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SYNTHESIS OF POTASSIUM HYDROXIDE (KOH) FROM RIPE PLANTAIN PEELS DOPED WITH RICE HUSK AND ITS APPLICATION IN BIODIESEL PRODUCTION USING CASTOR OIL (*RICINUS COMMUNIS*)

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Abstract

The goal of this study was to produce an energetic catalyst from ripe plantain peels and rice husk for biodiesel production. Caustic potash doped with Rice Husk, a heterogeneous solid catalyst, was made by wet impregnation at totally different conditions of calcination before doping and doping before calcination labelled catalysts A and B respectively. The properties of the catalysts were characterized utilizing Brunauer-Emmett-Teller (BET), Scanning electron microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), and Fourier Transform-Infrared spectrum analysis (FT-IR). The characterized catalysts showed improved and increased chemical process properties for reaction. The synthesized catalysts A and B were used for biodiesel production through Transesterification reaction exploiting castor oil, at a latent period of 3 hour, temperature of 60 oC, catalyst loading of 2.0 wt/wt% and alcohol to oil proportion of 6:1. each catalysts showed chemical process activity, but catalyst A had a stronger proportion yield of 91.5 % biodiesel as compared to that of catalyst B of 88.6 % biodiesel.

Keywords: *Catalyst, Castor Oil, Biodiesel, Transesterification, Potassium Hydroxide*

Introduction

The use of energy has been considered the greatest essential requirement for human existence (Ling Zhou 2013). In the world's energy supply radar, petroleum constitutes the majority among other different kinds of fuels. Petroleum is found to play a significant role in industry, transportation, and agriculture, as well as to meet many other basic human needs (Saydut et al., 2016). Enormous increase in population size, increase in energy demand, exhaustion of fossil fuel reserves all conglomerate with the environmental

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problems associated with fossil fuel usage and these, in turn, have led to the search for alternative fuels which can be obtained from renewable sources (biofuel) (Ahmed et al., 2016).

High capital and production cost, as mentioned by Amin and Amin (2015), have stood as the main impediment in the industrialization of biodiesel which has led researchers to focus on non-edible and waste oils (WO) as raw material to enhance biodiesel production.

Homogeneous alkali catalysts can convert triglycerides to their corresponding fatty acid methyl esters (FAMES) with high yield, less time and low cost but the process of renewing, separating the catalyst from the product mixture and the environmental hazards during disposal poses some challenges in the use of these catalysts (Feng and Zhen 2016). These challenges can be minimized or eliminated by the use of heterogeneous catalysts (Nasreen et al., 2018).

Potassium is the most abundant mineral in plantain peels with an estimated value of 37gkg⁻¹ in the green peel. This value is increased by a small amount during the ripening process (Efeovbokhan et al., 2016). Potash alkali and metal contents of ashes obtained from plantain peels have been investigated by a number of researchers and showed that the alkali content of the ash ranged from 69 to 81.9% and the analyzed potassium concentration in the peels gave as high as 750 mg/kg. According to Efeovbokhan et al., (2016), under the same process conditions of trans-esterification, KOH extract from ripe plantain peels ash gives higher percentage conversion than the commercial KOH.

Rice husk (RH) is a promising feedstock with very high abundance in nature and wide composition and these properties have given it a good edge for industrial applications. Just as other lignocellulosic materials, a typical rice husk contains cellulose, hemicellulose, lignin and ash (Touhamia et al., 2017). The striking surprise is that this biomass waste possesses exceptional properties like its high silica content, high porosity, light weight and high external surface area (Soltani et al., 2015). These properties have made rice husk an ideal biomass waste for use as a potential metal adsorbent, a ligand in construction material, a silica source in ceramics, a catalyst or a catalyst support for other uses such as biodiesel production (Touhamia et al., 2017). Rice husk, an agricultural waste, has been reported to contain about 92–95% silica (SiO₂) in the ash. It is highly porous with lightweight and great surface area. There are many publications with the report of the use of rice husk ash as catalyst support for metals (Thabet et al., 2015).

