

PREPARATION AND APPLICATION OF KF/EGGSHELL CATALYST IN TRANSESTERIFICATION OF NEEM OIL: OVAT APPROACH

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ABSTRACT

A solid base KF/Eggshell catalyst was prepared by wet impregnation method and applied for biodiesel production from high FFA neem oil. The XRF and XRD analyses confirmed the presence of CaO in the eggshell and crystalline phases of the desired catalyst. The 79 nm sized crystallites of the best catalyst having hexagonal shapes determined by SEM images were systemically arranged to give a BET specific surface area of 128 m²/g, pore size 3.24nm and pore volume 0.045 cm³/g. The parameters affecting the preparation of the catalyst were investigated using OVAT approach. The best synthesis conditions were found to be 900°C eggshell calcination temperature for 2h, 30 wt. % KF dosage, and 600°C KF/Eggshell post-impregnation calcination temperature for 3h. The catalyst was applied in a single stage transesterification of neem oil having FFA of 4.2% to produce 94.8% yield of biodiesel. The biodiesel produced was confirmed using FTIR and GC-MS and comparable to the ASTM commercial standard. The reusability test shows that the catalyst was active recording high yield of 90% even after the fifth run and more efficient than KF/commercial CaO. Accordingly, eggshell can serve as a very good source of CaO for catalysing biodiesel formation.

Keywords: Biodiesel, Transesterification, Waste Eggshell, Neem oil,

1. INTRODUCTION

In recent time, continuous crude oil price crash in the international market and discovery of more shale oil reserves have stirred a strong debate on the competitive advantage of biodiesel as compared to fossil diesel based on production cost. Also, environmental benignity and renewability of biodiesel remain unbeatable. The Nigerian biofuel and incentive policy stipulated usage of B20 biodiesel blend in automobiles by the year 2020, while currently countries like United States of America, Brazil, Indonesia, Malaysia, France and Germany uses biodiesel (Libai *et al.*, 2010). Biodiesel is conventionally produced via transesterification of vegetable oils and animal fats with methanol in presence of homogeneous alkali (Encinar *et al.*, 2002), acid (Rashid *et al.*, 2008), chemical catalytic conversion (Verhéet *et al.*, 2011) and enzyme catalysts (Xu *et al.*, 2005). Homogeneous catalyzed transesterification yields catalyst-contaminated biodiesel and glycerol, and generate huge quantity of effluents during product purification stage (Venkat Reddy *et al.*, 2006). Heterogeneous catalysts could provide a viable solution to the product purification problems associated with homogeneous catalysts. Alkali-earth metal oxides (CaO, MgO, SrO and BaO), transition metal oxides (ZrO, TiO and ZnO) and zeolite have been reported to successfully catalyzed various vegetable oils producing biodiesel yields according to the specific surface area and basic strength of the catalysts (Zabetiet *et al.*, 2009; Suppes *et al.*, 2001). Chicken eggshells are renewable resources containing CaCO₃ in varying amounts, calcination of these eggshells above 700°C produces heterogeneous CaO-

catalyst for biodiesel production (Wei *et al.*, 2009). According to the report of the United State Department of Agriculture (USDA, 2013), Nigeria ranks as the largest chicken egg producer with a progressive trend from 500,000 metric tons egg production in 2005 to 650,000 metric tons in 2013, as depicted in Figure 1. These figures ensure adequate and continuous availability of eggshell wastes from which CaO can be obtained when treated, as untreated waste eggshells are usually disposed in landfill and its degradation often leads to pollution.

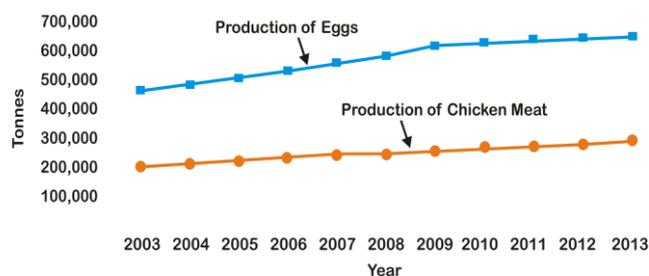


Figure 1: Nigerian poultry industry growth trend (Source: USDA, 2013)

CaO is the most promising and frequently applied metal oxide catalyst for biodiesel production, due to its cheap price, relatively high basic strength and less environmental impacts (Madhuet *et al.*, 2017). Pure metal oxide like CaO usually possess a less catalytic activity in comparison with mixed metal oxides (Lee and Taufiq-Yap, 2014; Hodnett, 2000 and Centi *et al.*, 2001). Apparently, large number of mixed oxides such as

