

Kariya Pod-Husks: A Novel Biocatalyst in Biodiesel Production

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ABSTRACT

Diverse challenges faced with the use of homogeneous catalysts in biodiesel production coupled with the interest in converting waste resources to useful products in solving occurring climatic and environmental challenges around the world have triggered research into the use of various heterogeneous catalysts. In this study, the catalytic properties of kariya pod-husks were investigated to examine their suitability in biodiesel production. Kariya pod-husks were ash and calcined at 600°C for 4 h. In the morphological structure examination, the scanning electron image of calcined kariya pod-husks shows that it has a more compact microstructure with a cluster of big crystals but irregular pores which is an attribute of high catalytic potentials. The elemental composition of the calcined kariya pod-husks reveals that it contains a higher percentage weight of calcium (42%) and potassium (31%) which makes it a more suitable catalyst for biodiesel production. The developed catalyst was further used in the production of kariya biodiesel. A biodiesel yield of 94% was obtained. This study shows that calcined kariya pod-husks could catalyze biodiesel production. It also helps in proving suitable biocatalyst to solve the challenges associated with the separation of catalyst from the product stream which consequently aids in the creation of continuous chemical processes.

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Introduction

Catalyst hastens chemical reaction via the reduction of activation energy whereby the catalyst itself is not consumed during the reaction. The most industrial process relies on the use of solid catalysts such as in petrochemistry and fine chemicals. 85% of all chemical processes have used catalysts, for at least one step during their preparation [1]. In biodiesel production, the use of homogeneous catalysts has posed serious challenges in its separation from the product stream. Though, utilization of heterogeneous catalysts has been investigated by some researchers and it was found to be more tolerant of extreme operating conditions than homogeneous catalysts yet there is little information on the use of waste bio-materials as heterogeneous catalysts in producing biodiesel.

In contrary to homogeneous catalyst, the heterogeneous catalyst phase varies from the reactants or products phase, eliminates expensive and timewasting water purification and neutralization process in separating and recovering used catalyst [2]. Also, the purified glycerol by-product produced with heterogeneous catalyst (98%) is higher than that of homogenous catalyst (80%) and heterogeneous catalyst is cheap and easy to adjust to accommodate required properties for preventing FFA or water from negatively affecting the reaction process during biodiesel production [3-5].

Heterogeneous catalyst is usually prepared by pretreating and ashing (calcination) the catalyst materials in muffle furnace at high temperature to eliminate the carbon content of the materials. According to Aransiola EF et al., after calcination, the catalyst properties determination; the X-ray diffraction (XRD) analysis, and the Scanning electron-microscope test are usually examined [6]. Table 1 shows some heterogeneous catalysts preparations.

S/N	Heterogeneous catalyst	Catalyst preparation
1	Calcium-Oxide solid base [5]	Preparation of Calcium-Oxide was carried out through the decomposition of pulverized Calcium-carbonate at 960°C for 3½h.
2	Ca ₂ Fe ₂ O ₅ [7]	Preparation of Dicalcium-diiron pentaoxide (Ca ₂ Fe ₂ O ₅) was carried out by milling and calcining the mixture of 1:2 molar ratio of Iron (V) oxide and calcium carbonate to 900°C at 2°C min ⁻¹ and thereafter at 1050°C for 4h.
3	Al ₂ O ₃ /KI solid base [8]	The preparation of this catalyst was carried out by impregnating potassium-iodide solution, dring and activating it at 120°C and 500°C for 3 h respectively.
4	Al ₂ O ₃ /PO ₄ ³⁻ solid acid [8]	Al (NO ₃) ₃ was dissolved in 9 mol of water and 85% H ₃ PO ₄ acid was added. The Ph value was adjusted at 7 using ammonia solution. After the filtration of the precipitation, it was washed and oven-dried at the temperature of 383K for 12h and later calcined at 400°C for 3h.
5	Mg/Al hydrotalcites [9]	The preparation of this catalyst was carried out by co-precipitating the supre saturated mixture. The two solutions were stirred together at 40°C. The first solution contains a 200ml saturated solutions of Mg and Al metal nitrates while the second solution contains a dissolved 14g NaOH and 15.9g Na ₂ CO ₃ in a 200ml deionized water. After the first and the second solutions have reacted together for 2h, it was allowed to precipitate in thermostatic bath of 65°C. It was then filtered and washed properly using deionized water till NaOH is not noticed in the filtrate. This was then dried at 90°C for 24h.
6	La ₂ O ₃ mixed with ZnO and catalyzed by alumina (La ₂ O ₃ / Al ₂ O ₃) [4]	This was prepared by wetness impregnation, oven-drying and then by calcination. A mixture of 10g of Lanthanum (III) nitrate hexahydrate solution and 7.5g of Zinc oxide was stirred and oven dried at 150°C for 3h. The catalyst calcination was carried out at 470°C for 3h. A 5g of Lanthanum (III) nitrate hexahydrate solution and 20.3g of Aluminium oxide stirred and dried at 150°C for 3h and then calcined at 600°C for 3h.
7	ZnO/Ba solid base [8]	This catalyst was prepared by impregnation using Ba (NO ₃) ₂ as a precursor to Zinc oxide. This was dried and then calcined at 600°C for 5h.
8.	ZnO/KF solid base [8]	This catalyst was prepared by impregnation with Potassium fluoride solution. Then it was dried at 393K and calcined at 600°C for 5 h.