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Methodology

The raw ripe plantain peels were collected from eateries and restaurants in Gidan Kwanu, Niger State while the castor oil was obtained from NARICT (National Research Institute for Chemical Technology). The raw rice husk was obtained from Kpakungu Rice Mill, Niger State.

Sample Preparation

The raw ripe plantain peels were washed with distilled water and then dried in an oven at 60°C until they were dried enough for combustion. The samples were then burnt in an open air, with absolute caution, to prevent the ash from being blown off by air current. The ash obtained were carefully collected to minimize loss and stored in a polythene bag for the prospective extraction processes to be carried out (Efeovbokhan *et al.*, 2016).

Synthesis of KOH

20 g each of the plantain ash sample was weighed and mixed with the required volume (10 ml/g ash) of mineral free-water in 500ml beakers. The container with its mixture was then placed on a hot plate magnetic stirrer, kept under stirring and heating at the temperature of 50 °C for a duration of 3 hr. The resultant solution was then filtered using filter paper and stored. Then the residue was further extracted under the same conditions as above. The resultant solution was again filtered. The procedure was repeated until the solution from the residue tested neutral or almost neutral to pH paper. The filtrates from the stages were collected respectively in separate stainless steel containers and evaporated to dryness in an oven. The dried sample was collected, weighed and bottled in a plastic container (Efeovbokhan *et al.*, 2016).

Rice Husk Preparation and Pre-treatment

30 g of clean rice husk was stirred with 750mL of 1.0M H₂SO₄ at room temperature for 24h. The cleaned RH was washed with copious amount of distilled water to constant pH, then dried in an oven at 100°C for 24h (Thabet *et al.*, 2015).

Preparation of KOH doped Rice Husk Catalyst For Catalyst A

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The oven dried sample was burned in a muffle furnace at 600oC for 4 hr so as to obtain white rice husk ash (Thabet *et al.*, 2015). 30 g of KOH was impregnated by introducing it into 30 g of white rice husk ash and was allowed to age at room temperature for 18 hr. The resultant sample was dried in an oven at 110oC for 24 hr and was finally calcined in a muffle furnace at 500oC for 3 hr (Maniam, *et al.*, 2015).

For Catalyst B

The 30 g of KOH was impregnated by introducing it into 30 g of the oven dried and was allowed to age at room temperature overnight. The gel was dried in an oven at 110oC for 24 hr and was calcined in a muffle furnace at 600 oC for 4 hr (Thabet *et al.*, 2015).

Characterization of Catalyst

The catalysts were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX).

Characterization of Castor Oil

The castor oil was investigated for its specific gravity, density, flash point, kinematic viscosity, acid value, iodine value, moisture or water content and free fatty acid (FFA). The experimental description reported by the American Standards and Testing Materials (ASTM) were utilized in the determination of the above-mentioned properties.

Transesterification of Castor Oil

The castor oil was trans-esterified utilizing the two synthesised catalysts A and B. In each of the processes, the catalyst was placed in a 250 cm³ round bottom flask with methanol and the oil with the process parameters of methanol to oil molar ratio of 6:1, catalyst loading of 2.0 wt/wt %, reaction time of 3 hr and temperature of 60°C, under constant stirring. After completion of the reaction, the products were clamped in a separating funnel and allowed to settle overnight and the biodiesel was collected and washed (Nurdin *et al.*, 2015; Yacob *et al.*, 2017).

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Results and Discussion

Catalyst Characterization

The surface area, functional group, surface morphology and crystallinity of the synthesized catalysts as revealed by their characterisation are shown in the table below.