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KF/CaO-Fe₃O₄ (Hu *et al.*, 2011), KF/ZnO (Xie *et al.*, 2006) and KF/Ca-Mg-Al (Gao *et al.*, 2009) have been reported for the transesterification reactions. Basic heterogeneous catalysts performed more actively, react faster and are less corrosive in comparison with acidic heterogeneous catalyst (Helwani *et al.*, 2009), but they are unfavourable for feedstocks with high FFAs and moisture content leading to saponification and hydration respectively (Wei *et al.*, 2009; Gao *et al.*, 2010). To mitigate this problem, two-step method is most commonly used (Wei *et al.*, 2009). The first step is the FFA esterification reaction, this reaction is commonly carried out using homogenous acid catalyst (Wei *et al.*, 2009). The second step is transesterification reaction mostly using base catalysts (Wei *et al.*, 2009). However, the two-step method increases system complexity and the cost of production (Wei *et al.*, 2009). Thus, synthesis of a heterogeneous catalyst from adequately available and cheap spent eggshell impregnated with potassium fluoride (KF) for a single stage transesterification process can be an ideal cost-effective process for biodiesel production from vegetable oils having high FFA (Wen *et al.*, 2010 and Liu *et al.*, 2012). Accordingly, the paper sets out to synthesis, characterized and optimize the synthetic and operational conditions using OVAT for a catalyst from spent eggshell for a single stage transesterification of neem oil.

2. EXPERIMENTAL

2.1 Materials

3.5kg spent eggshells were collected at Frizlers restaurant in Ahmadu Bello University main campus, Zaria, and wet beneficiated. The neem oil was provided by National Research Institute for Chemical Technology, Zaria, Nigeria. The oil had FFA of 4.2%. It contains 0.02% (wt) water and its molecular weight was 870g/mol⁻¹. Analytical grade anhydrous methanol used was purchased from Zayo Chemicals Limited, Jos, Nigeria. The Commercial CaO and KF used were analytical reagents purchased at Hadis Chemicals Limited, Zaria, Nigeria.

2.2 Method

The collected waste eggshells were parboiled, satisfactorily washed and dried overnight in hot air oven at 105°C. The dried eggshells were crushed, ball milled and then sieved using a 63µm mesh sized sieve. The powdered eggshell obtained was calcined in a muffle furnace under static air condition at 900°C at holding time of 2hr (Viriya-Empikul *et al.*, 2012 and Singh *et al.*, 2012). The highly active CaO species derived from eggshell calcined at varied holding times and commercial CaO were hydrated at 60°C, dehydrated at 140°C and recalcined at 600°C for 3h to convert the hydroxide formed to a highly porous oxide.

2.2.1 Catalyst Synthesis: wet impregnation of KF/Eggshell

10g each of the dehydrated-activated-CaO eggshell based catalysts was mixed with previously prepared aqueous solution of potassium fluoride (KF) with dosage (in wt%) of 20 to 40. The resulting slurries were dried at 105°C overnight in an oven and was subsequently calcined at temperatures ranging between 200°C and 600°C at holding times of 2 to 4hrs. These as-prepared catalysts were applied in a transesterification process to investigate their efficacies.

2.2.2 Transesterification: catalyst efficacy tests

The procured neem oil was pre-treated and analysed for physicochemical properties. The transesterification reaction parameters used in this study for the purpose of testing the efficacy of the catalysts were derived from the report of Libai *et al.*, (2011) with some modifications. In this study, 5wt. % catalyst weight was used for a reaction time of 1.5h with oil-methanol ratio and reaction temperature of 1:12 and 65°C, respectively. Typically, a 250ml 3-neck flat bottom flask was charged with 23g of the pre-treated neem oil and 5 different catalysts prepared in section 2.2.1, while the reaction condition employed are as mentioned earlier. The medium was stirred at 500r.p.m and refluxed with a water-cooled condenser, placed on a calibrated magnetic stirrer. At the stipulated reaction time, the product was cooled down and allowed to separate into three distinct layers after staying for 24hrs in a separating funnel. The topmost layer consisted majorly of the methyl ester, middle-dissolved methanol and bottom-unreacted triglycerides. It was decanted, washed with distilled water and the residual methanol was separated by distillation at 75°C. The biodiesel yield was determined as ratio of the weight of decanted topmost oil layer to the weight of neem oil used in the reaction. The catalyst having the highest yield of biodiesel was chosen as the best and subjected to further upgrade.

2.2.3 Comparative and Reusability Tests

Four different types of catalysts were prepared based on the selected favourable conditions, namely; KF/eggshell, KF/Commercial CaO, Eggshell and Commercial CaO were applied in transesterification reaction. The as-synthesized KF/eggshell based catalyst was repeatedly used in the transesterification reaction. After each complete cycle of transesterification, the catalyst was centrifuged from the mixture, washed with methanol, dried and weighed before applying them in another cycle. The biodiesel yield and catalyst weight after each run were determined and noted.