In its fruiting season after flowering, a kariya tree bears abundant reddish-gold-one seeded pods containing a nut inside which a kariya kernel is encased as shown in Plate 1c-e. But often, these pods end up in the garbage; whereas it has been discovered that the seed contains a high quantity of oil with good physicochemical properties and fuel properties which can be explored for biodiesel production [10,11]. In this study, kariya pod-husks will be explored as a biocatalyst in kariya oil biodiesel production.

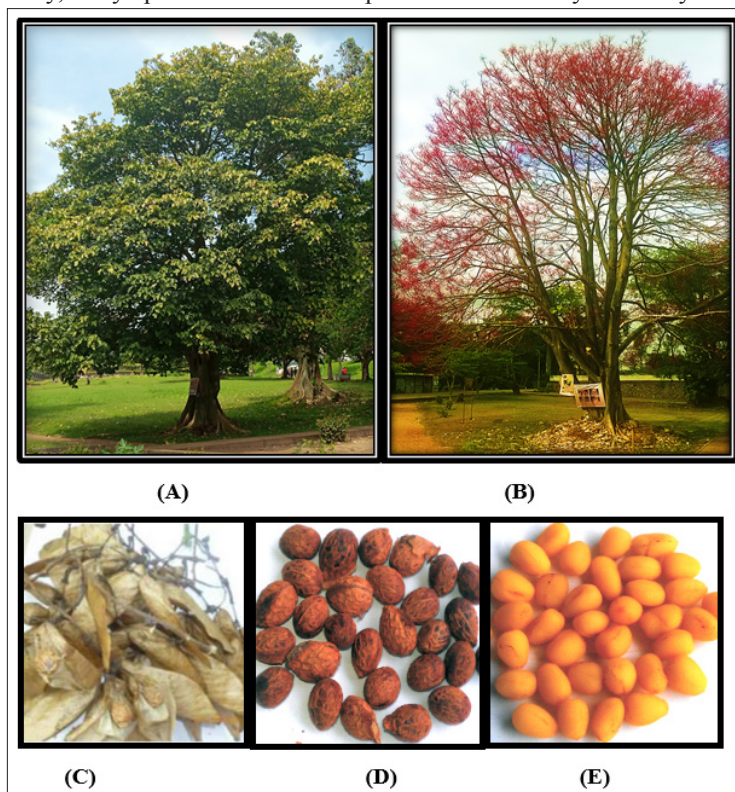


Plate 1: (A)Kariya tree during rainy season (B) Kariya ornamental tree during the dry season (C) Matured dried kariya pod-husks (D) Kariya seeds (E) Kariya kernels.

Methodology

Kariya seed oil and kariya pods were obtained from the Agricultural and Environmental Engineering Department and campus environs of Obafemi Awolowo University, Ile-Ife, Nigeria respectively. The biodiesel production process was performed using ethanol as alcohol and calcined kariya pod-husks as a catalyst. Scanning Electron-Microscope (SEM) and 1.7 MV tandem electrostatic ion accelerator (Model 5 SDH Pelletron) were employed for the determination of the morphological structure and the elemental composition of calcined kariya pod-husks.

Catalyst Preparation

Kariya pod husks were sorted to remove foreign materials, after which it was dried in an oven for 4 h at 105°C. The dried sample of the kariya pod husks was then burnt in the open-air and was sieved into a fine particle of 75 µm. After which, the sample was calcined in a muffle furnace at 600°C for 4 h to eliminate the carbon content and make the catalytic properties of the sample to be more active. The calcined sample was used in the production of biodiesel as a heterogeneous catalyst.

Determination of Catalyst Morphological Structure

The calcined sample was examined using scanning electron microscopy (SEM, Model: ASPEX 3020, PSEM 2). 50 g of the calcined samples were placed in the SEM and the surface micrograph was obtained by examining the longitudinal view of the sample at a displayed magnification of 250 and acceleration voltage of 16.0 kV.

Determination of Catalyst Elemental Composition

1.7 MV tandem electrostatic ion accelerator (Model 5 SDH Pelletron) was used to determine the elemental compositions of the calcined kariya pod-husks. Hydrogen and Nitrogen gas was used as ion source and accelerator stripper respectively.

The characteristic x-ray generated was captured with PIXE-detector. The spectral displayed was observed and examined, and the elements present were obtained.