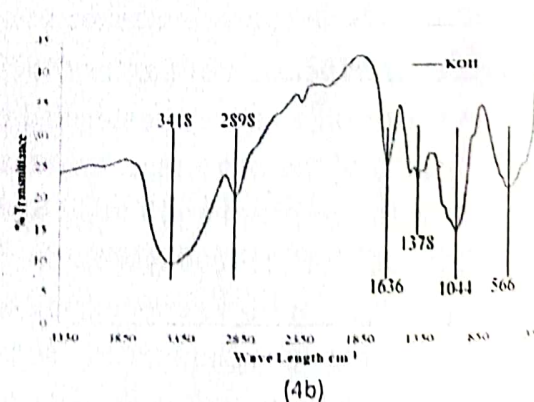
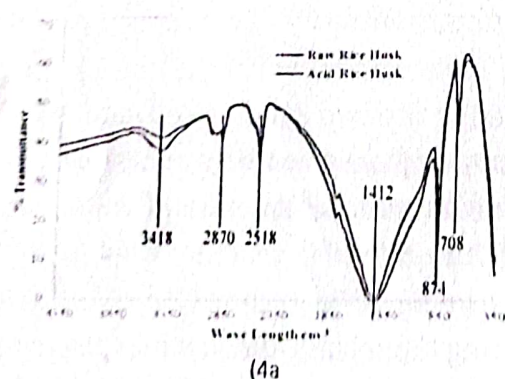
Brunauer-Emmet-Teller (BET) analysis

Table 4.1: BET Analysis for Catalyst A and Catalyst B

Sample	Specific Surface Area at 300 oC (m ² /g)	Pore Size Distribution at 40-100um (micron)
Raw Rice Husk	80.70	48.20
Acid-Treated RH	68.70	45.00
KOH	77.43	50.20
Catalyst A	67.30	54.00
Catalyst B	62.30	54.20

The BET analysis of both catalysts A and B produced no appreciable difference in their pore size distribution, but Catalyst A had a higher specific surface area of 67.30 m²/g than Catalyst B with 62.30 m²/g. It also showed that the specific surface area and the pore size distributions of the synthesised catalysts were within the range of values reported by Thabet *et al.*, 2015.

4.1.2 Fourier-transform infrared spectroscopy (FTIR) analysis



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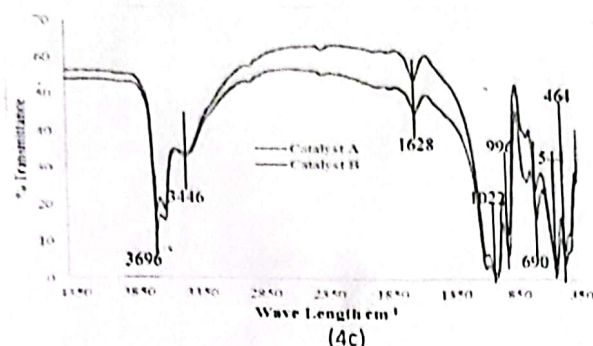


Figure 4.1: FTIR Spectra of Raw Rice Husk and Acid-Leached Rice Husk (4a), KOH (4b), and Catalysts A and B (4c)

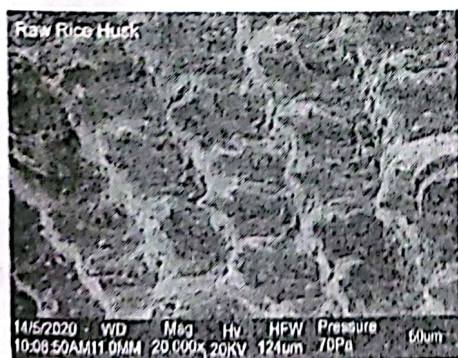
Figure 4a showed the IR spectra of both the raw rice husk and the acid-treated rice husk samples. Figure 4b showed the IR spectrum of the synthesised KOH. While figure 4c showed the spectra of catalysts A and B. The peaks found within the region of 3700cm^{-1} – 3200cm^{-1} were due to the stretching vibrations of the O–H bonds of water molecules adsorbed onto the matrices of the samples (Muniandy *et al.*, 2014).

The weak bands found within 2800cm^{-1} – 3000cm^{-1} indicated the stretching vibrations of the C–H bonds of the methylene groups (CH_2) (Muniandy *et al.*, 2014).

The band at 1620cm^{-1} – 1680cm^{-1} were attributed to the stretching vibrations of C=C bands (alkene).

The band at 1378cm^{-1} – 1480cm^{-1} could be attributed to the bending vibrations of C–H band (alkane group). The vibrations noticed at 1022cm^{-1} - 1044cm^{-1} was as a result of the stretching vibrations of C–O bands of the ether group (Muniandy *et al.*, 2014).

