Original Research Article

Investigating Calcination Temperatures' Impact on Kola Nut Pod Residue as Catalyst for Biodiesel Synthesis

Evaluation of Impact of Calcination Temperatures on Kola Nut Pod Residue as Catalyst for Biodiesel Synthesis

Abstract

The research explores the viability of Kola Nut Pod (KNP) residue, derived from kola fruit in West African countries, as a catalyst for biodiesel synthesis. The abundant KNP husk, a byproduct, raises environmental concerns if discarded directly. The study aims to utilize KNP as a biocatalyst to address environmental issues and reduce biodiesel feedstock costs. Applying calcination temperatures from 500 to 900 ℃, the resulting ash undergoes chemical analysis to determine the optimal temperature for catalyst formation. The material undergoes pre-treatment, including drying and grinding, with varied calcination temperatures to obtain ash products. Chemical, elemental, and XRD analyses characterize both uncalcined and calcined samples. The uncalcined sample contains SiO_2, Al_2O_3, CaO, MgO, K_2O, and other oxides, with CaO as the predominant component. Calcination temperature effects indicate increased SiO_2 and Al_2O_3, while CaO remains stable, presenting KNP as a promising biodiesel catalyst feedstock. Elemental composition analysis identifies potassium as the key catalytic contributor. XRD analysis confirms CaO as the primary compound in calcined KNP ash, with $Ca(OH)_2$ and KCl occurrences. The study offers insights into the optimal calcination temperature for KNP-derived catalysts, underscoring Kola Nut Pod residue's potential as a cost-effective and eco-friendly source for biodiesel production.

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Keywords: Calcine, Kola nut pod, Residue, catalyst, biodiesel

1.0 Introduction

Kola nut pod husk, a waste biomass originating from kola trees prevalent in West African countries, presents significant social and economic value, particularly with species like Cola Acuminata and Cola Nitida being crucial in African nations, such as Nigeria. In 2020, global kola nut production reached 304,950 tonnes, with Nigeria contributing 166,895 tonnes, making up 54.7% of the total output and establishing Nigeria as one of the leading global producers (Asuquo *et al.,* 2023).The abundant availability of this resource raises concerns about environmental hazards if it is directly discarded, potentially releasing harmful greenhouse gases like methane (Betiku*et al.,* 2019).

Consequently, there is a growing interest in developing a biocatalyst from kola nut pod husk, with the suggestion that it could serve as a foundational catalyst for biodiesel production (Betiku*et al.,* 2019). Recent research has concentrated on creating environmentally friendly heterogeneous catalysts for FAME synthesis, leveraging the rich minerals present in biomass and agro-residue materials suitable for green heterogeneous catalyst production, as outlined in Table 1. This approach is favored because solid base catalysts utilized in the process remain unaffected, allowing easy separation from the biodiesel product. These solid base catalysts exhibit activity at the boiling point of methanol (MeOH) during the transesterification process (Asuquo *et al.*, 2023).

Table 1: Some residues used as heterogeneous catalysts with operation conditions

Source of catalyst	Biodiesel feedstock	Preparation condition	Biodiesel yield (%)	Authors
Shrimp shell	Rapeseed	Carbonization + Impregnation + calcination for 2 h	89.1	(Konwar, 2012)
Waste animal bone	Palm oil	Calcination at 900 ^{o}C for 3.5 h	87.28	(Jazie *et al*,., 2013)
Modified–Peanut husk ash	Soybean oil	Heating of husk at 900 ^{o}C for 2 h + mixing with Li_2CO_3 + calcination for 4 h	98.4%	(Dai *et al*,., 2014)

Barium–modified montmorillonite (BMK10)	Waste cooking oil	Impregnation + calcination at 500 °C for 5 h	88.38	(Buasri *et al*,., 2015)
Quail eggshell	Palm oil	Calcination at 800 °C	98	(Buasri *et al*,., 2015)
Ostrich eggshell	Waste cooking oil	Calcination at 1000 °C for 4 h	96	(Ismail *et al*,., 2016)
Fishbone	Palm oil	Calcination at 900 °C for 2 h	77.2	(Lesbani *et al*,., 2016)
Chicken eggshell	*Pongamia pinnata*	Calcination at 900 °C for 2 h	95	(Lani *et al*,., 2019)
Chicken eggshell	Soybean oil Calcination	Calcination at 1000 °C for 2 h	95%	(Lani *et al*,., 2019)

Biodiesel, derived from sources like Jatropha, Soybean, palm oil, rapeseed oil, and Carica papaya seed oils, has been shown to significantly decrease hydrocarbon, CO, and soot emissions (Tan *et al.*, 2023). Substituting conventional fossil-derived transport fuels with biodiesel could contribute to this objective. Biodiesel offers various advantages, including renewability, lower carbon emissions, environmental friendliness, and compatibility with petro-diesel. Nevertheless, the widespread adoption of biodiesel is hindered by the high cost of feedstock, accounting for approximately 80–85% of biodiesel production costs (Betiku*et al.*, 2019). A promising strategy to mitigate this cost is the utilization of low-cost feedstock from biomass residue.