2.2.4 Characterization Technique

The chemical composition of the eggshell was determined by XRF spectrometry using Shidmadzu EDX-720 spectrometer. The morphology and specific composition for each stage of the transformation of the eggshell were observed under Scanning Electron

Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) using Hitachi S-4500 field emission SEM with a Quartz PCI XOne SSD X-ray analyzer. The crystalline phase of each stage of the transformation of eggshell into the desired catalysts was studied using the Shimadzu XRD-6000 Diffractometer. The XRD patterns were identified and analyzed by comparing their diffraction lines and intensities using the Joint Committee on Powder Diffraction Standards (JCPDS). The Quantachrome Nova 4200e BET machine was employed to determine the specific surface area, pore diameter and volume of the catalyst produced under optimal conditions using the N₂ adsorption-desorption technique. The FTIR analyses on the catalyst performed using the Agilent machine. The fresh biodiesel produced from the best condition was analysed qualitatively using FTIR and GC-MS.

3. RESULTS AND DISCUSSION

3.3.1 Eggshell and Catalysts

The result of XRF analysis of the beneficiated eggshell suggests, shown in Table 1, that the choice of eggshell as a raw material in this study is justified by the rich content in calcium needed basically for the catalysis. Hunton (2005) reported that the chicken eggshell is 97% calcium carbonate crystals, which are stabilized by a protein matrix, he also mentioned that an amount as low as 78% has been reported. The variance in the values of the main component, i.e CaO seen in Table 1 with the literature (Eletta *et al.*, 2016 and Amal and Manusamy, 2015) might be attributed to difference in the chicken feeding culture and/or location.

Table 1: Chemical composition (wt. %) of eggshell

Composition	CaO	SO ₃	Na ₂ O	Al ₂ O ₃	Fe ₂ O ₃	CeO ₂	BaO	SiO ₂	TiO	MgO	P ₂ O ₅
Present work	98.04	0.21	0.08	0.28	0.08	0.03	0.06	0.36	0.02	nd	nd
Eletta et al (2016)	89.85		0.21	0.32	0.03	nd	nd	0.1	nd	0.01	0.26
Amal and Manusamy, 2015	76.99	0.33	0.11	nd	0.02	nd	nd	nd	nd	0.93	0.42

nd-not determined

The result of thermal transition, crystalline phase and morphology of samples are detailed here. The most intense peak observed occur at $2\theta = 29.32^\circ$ in Figure 2 (a) having crystalline plane of (104) and other minor peaks were noted at $35.95^\circ(110)$, $39.37^\circ(113)$, $43.08^\circ(202)$,

according to JCPDS card number; 01-085-1108 for calcium carbonate. It should be noted that the results displayed in Figures 2 and 3 as well as the BET data were for the starting material and best catalyst in transesterification reaction.

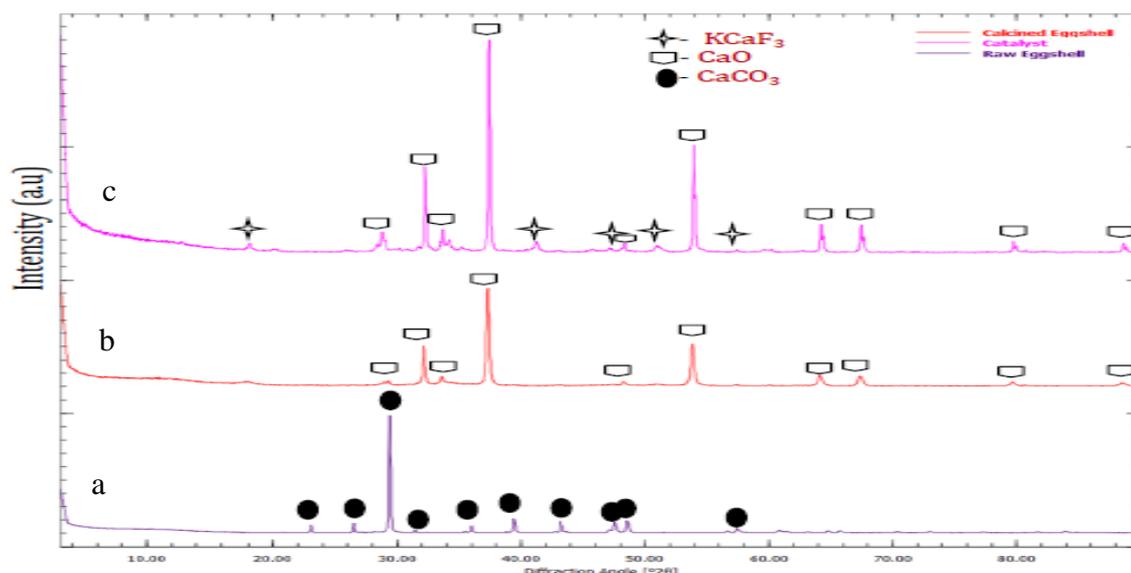


Figure 2: XRD patterns for raw eggshell, calcined eggshell and KF/eggshell catalyst