4.1.3 Scanning electron microscopy (SEM) analysis



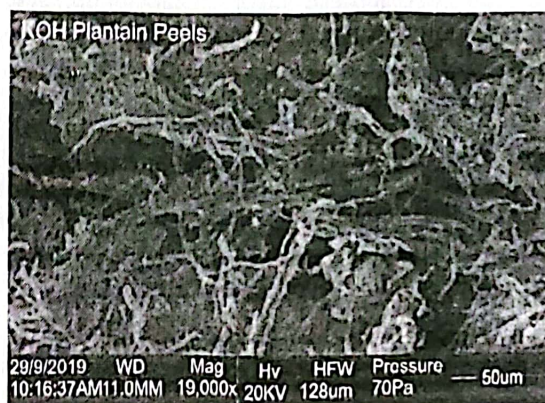
(5a)



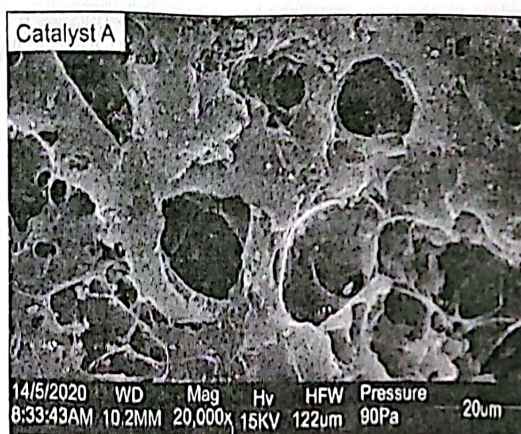
(5b)

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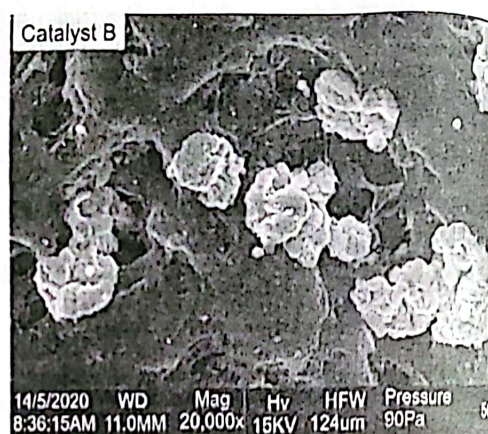
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(5c)



(5d)



(5e)

Figure 4.2: SEM micrograph of Raw Rice Husk (5a), Acid-Leached Rice Husk (5b), KOH (5c), Catalyst A (5d) and Catalyst B (5e)

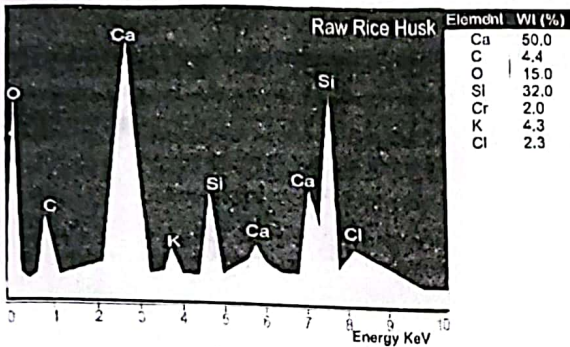
Figure 5b exhibits the highly developed porous structure of the acid-leached rice husk sample from the relatively non-porous raw rice husk with corrugated structure (Fig. 5a). The acid leaching was confirmed to have induced the porosity of the rice husk material with high surface area and large pore volume. It was observed that the raw rice husk was fibrous and had no hollow structures could be attributed to the fact that the pores of the raw rice husk were filled with carbonaceous products (Touhamia *et al.*, 2017). The calcination process showed more impact in figure 5d than in 5e which indicated that the pre-heat treatment process before doping is very important to increase the specific surface area of

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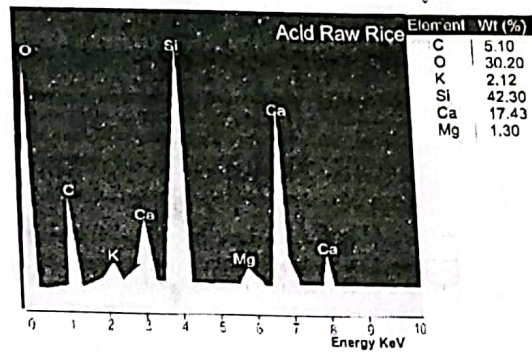
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the samples. This conversion is ascribed to the decay of the volatiles due to the calcination process at high temperatures (Muniandy *et al.*, 2014).

