for the three forms of catalyst used. Beyond (2.0–3.0) wt/wt% Oil, the excess CaO catalyst reacted with the reactants to form by-products, thereby reducing the yield of biodiesel [7].

Also, it could be deduced from Table 3, Figures 1 and 2 that higher yield of biodiesel was obtained when CaO with impregnated KNO_3 was used, followed by the operation involving CaO impregnated with $NaNO_3$ and operation with no impregnation. These trends reveal the importance of the impregnation of CaO, as well as the superiority of KNO_3 over $NaNO_3$ (as impregnating reagents). The higher biodiesel yield of CaO impregnated with KNO_3 (compared to the yield from CaO impregnated with $NaNO_3$) could be traced to the reactive nature and arrangement of electrons of both Potassium and Sodium [5,9].

That is, since the atomic radius of K is greater than that of Na, hence the single valence electron that exists in the former is located farther from the nucleus than that for Na, therefore lesser energy is required to excite the singe valence electron in K compare to that involved in Na during chemical reaction [5].

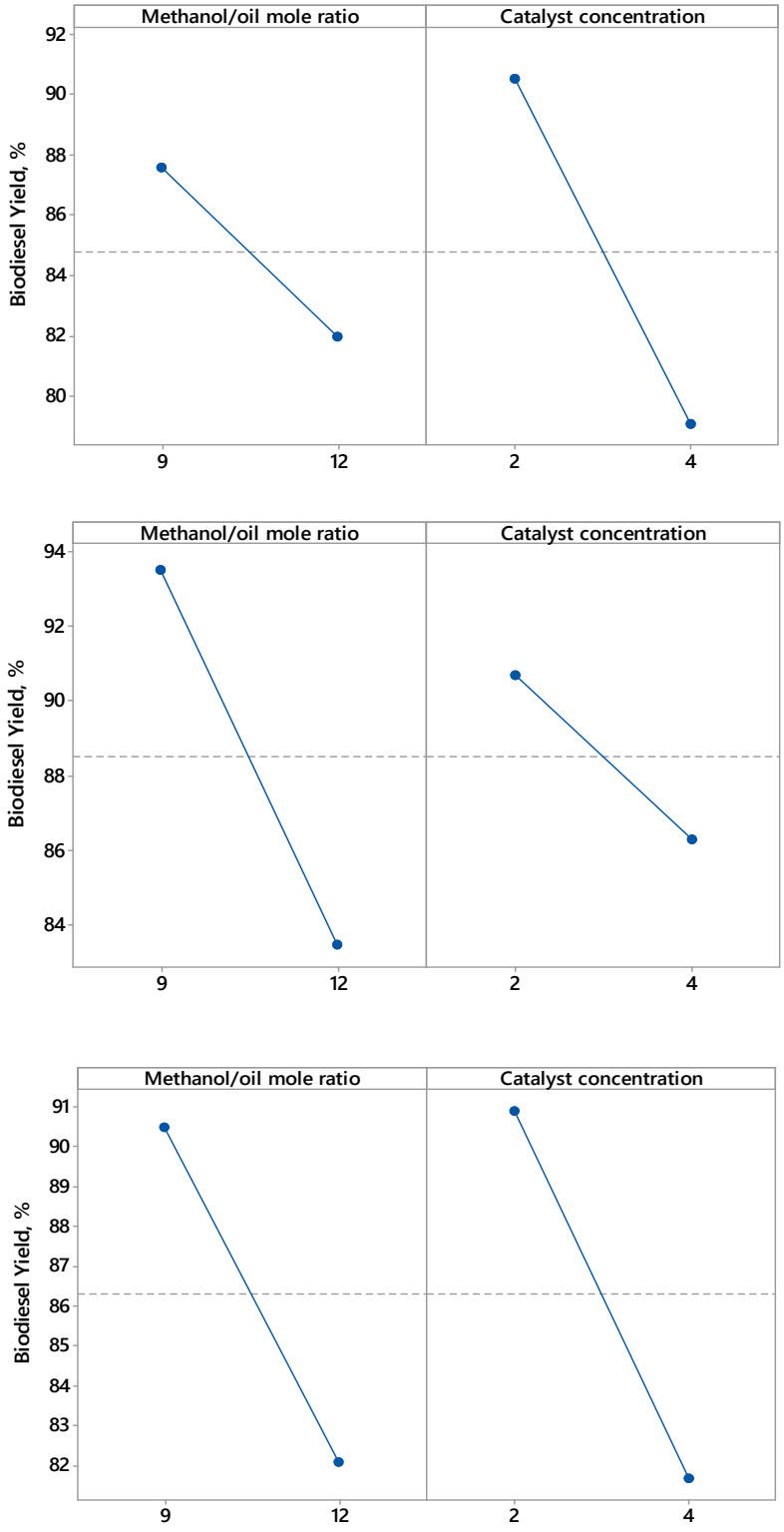

Figure 1. Main effects of the two processing variables on biodiesel yield obtained using (i) unimpregnated CaO, (ii) KNO_3 impregnated on CaO, (iii) $NaNO_3$ impregnated on CaO.

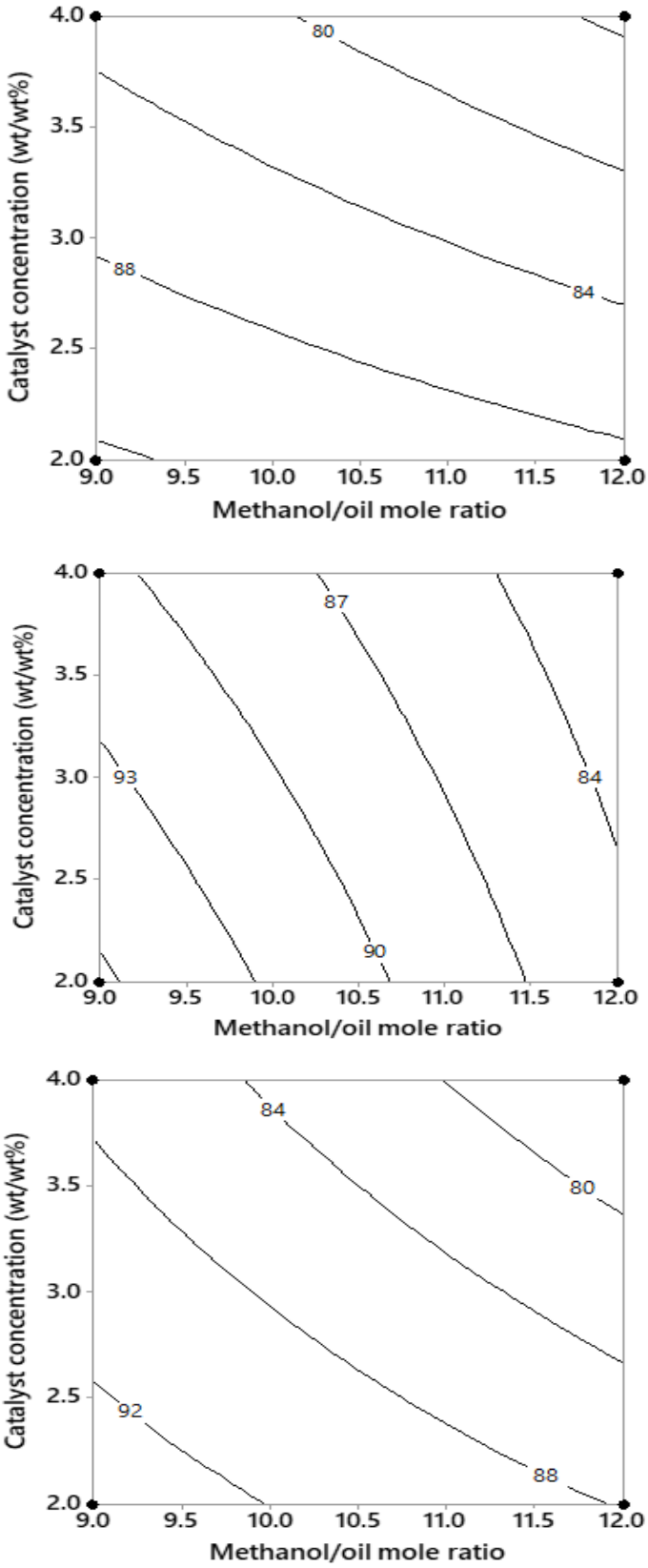

Figure 2. Contour plots of the two process variables on biodiesel yield obtained using (i) unimpregnated CaO, (ii) KNO_3 impregnated on CaO, (iii) $NaNO_3$ impregnated on CaO.