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This is in agreement with the XRF result in Table 1 which showed that beneficiated raw eggshell is majorly composed of CaCO_3 . Thermal treatment of the calcite at the optimum operating condition assisted in the transformation of the CaCO_3 into CaO as depicted by Figure 2 (b). The peaks prominent for lime were observed at $2\theta = 32.03^\circ(111)$, $37.26^\circ(200)$, $53.71^\circ(220)$, which corresponds with the JCPDS card number- fm-3m: 01-077-2376 for face-centred cubic lime lattice. The peaks corresponding to the KCaF_3

were consistent with the standard pattern reported in JCPDS file (3-567) for KCaF_3 crystal, having intense peaks of the magnetite observed at $2\theta = 30.04^\circ(220)$, $43.08^\circ(400)$ as depicted in figure 2(c) contained in the file number (79-0417). According to XRD analysis, the crystallinity (%), size (nm) and shape for beneficiated eggshell, calcined eggshell, catalyst and magnetic catalyst, respectively, are 94, 100, hexagonal; 92, 84, cubic; 87, 79, hexagonal and 98, 108, orthorhombic.

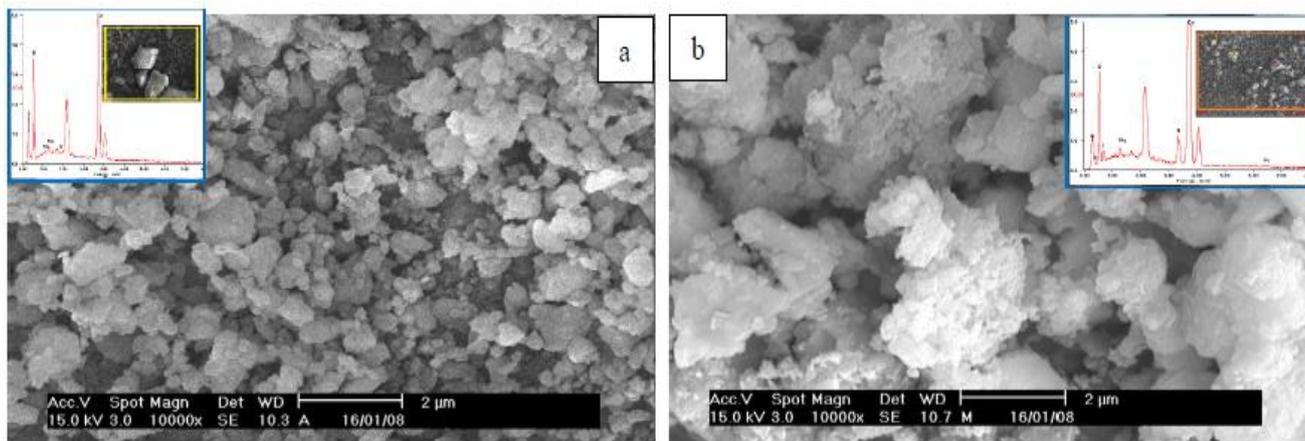


Figure 3: SEM for beneficiated eggshell and magnetite KF/Eggshell catalysts

Figure 3(a) is the SEM image of the beneficiated eggshell, shows irregular agglomerates of rod-like particles of eggshell indicative of a low specific surface area, which is similar to report Khemthong *et al.*, (2012) and Nijuet *et al.*, (2014). Figure 3(b) is the SEM micrograph of the magnetic catalyst, shows an irregularly shaped structure, but having some closely parked agglomerates probably resulting from the magnetic nature of the catalyst. This feature may possibly be an advantage in catalyst activity and recoverability. The EDS gave an indication of the introduction of magnetite in the final catalyst and its result for the beneficiated eggshell was found to corroborate the XRF result.

The hydration-dehydration technique after initial calcination was reported by (Yoosuk *et al.*, 2010) to play an important role in improving the specific surface of CaO catalyst. The specific surface area, pore size and pore volume of the catalyst were determined to be $128\text{m}^2/\text{g}$, 3.24 nm and $0.046\text{ cm}^3/\text{g}$, respectively, an indication of its mesoporosity.

3.3.2 Transesterification reaction

Figure 4 shows the combined effects of post-impregnation calcination time (PICtime) and KF dosage at post-impregnation calcination temperature (PICtemp) of 600°C . The biodiesel yield was observed to increase with increase in PICtemp and KF dosage but climaxed at KF dosage of 30wt%. Further increase in the dosage led to drop in biodiesel yield, which suggest that the excess KF have

negatively affected the activity of the catalyst resulting in the promotion of reverse reaction (Singh *et al.*, 2012). The increase in biodiesel yield was spontaneous as the value spike from 70.3% for PICtemp of 200°C to 91.8% at PICtemp of 600°C . Accordingly, the PICtemp of 600°C and KF 30wt% were chosen as the best point for these parameters of investigation. This suggest that the dosage and temperature are favourable for the synthesis of an active highly porous catalyst with good surface area.