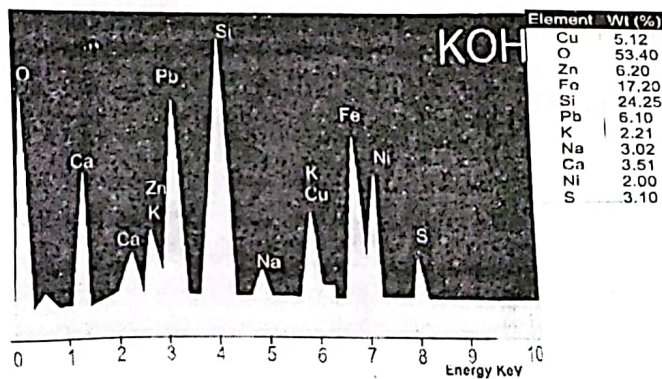
4.1.4 Energy Dispersive X-ray (EDX) analysis



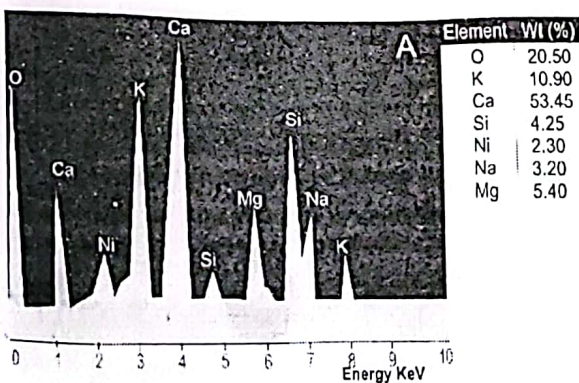
(6a)



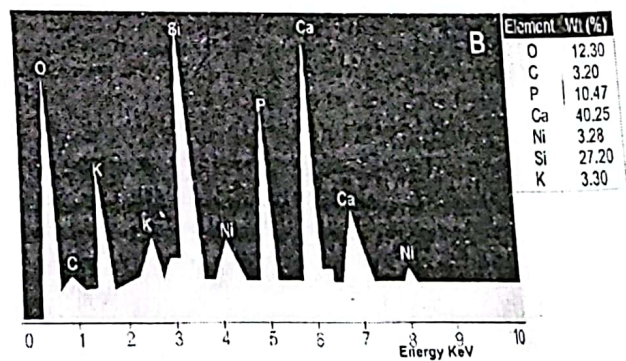
(6b)



(6c)



(6d)



(6e)

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Figure 4.3: Elemental Weight Composition of the Raw Rice Husk (6a), Acid-Leached Rice Husk (6b), KOH (6c), Catalyst A (6d) and Catalyst B (6e)

The Energy Dispersive X-ray (EDX) of all the samples revealed the presence of several elements. The presence of silica was noticed in all the samples. It was observed in the acid-leached sample (6b) that the weight of Si increased from 32.0 wt(%) in raw rice husk to 42.30 wt(%) after leaching. KOH sample (6c) also displayed the presence of Si 24.25 wt(%). Catalyst B (6e) 27.20 wt(%) showed evidence of more silica content than Catalyst A (6d) 4.25 wt(%). However, the Energy Dispersive X-ray (EDX) also revealed the presence of other compounds like Ca, O and K in all the samples.