Table 3. Biodiesel yields obtained from the three forms of catalysts used.

Methanol/oil mole ratio mol/mol	Cat. conc. wt/wt %	Yield (using unimpregnated CaO) %	Yield (using impregnated KNO_3 on CaO) %	Yield (using impregnated $NaNO_3$ on CaO) %
9	2	92.4	96.4	94.0
9	4	82.8	90.6	87.0
12	2	88.6	85.0	87.8
12	4	75.4	82.0	76.4

3.4. Modelling of biodiesel yields

Regression analysis which involves the establishment of model of biodiesel yield and the two process variables (methanol/oil mole ratio, X_1 and catalyst concentration, X_2) was carried out. The results obtained were expressed in Eqs 1–3.

$$Yield_{unimpregnated} = 224.6 - 11.47X_1 - 47.20X_2 + 3.967X_1X_2 \quad [Rsq = 98.7, Adj.\ Rsq = 90.4] \quad (1)$$

$$Yield_{KNO_3} = 205.0 - 9.80X_1 - 41.20X_2 + 3.333X_1X_2 \quad [Rsq = 96.2, Adj.\ Rsq = 85.7] \quad (2)$$

$$Yield_{NaNO_3} = 97.60 - 3.32X_1 - 17.00X_2 + 1.733X_1X_2 \quad [Rsq = 97.5, Adj.\ Rsq = 88.6] \quad (3)$$

3.5. Optimum conditions of the biodiesel produced

Table 4 shows the optimum conditions for the production of biodiesel obtained, using 2 level–2 factors Factorial method (Minitab 17). That is, at optimum conditions of methanol/oil mole ratio of 9.0 and catalyst concentration of 2.48 wt/wt% oil, biodiesel yields are 95% (using CaO impregnated with K_2NO_3), 92.3% (using CaO impregnated with $NaNO_3$) and 90% (using CaO without impregnation).

Table 4. Optimum conditions of the biodiesel produced.

Properties	Methanol	Catalyst
High value	12.0	4.0
Optimal value	[9.0]	[2.4828]
Low value	9.0	2.0
Yield (K)	Yield (N)	Yield (U)
y = 95.00	y = 92.31	y = 90.08
d = 1.000	d = 0.770	d = 0.966

K = CaO impregnated with KNO3, N = CaO impregnated with NaNO3,

U = unimpregnated CaO, d = desirability level, y = percentage biodiesel yield.

3.6. Biodiesel properties

The properties of the biodiesel obtained are as shown in Table 5. the results of the various tests and analysis reveal that quality biodiesel were produced form the three forms of catalyst used. This is because, each of the values of the properties falls within the ASTM standard [21].

Table 5. Biodiesel properties of the biodiesel obtained.

Properties	Yield (using unimpregnated CaO)	Yield (using impregnated KNO_3	Yield (using impregnated $NaNO_3$	ASTM standard
Density 40 ℃ g/mL (ASTM D4052)	0.887	0.878	0.87	0.860–0.890
Viscosity at 40 ℃ mm^2/s (ASTM D445)	4.93	4.35	3.81	1.9–6.0
Flash point (ASTM D93)	230	182	181	>93
Pour point (ASTM D97)	−7	−6	−7	≤15
Water content, wt %. (ASTM ASTM D6304)	0.03	0.04	0.04	≤0.05
Ash content, wt % (ASTM D874)	0.01	0.01	0.01	≤0.02

4. Conclusions

The research work revealed that the treatment of used vegetable oil and calcination of $CaCO_3$ into CaO (as well as its impregnation using KNO_3 and $NaNO_3$ separately) can produce high yield and quality biodiesel. Similarly, optimum conditions of methanol/oil mole ratio of 9 and catalyst concentration of 2.4 wt/wt% Oil would produce biodiesel yields of 90% (for unimpregnated catalyst), 92% (using CaO impregnated with $NaNO_3$) and 95% (using CaO impregnated with KNO_3). Also, the research work reveals that CaO catalyst impregnated with KNO_3 produced higher yield compared to CaO impregnated with $NaNO_3$. This could be explained in terms of the chemical reactivity of both K and Na, as well as the chemical arrangement of the atoms of the two elements. Since the atomic radius of K is greater than that of Na, hence the single valence electron that exists in the former is located farther from the nucleus than that for Na, therefore lesser energy is required to excite the singe valence electron in K compare to that involved in Na during chemical reaction.