The produced KF/eggshell catalyst produced from post-impregnation calcination temperature of 200°C to 600°C and PICtime of 2 to 4hrs using 30wt% KF was tested in the transesterification reaction and the biodiesel yield obtained are depicted in Figure 5. The result in figure 4 shows that holding time does not have significant effect on biodiesel yield as the increase in its value is less than 2% for holding time up to 4hrs, irrespective of the post-impregnation temperature. On the contrary, the temperature of thermal treatment had a positive effect on the biodiesel yield. For holding time of 2hr, the yield increases from 69.2% at 200°C to 89.5% at 600°C , an improvement was noticed when the holding time was increased to 4hrs, recording 70.3% and 91.8% at 200°C and 600°C , respectively. This is an indication that the reaction between CaO and KF was highly favoured at higher temperature, leading to highly active catalyst producing high biodiesel yield (Wen *et al.*, 2010).

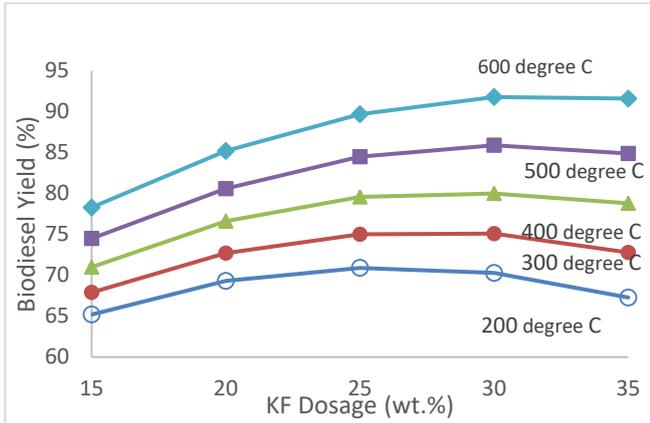


Figure 4: Biodiesel yield obtained at PICTime of 3hrs under studying PICTemperature and KF dosage

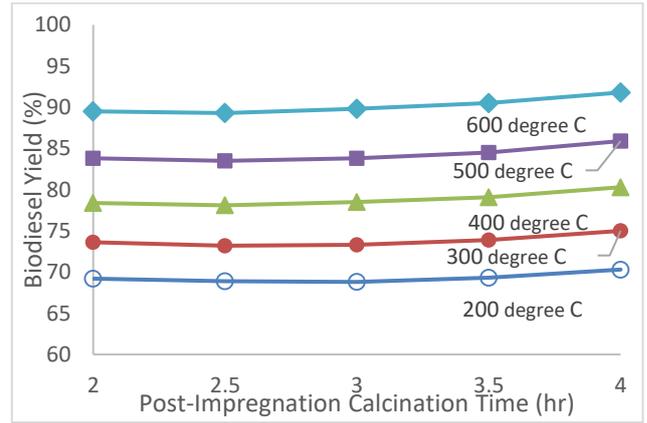


Figure 5: Biodiesel yield obtained at KF-30wt% under studying PICTemperature and PICTime.

Figure 6 shows the effect of KF dosage and PICTime at fixed PICTemperature of 600°C of biodiesel yield. It was found to increase with increase in both parameters, suspected to have resulted from formation of the desired catalyst at this temperature and appropriate dosage of KF. The biodiesel yield increased from 75.9% for KF dosage of 15% at PICTime of 2hrs to 89.2% for KF dosage of 30%

and same PICTime. Increasing the PICTime to 4hrs, biodiesel yield of 78% and 91.2% were respectively, obtained for KF dosage of 15 and 30%. It should be mentioned here that, the biodiesel yield obtained for KF dosage of 30 and 35wt % were observed to be close in terms of value, which implies that further increase in KF dosage does not favour biodiesel yield.

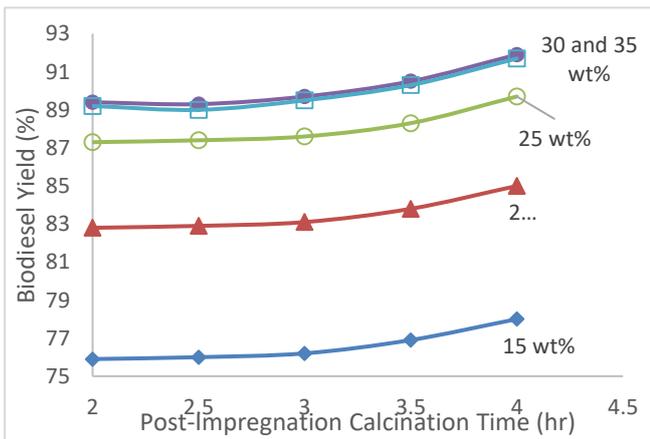


Figure 6: Biodiesel yield obtained at KF-30wt% under studying PICTemperature and PICTime.

A KF dosage of 30wt%, PICTemperature of 600°C and PICTime of 3hrs were observed to be a favourable condition for the formation of an active KF/eggshell based biodiesel catalyst. Accordingly, the proposed transesterification reaction mechanism for KF/eggshell based catalyst is presented in Figure 7.