The method of converting these agricultural residues to catalysts is mostly through thermal decomposition known as calcination. The calcination is done at varying temperatures usually commonly above 400 °C in furnace to form ash. The temperature of calcination is chosen based on the properties of the biomass after calcination. Calcium oxide (CaO—based) catalysts are heterogeneous, low-cost, available materials in abundance in nature that can be produced from residue feedstocks. Cao-based catalysts have relatively high activity, and their leaching problem can be overcome by supporting it on different carriers or mixing with other oxides (Mazaheri *et al*., 2021

Several synthesis conditions on the thermal decomposition of kola nut pod at different temperatures and under different atmospheric conditions were reported (Adepoju *et al*., 2020, Falowo *et al*., 2020, Asuquo *et al*., 2023). However, the effect of calcination temperature on physical and chemical has not been reported. In this work, the effect of calcination temperature on chemical properties of CaO-catalyst derived from KNP was investigated to find the appropriate temperature to calcine kola nut pod residues for heterogeneous catalysts.

2.0 Materials and Methods

2.1 Materials C~~c~~ollection and P~~p~~re-treatment

The Kola Nut Pod (KNP) that was used in this work was freshly obtained from a local farm in Ile Ife (7.49^{o}N 4.55^{o}E), Osun State, Nigeria, because of its abundance in the region. Sorting of the dirt, immature pod and fresh husks was carried out manually. The fresh pods were cut into pieces, washed with clean tap water and sun-dried. The sun-dried pods were further dried in the oven at 105 °C to a constant weight to remove moisture content from them (Betiku *et al*., 2016). The oven-dried residue was ground into powder form using a disk mill and sieved into a uniform powder particle size of 150 µm using a standard sieve via a mechanical shaker machine. The sieved sample was kept in airtight containers for further analysis. The method reported by Betiku *et al.* (2016); Oladipo *et al.(*2018) and Oladipo *et al*.(2020) was used for sample preparation.

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2.2 Catalyst ~~P~~Preparation

A portion of each KNP, powder was kept as the raw sample for further usage. The other portions were calcined at varying temperatures of 500 to 900 ℃ at 100 ^{o}C intervals, for four hours per sample in a muffle furnace (Galenkamp) to remove carbonaceous and volatile matter from them and to obtain ash products. The calcined KNP ash sample was put in a desiccator and then stored in airtight bags to ensure that no moisture interacted with the sample before further usage. The raw (uncalcined) kola nut pod and calcined ashes were designated as CKNPA and UKNP respectively. The catalyst preparation followed procedures detailed by Betiku *et al,*. (2016) and Oladipo *et al,*. (2018).

2.3 Catalyst Characterization

The samples were characterized by the X-ray fluorescence Spectrometer (XRF) method following the procedures of Betiku *et al,*. (2017) and Etim *et al,*. (2020)using Rigaku ZSX Primus XRF machine equipped with an end window 4.kW R^H-anode X-ray tube. The elemental composition of the sample was determined through EDX analysis. The phase composition of the uncalcined and calcined samples was determined by the XRD analysis of the sample with Bruker X-ray Diffractometer model operating with a CuKα radiation source (Kα=1.5406 A_O).

3.0 Results and Discussion

3.1 Chemical Analysis

The elemental composition of the uncalcined sample revealed the presence of SiO2 (4.05%), Al_2O_3 (5.33%), CaO (29.52%), Fe_2O_3 (1.41%), MgO (21.04%), K_2O (27.61%), P_2O_5 (0.82%), SO_3 (4.27%), TiO_2 (0.28%), and MnO (0.58%) (Table 2). The identified oxides, namely SiO2, CaO, and MgO, are significant components known to support heterogeneous catalysts in biodiesel production (Mohadesi *et al*., 2014; Adepoju *et al*., 2020; Falowo*et al*., 2020; Asuquo *et al*., 2023). Notably, CaO exhibits the highest composition among the compounds detected in the uncalcined KNP through XRF. This result implies that KNP serves as a suitable feedstock for heterogeneous production.