Acknowledgement

The authors appreciate the financial assistance of CUCRID Covenant University towards the publication of this research work.

Conflict of interest

The authors declare that there is no conflict of interest in this research work.

References

1. Tomkute V, Solheim A, Sakirzanovas S, et al. (2016) Reactivity of CaO with CO_2 in molten CaF_2–NaF: Formation and decomposition of carbonates. *Energy Sci Eng* 4: 205–216.
2. Ayoola AA, Hymore KF, Omnhinmin CA (2016) Optimisation of biodiesel production from selected waste oils using response surface methodology. *Biotechnology* 16: 1–9.

3. Anr R, Saleh A, Islam MS, et al. (2016) Biodiesel production from crude jatropha oil using a highly active heterogeneous nanocatalyst by optimizing transesterification reaction parameters. *Energy Fuels* 30: 334–43.
4. Zahira Y, Masita M, Mohammad A, et al. (2013) Overview of the production of biodiesel from waste cooking oil. *Renewable Sustainable Energy Rev* 18: 184–193.
5. Ayoola AA (2015) Production and life cycle assessment of biodiesel produced from three waste oils, Ph.D. Thesis, Chemical Engineering Department, Covenant University, Nigeria.
6. Ayoola AA, Adeniyi DO, Sanni SE, et al. (2018) Investigating production parameters and impacts of potential emissions from soybean biodiesel stored under different conditions. *EER* 23: 54–61.
7. Math M, Kumar S, Chetty S (2010) Technologies for biodiesel production from used cooking oil—a review. *Energy Sustainable Dev* 14: 339–45.
8. Bifubara H, Obot N, Chendo M (2014) Potential of waste vegetable oil for biodiesel in Nigeria. *Curr J Appl Sci Technol* 4: 3716–3725.
9. Borges M, Díaz L (2012) Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renewable Sustainable Energy Rev* 16: 2839–2849.
10. Madhuvilakku R, Piraman S (2013) Biodiesel synthesis by TiO_2-ZnO mixed oxide nano catalyst catalyzed palm oil transesterification process. *Bioresour Technol* 150: 55–59.
11. Efeovbokhan VE, Ayoola AA, Anawe PA, et al. (2012) The effects of trans-esterification of castor seed oil using ethanol, methanol and their blends on the properties and yields of biodiesel. *Int J Eng Technol* 2: 1734–1742.
12. Ullab Z, Bustam M, Man Z (2015) Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst. *Renewable Energy* 77: 521–526.
13. Ayodeji AA, Ojewumi ME, Rasheed B, et al. (2018) Data on CaO and eggshell catalysts used for biodiesel production. *DIB* 19: 1466–1473.
14. Ayodeji AA, Blessing IE, Sunday FO (2018) Data on calcium oxide and cow bone catalysts used for soybean biodiesel production. *DIB* 18: 512–517.
15. Viriya-empikul N, Krasae P, Puttasawat B, et al. (2010) Waste shells of mollusk and egg as biodiesel production catalyst. *Bioresour Technol* 101: 3765–3767.
16. Ayoola AA, Fayomi OSI, Adeeyo OA, et al. (2019) Impact assessment of biodiesel production using CaO catalyst obtained from two different sources. *Cogent Eng* 6: 1615198
17. Fayomi OSI, Popoola API, Oloruntoba T, et al. (2018) Inhibitive characteristics of cetylpyridinium chloride and potassium chromate addition on type A513 mild steel in acid/chloride media. *Cogent Eng* 4: 1318736.
18. Wen L, Wang Y, Lu D, et al. (2010) Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. *Fuel* 89: 2267–2271.
19. Irmawati R, Shafizah I, Nur Sharina A, et al. (2014) Transesterification of palm oil by using silica loaded potassium carbonate catalysts to produce fatty acid methyl esters. *Energy Power* 4: 7–15.
20. Ayoola AA, Hymore FK, Omonhinmin CA, et al. (2019) Analysis of waste groundnut oil biodiesel production using response surface methodology and artificial neural network. *CDC* 22: 100236.

21. Parag S, Sayali J, Milind J (2013) A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Eng* 51: 395–402.