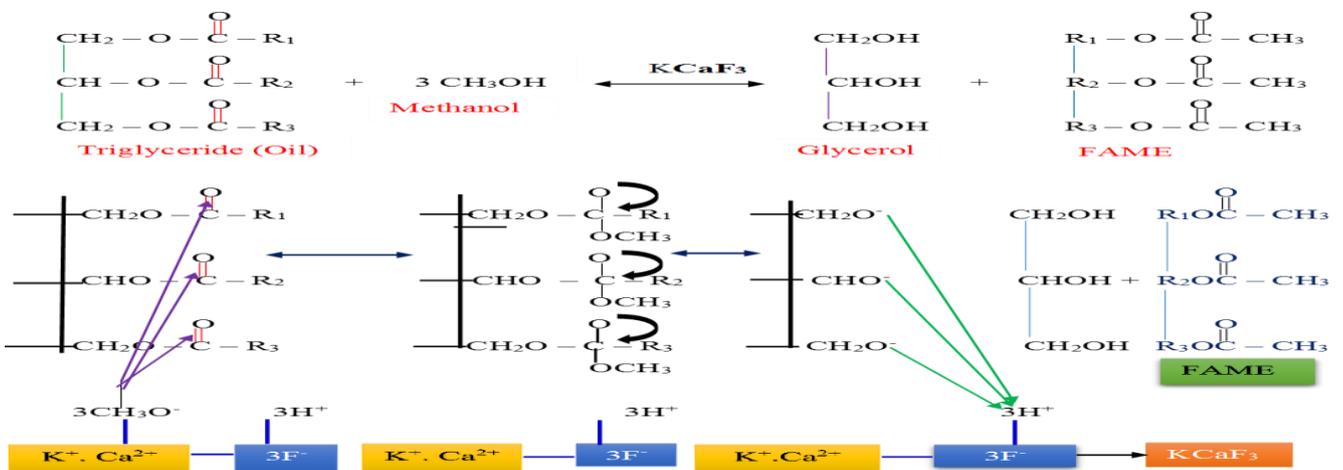


Figure 7: Proposed transesterification reaction mechanism in the presence of KF/eggshell catalyst.

3.3.3 Comparative and Reusability Test

Figure 8 showed the biodiesel yield produced from four different catalyst. It worth mentioning that the eggshell based CaO was more active than its commercial counterpart, for the former recorded 68.6%, while the commercial had only 60.8%.

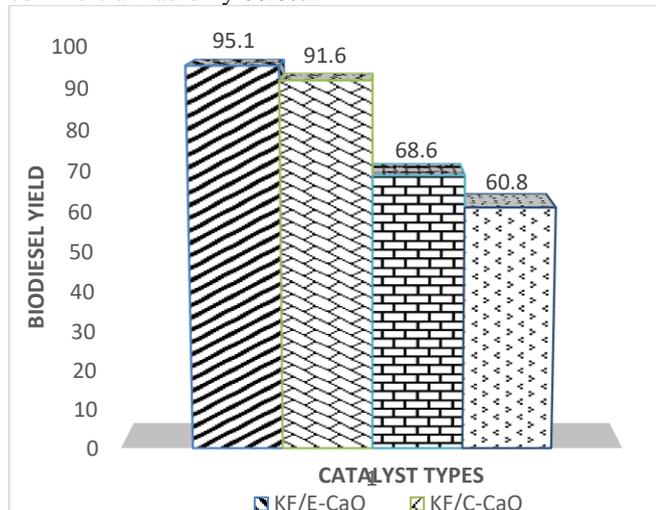


Figure 8: Comparative transesterification yield study.

It is suggestive that the eggshell based CaO have less resistance to thermal activation compare with the commercial one, that might have gone through several processes during its production. The KF/eggshell catalyst was also found to be more reactive than the KF/C-CaO, producing biodiesel yield of 95.1% compared with 90.1% from the other. The reason for this might be partly what was stated earlier and/or inability of the KF to interact properly with a more rigid structure of the commercial CaO.

The reusability study conducted showed that the catalyst can be economically used for more than four runs with biodiesel yield of 79% at the fifth run, as depicted in Figure 9. The test was further conducted for yet other runs and it was observed that as the weight of the recovered catalyst drop, the yield dropped in same trend. This suggests that the quantity of catalyst viz-a-viz the needed active were reduced hence less biodiesel formation, resulting from leakage of K and Ca to water and methanol (Liu *et al.*, 2012).

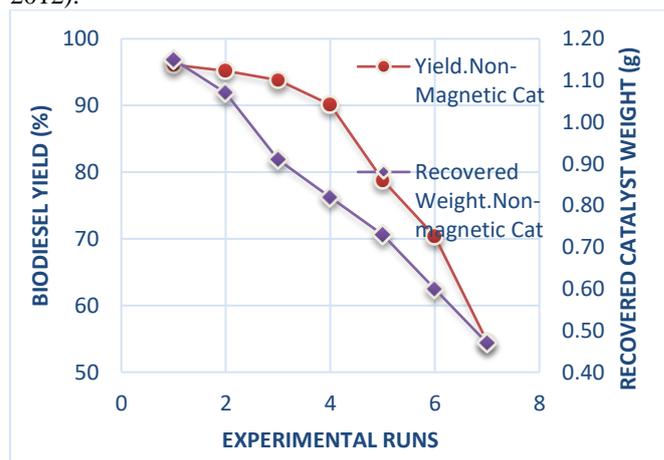


Figure 9: Catalyst reusability study.