4.1.5 X-ray Diffraction (XRD) analysis

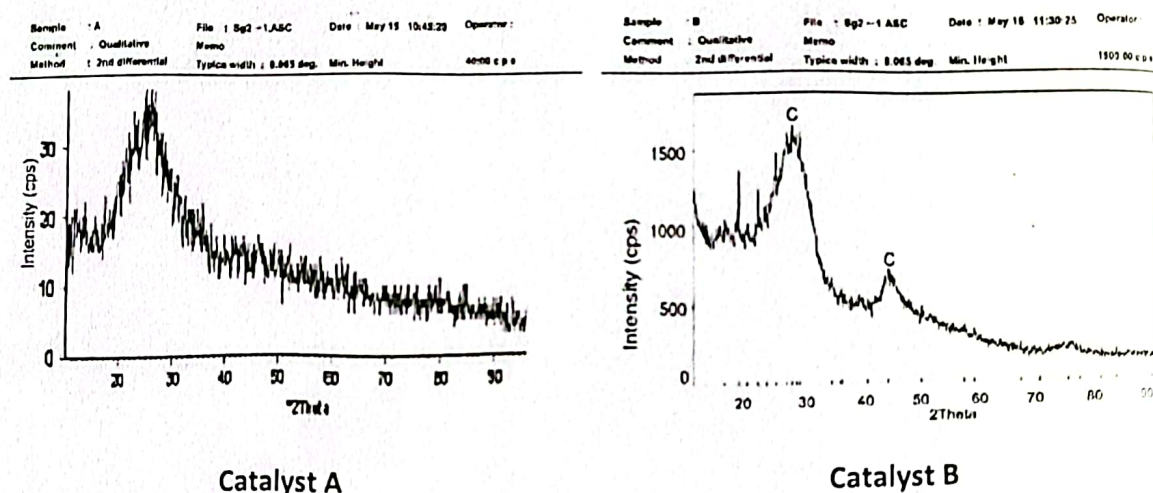


Figure 4.4: X-ray Diffraction (XRD) analysis of Catalysts A and B

The characteristic peaks at 2θ value obtained from the XRD diffractograms of both catalysts (A and B) at $(20-30)^\circ$ and 45° are similar as the typical KOH doped with rice husk peaks reported by Muniandy *et al.*, (2014). The XRD patterns of the synthesized catalysts (A and B) are also similar to that reported by Touhamia *et al.*, (2017). Muniandy *et al.*, (2014) reported that it could be right that there are some mark of micro-crystallinity with turbostratic graphite structure in both samples. The broad nature of the peak as reported by Touhamia *et al.*, (2017) could be attributed to hydrogen bond transformation in cellulose during the heat treatment. Furthermore, the low crystallinity is believed to be due to the large amount of amorphous cellulose in the catalysts.

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Biodiesel production

Comparison of the produced biodiesel with standard exposed that it is in conforms with the standard as shown in Table 4.2 below.

Table 4.2: The conformity of Synthesized Biodiesel with the Standard Biodiesel

Properties	Units	Castor Oil Biodiesel using catalyst A	Castor Oil Biodiesel using catalyst B	ASTM D6751
Density 40oC	g/cm ³	0.946	0.943	-
Kinematic Viscosity at 40oC	mm ² /s	4.9	5.4	1.9 - 6.0
Flash Point	-	162	135	130 min
Pour point	o C	-7	-5	-
Cetane Index	-	62	51	47 min
Cloud point	-	4 o C	6 o C	-
Iodine value	mg I/100g	85	86	-
Ester value	wt. %	169.12	99.4	-
pH Value	-	7.18	7.39	-
Biodiesel Yield	%	91.5	88.6	-

Conclusion

The characterization of both catalysts A and B has shown the dominance in reactivity of catalyst A over catalyst B. This fact was validated by the BET and SEM analysis where catalyst A showed a higher specific surface area than catalyst B indicating the presence of more pore volume in the catalyst A than in catalyst B.

In the application of these synthesized catalysts for biodiesel synthesis, catalyst A has shown better reactivity with a yield of 91.5% as against a yield of 88.6% obtained with catalyst B. Also, the cetane number of the Fatty Acid Methyl Ester produced with catalyst A showed a higher index of 62 as against that of catalyst A with an index of 51. Other biodiesel properties such as flash point, kinematic viscosity at 40oC and the ester value all favoured the use of catalyst A for biodiesel production.

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