Table 2: The oxides composition of the raw residues

Oxide	Uncalcined	Calcination temperatures (^oC)				
		500	600	700	800	900
SiO_2	4.05	24.39	27.11	27.08	27.41	27.53
Al_2O_3	5.33	5.37	4.31	5.44	5.63	5.72
CaO	29.52	42.81	42.81	41.53	41.72	41.46
Fe_2O_3	1.41	2.00	1.43	2.46	2.50	2.31
MgO	21.04	1.26	1.65	3.14	2.45	2.29

K_2O	27.61	12.08	10.03	10.26	10.00	10.31
P_2O_5	0.82	2.44	2.29	2.32	2.40	2.32
SO_3	4.27	4.00	4.21	2.16	2.03	2.11
TiO_2	0.28	0.85	0.80	0.63	0.74	0.61
MnO	0.58	1.40	1.40	1.51	1.59	1.38

3.2 Effect of calcination temperatures on the chemical composition

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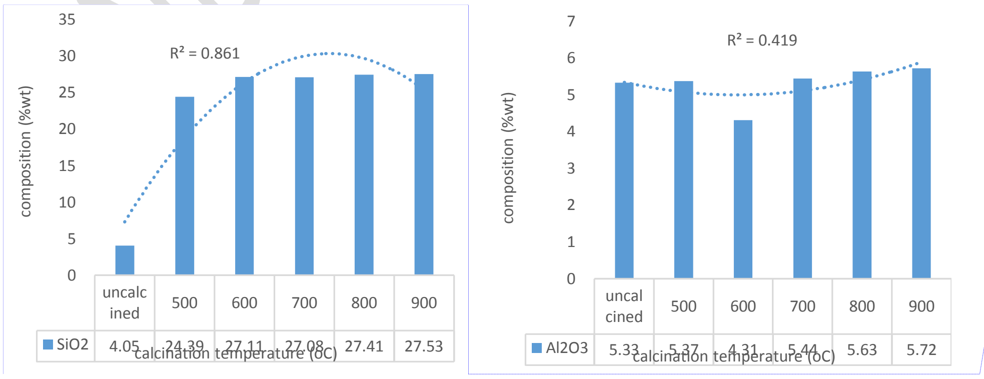
Figure 1 presents the chemical compositions of KNPA for major oxides detected by XRF. A notable observation is the significant increase in SiO2 composition with calcination, as illustrated in Figure 1a. Moreover, the SiO2 content rises with escalating calcination temperatures, indicating that thermal application converts KNP to SiO. A similar trend is observed for Al_2O_3, as depicted in Figure 1b. The CaO content shows an increase from the uncalcined state (29.52%) to 42.81% at 500 and 600°C, remaining relatively stable at 41% (Figure 1c) from 700 to 900°C. On the other hand, the compositions of MgO and K2O decrease significantly upon calcination, suggesting that these oxides are not stable under thermal application. The overall outcome reveals that CaO maintains its highest composition at all calcination temperatures. This aligns with various studies that have utilized CaO as a foundational element for KNP as a heterogeneous catalyst in biodiesel production (Osakwe *et al*., 2018; Betiku*et al*., 2019; Adepoju, 2020).



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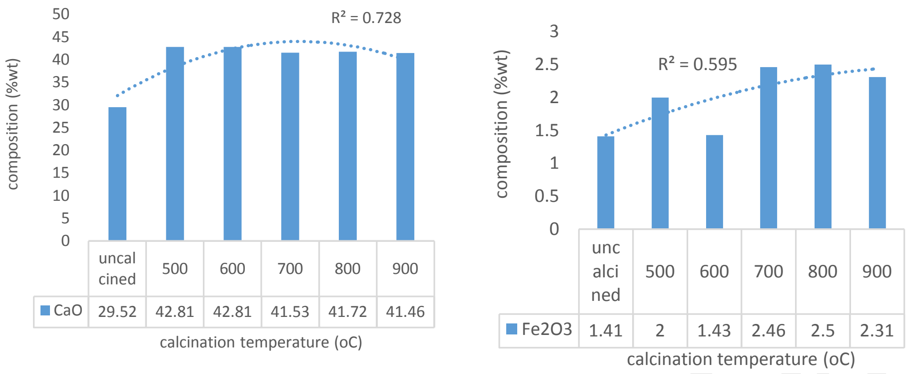
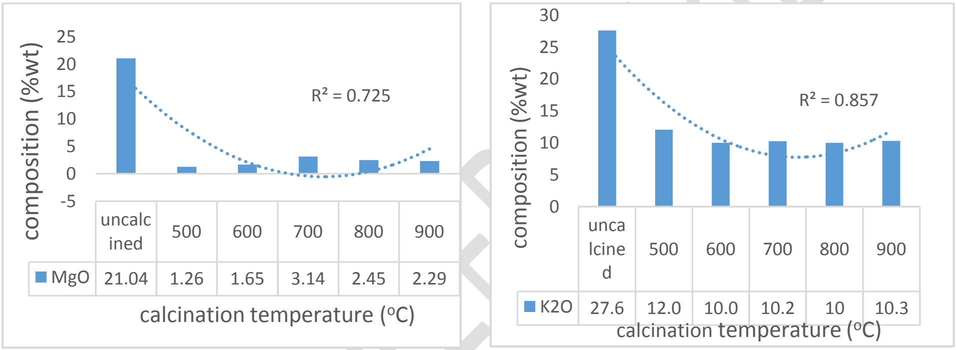
(a) SiO_2 (b) Al_2O_3