3.3.4 Biodiesel Characterization

Figure 10 depicting the FTIR for biodiesel produced, showed a slight absorption in the 3600-3300 cm^{-1} range indicating a very little presence of moisture this is also complimented by the “water and sediment” result in Table 2.

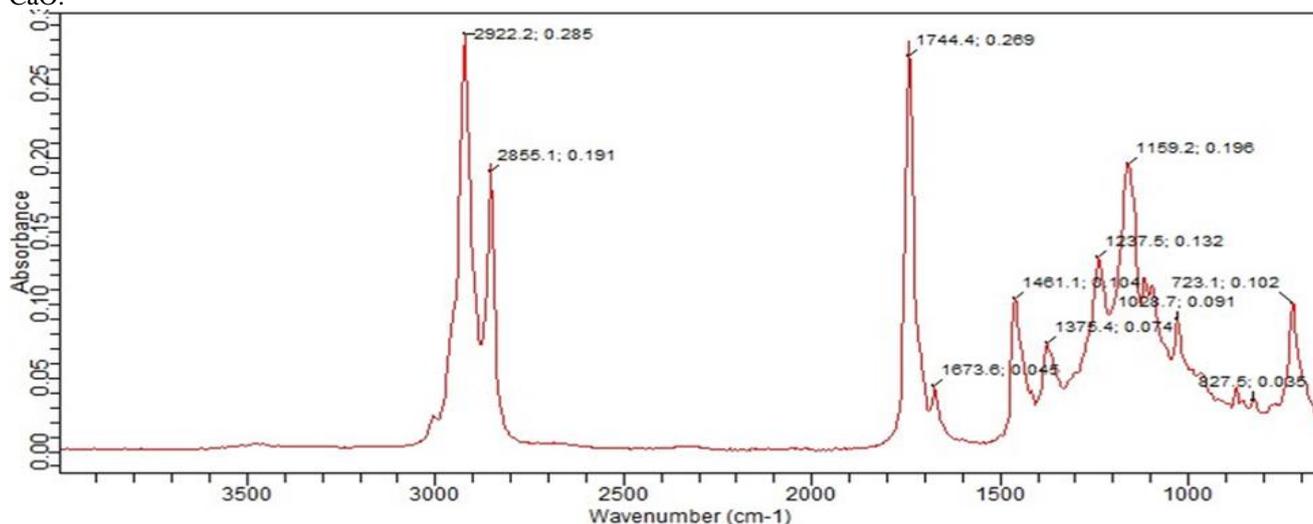


Figure 10: FTIR spectra of biodiesel fuel produced over the KF/Eggshell catalyst

This also suggests absence of unreacted alcohol in the fuel produced, resulting from the distillation of the fuel after the transesterification process. The slightly sharp peaks in the 1147 – 1122 cm^{-1} indicates low presence of unsaturated compounds in the fuel produced. This is evident in the

observed reduction of the iodine value of the fuel which is probably due to transformation during the transesterification process. There is a very strong ester absorption in the range 1750 – 1730 cm^{-1} depicted by a

very sharp peak suggesting, almost complete conversion of triglycerides to methyl esters (Tanwari *et al.*, 2013)

Table 2: Physicochemical Properties of Neem Oil and Biodiesel

Properties	Neem Oil Measured value	Biodiesel (B100) Measured value	ASTM Standard B100	Test Methods
Density at 40°C (g/cm ³)	0.92	0.89	0.86 – 0.89	ASTM D1298
Iodine value (mg I/100g oil)	71.4	42.5	-	ASTM D5554
Viscosity at 40°C (mm ² /s)	26.09	4.78	1.9 – 6.0	ASTM D445
Acid value (mg KOH/g)	8.36	0.264	0 – 0.5	ASTM D664
Flash point °C	-	137	93 -170	D93
Cloud point °C	-	10	(-3) - 12	Refrigeration
Pour point °C	-	4	(-15) - 10	Refrigeration
Water & sediment (% vol)	-	0.02	0 – 0.05	ASTM D2709
Molecular weight (g/mol)	870	-	-	(Xu <i>et al.</i> , 2006)
Colour	Dark brown	Light brown	-	-

The major shift from direct use of vegetable oil in diesel engines to transesterified oil is because of its high viscosity; this fuel property affects the flow and atomization characteristics of a liquid fuel. A 4.78 mm²/sec kinematic viscosity of the produced neem oil biodiesel can ensure a superior injection and atomization performance with added advantage of lubrication for the moving engine parts. High flash point temperatures for fuels ensure safe handling and storage. All the properties investigated in Table 2 were observed to fall within the ASTM standard.