Biodiesel Production Using Calcined Kariya Pod-Husks

A pretreated kariya seed oil, ethanol, and calcined kariya pod-husks were poured into a three-necked flask and placed on a magnetic stirrer. The solution was properly stirred at 400 rpm and heated at temperatures of 75°C for 3 h using 10:1 ethanol/oil molar ratio. The solution was then allowed to settle for 24 h under gravity in a separating funnel. Then the upper biodiesel layer was separated from the lower glycerol layer. According to ASTM, the biodiesel sample was mixed with water at 30°C temperature to remove residual glycerol [12]. This process was repeated until colorless water was obtained to provide purified biodiesel. After which it was separated from the water and dried over anhydrous calcium chloride to remove the residual water in the biodiesel. Biodiesel yield was determined and recorded using equation (1).

$$\text{Biodiesel Yield \% (w/w)} = \frac{\text{Weight of Biodiesel Produced}}{\text{Weight of Kariya Oil Used}} \times 100\% \dots \dots \dots (1)$$

Result and Discussion

Catalyst Morphological Structure

Plate 1 shows the scanning electron image of calcined kariya pod-husks. The image shows that calcined kariya pod-husks have a compact microstructure with a cluster of big crystals of irregular pores. This can be attributed to the heterogeneous distribution in the mechanical properties of the calcined kariya pod-husks, which indicate high catalytic activity of the catalyst [13,14]. The big pores in kariya pod-husks allow better diffusion of reactant

and product molecules in the production of biodiesel [15]. The characteristics heterogeneous morphological structure of CaO from kariya pod-husks is similar to that of eggshell investigated by Tshizanga, Navajas et al., and Niju et al., [15-17].

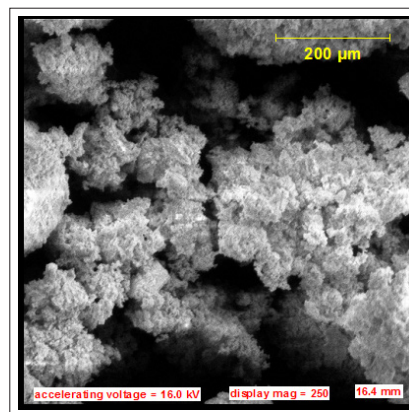


Plate 1: Scanning Electron images (250 Magnification) of calcined kariya pod-husks

Catalyst Elemental Composition

The result of the elemental composition of calcined kariya pod-husks shown in Table 3 reveals that the catalyst contains a high percentage weight of calcium and potassium of 42.349 % and 31.136 % respectively which is a suitable base catalyst in biodiesel production having a high basic strength, minor toxicity and better reaction with water [19].

Table 3: Elemental composition of calcined kariya pod-husks

Atomic Number	Symbol	%Composition	% Weight
		KP	KP
6	C	0.071 ± 0.014	0.102
11	Na	0.550 ± 0.020	0.791
12	Mg	5.385 ± 0.016	7.743
13	Al	0.154 ± 0.002	0.221
14	Si	3.221 ± 0.010	4.631
15	P	2.992 ± 0.017	4.302
16	S	1.606 ± 0.006	2.309
17	Cl	3.396 ± 0.006	4.883
19	K	21.654 ± 0.009	31.136
20	Ca	29.452 ± 0.100	42.349
22	Ti	0.060 ± 0.016	0.086
23	V	0.023 ± 0.015	0.033
25	Mn	0.099 ± 0.014	0.142
26	Fe	0.506 ± 0.019	0.728
29	Cu	0.008 ± 0.002	0.012
30	Zn	0.008 ± 0.002	0.012
33	As	0.004 ± 0.002	0.006
35	Br	---	---
37	Rb	0.029 ± 0.007	0.042
38	Sr	0.317 ± 0.038	0.456
40	Zr	---	---
56	Ba	0.011 ± 0.003	0.016

*KP – Kariya pod-husks, ±Conc. Error.

Biodiesel Yield

The biodiesel yield of 94% was obtained when the calcined biocatalyst was used for the production of kariya biodiesel. This result corresponds to the report of Endalew et al., in which a 100% optimum yield of biodiesel produced from jatropha was observed when a heterogeneous catalyst ($\text{CaO} + \text{Fe}_2(\text{SO}_4)_3$) was used at 6:1 methanol-oil molar ratio and 60°C for 3 hrs [5]. Chouhan and Sarma similarly stated that Calcium oxide derived from eggshell was an effective catalyst for trans-esterification of soybean oil, producing 97-98% biodiesel yield at 65 °C with alcohol/oil ratio 9:1. Likewise, Viriya-Empikul et al. used eggshells with palm oil, and a 95% biodiesel yield was produced in 2h at a 12:1 methanol to oil ratio. This result present calcined kariya pod-husks as a good biocatalyst in the production of biodiesel [19,20].

Conclusion

In this study, the use of calcined kariya pod-husks as a heterogenous catalysts in biodiesel production was examined. The biodiesel yield of 94 % was obtained at a temperature of 75°C, time of 3 h, and an ethanol-oil molar ratio of 10:1. This study shows that calcined kariya pod-husks could catalyze biodiesel production.

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