(c) CaO (d) Fe_2O_3



(e) MgO (f) K_2O

Figure 1: Effect of Calcine temperature on some oxide of KNPA

3.3 Elemental composition of the raw agricultural residues

Chemical analyses were conducted on uncalcined KNP to determine its elemental compositions using EDX analysis. The identified elements include O, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, and Ba. The elemental composition reveals that potassium is the most abundant element at 31.7%, followed by calcium (17%), and magnesium (7.4%). Several elements, including "K, Ca, Mg, Na, Al, Si, P, S, Cl," and others, were identified as contributors to the phases responsible for the catalysts' catalytic activity in biodiesel production. Transition metal oxides were also detected in trace amounts alongside these metal oxides, as shown in Table 3. The findings suggest that "K, in the form of KCl, K_2CO_3, and K2O components," primarily serves as the key basic metal responsible for catalytic activity in the transesterification reaction for biodiesel production, as indicated by Prajapati *et al*. (2023).

Table 3: The elemental composition of the uncalcined KNP residues

Element	O	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe	Zn	Ba
Concentration (%)	29.21	7.39	4.15	1.64	0.74	1.98	2.03	31.18	17.09	0.46	2.28	0.12	0.06

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3 4 XRD analysis of Kola Nut Pod ash (KNPA)

Figure 2 depicts the XRD pattern of the calcined fused catalyst. Prominent peaks appearing around 2θ are summarized in Table 4 at different temperatures of calcination. The peaks indicate that CaO is the main constituent compound present and it is constituted mostly from KNP. The existence of $Ca(OH)_2$ was also identified as a result of moisture absorption by the CaO due to its natural hygroscopic properties. There was also the existence of a potassium compound in the form of KCl. Other minor peaks indicating the existence of Na_2O were also found due to the fused mineral constituent of the two materials. All these contribute to the catalytic potential of the synthesized base catalyst in the efficient transesterification process.

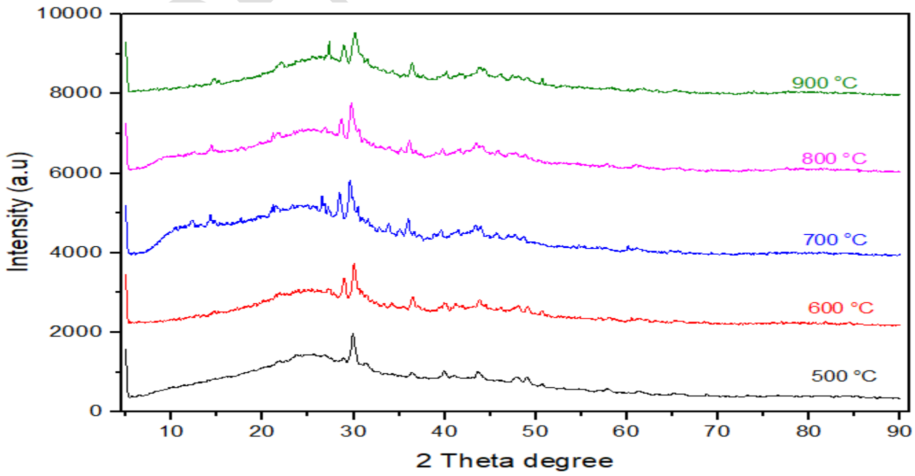

Figure 2:XRD spectra for KNP at different calcination temperatures

Table 4: summary of peaks at different calcination temperatures

Calcination Temperature (°C)	2θ (degree)
500	36, 40, 44, 48, 49, 50.5
600	30, 36, 40, 44, 48, 49
700	13, 14, 17, 22, 26, 28, 30, 34, 35.5, 40, 41, 44, 45.5
800	14, 22, 28, 30, 35.5, 40, 41, 44, 45.5
900	19, 27, 29, 30, 36, 40, 44, 50.5

4.0 Conclusion

Investigation of the viability of Kola Nut Pod (KNP) residue as a biodiesel synthesis catalyst, focusing on the impact of calcination temperatures on its chemical properties. KNP, an abundant byproduct of kolanut, is explored as a potential biocatalyst to address environmental concerns and reduce biodiesel feedstock costs. Calcination temperatures from 500 to 900 ℃ result in ash with varying chemical compositions. Chemical analysis identifies major and other oxides in the uncalcined and calcined samples, making KNP a promising biodiesel catalyst feedstock. The study contributes valuable insights to the development of sustainable and economically viable biodiesel catalysts.

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