Figure 11 shows the GC for fatty acid methyl esters, which contains about 34 methyl ester compounds. Eleven ester compounds out of the 15 observed were matched to the standard. Molecules of glycerine that is present in the

biodiesel may be due to insufficient purification after production. Squalene and octacosane are inherent compounds found in vegetable oils, squalene; an unsaturated alkene compound was observed to be present in a minute quantity. This was also confirmed by both the iodine value and FTIR peak. The relatively low amount of this compound, is beneficial to the oxidative stability of the biodiesel fuel. The ester content of the produced was found to be 96.82%, which compares favourably with the standard stipulated by ASTM is 96.5%.

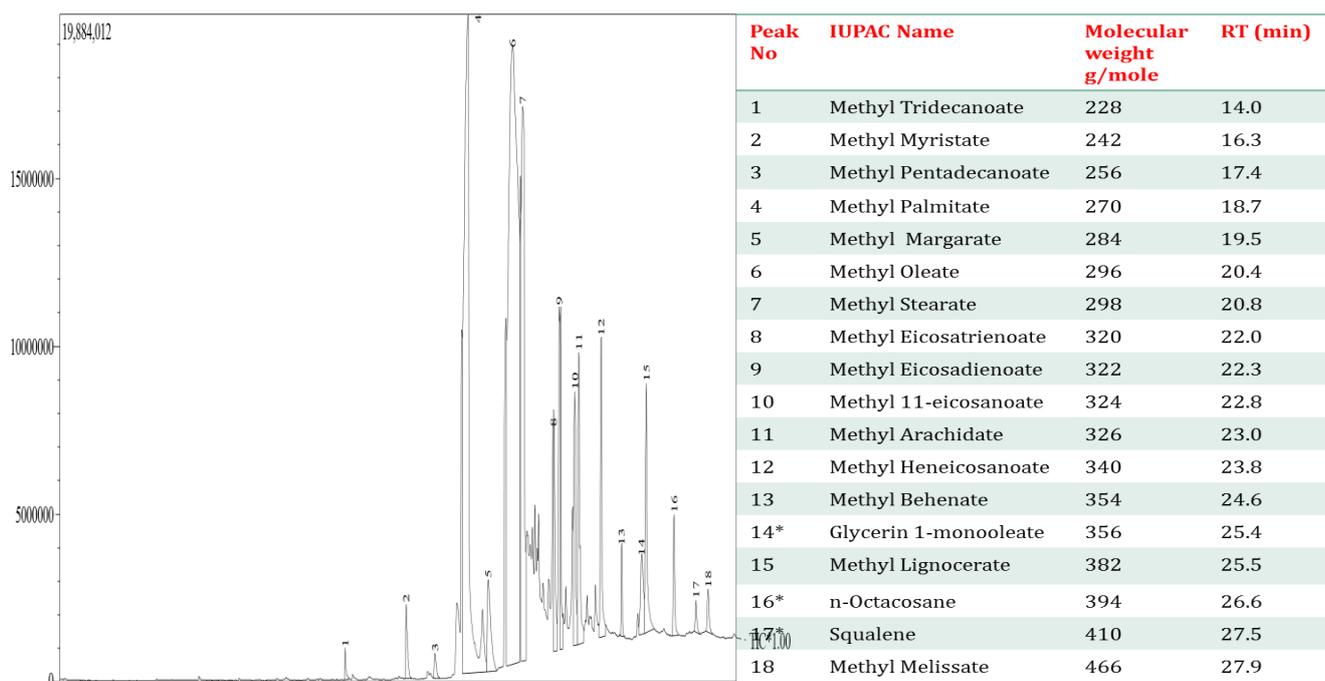


Figure 11: Gas Chromatogram of freshly prepared neem oil biodiesel

4.0 CONCLUSION

Chicken eggshell wastes are cheaply available rich source of CaCO_3 from which CaO can be synthesized as a catalyst for biodiesel production. The best temperature for calcination of chicken eggshell for the production of usable CaO -catalyst in biodiesel production was established to be 900°C for a period of 2h. The impregnation of KF in the calcined eggshell consequentially led to the formation of KCaF_3 crystals with probable higher basic strength than CaO . The KF/Eggshell synthesized after impregnation are more acid tolerant than CaO , hence usable in the transesterification of neem having FFA of 4.2%.

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30 wt.% of KF was found to be the best amount needed for the impregnation, calcination of KF/Eggshell at 600° for 2h were also found to be the optimal conditions for the preparation of the acid tolerant catalyst

The KF/Eggshell catalyst prepared at optimal conditions was found to be highly crystalline and porous with large hexagonal-like surface area. These structural properties together with the basic strength of the catalyst were believed to be responsible for its high catalytic activity. The catalyst was found to be reusable up to four and five turnovers respectively producing biodiesel of about 90% yield.

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