Ultrasound-assisted transesterification of waste cooking oil to biodiesel utilizing banana peel derived heterogeneous catalyst

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Abstract

Scientists are considering substitute energies as a consequence of the increasing global demand for energy. An eco-friendly and high flash point biofuel, biodiesel, can be obtained from different types of animal fats, vegetable oils, and algal oils through transesterification with methanol with the support of a catalyst. The current study focused on exploring a bio-based heterogeneous catalyst, Nendran banana peel (NBP), for biodiesel production from promising feedstocks like waste cooking oil (WCO) using ultrasound-based transesterification. Catalyst morphological characterization showed a microporous structure and shows the minerals like potassium and calcium present in it which help to catalyze the reaction. The resultant biodiesel yield calculated using ^{1}H NMR showed 72.25% conversion. The outcomes of this study showed that the Nendran banana peel can act as a potent catalyst for the biodiesel manufacturing process.

Keywords Nendran banana peel powder, Waste cooking oil, Calcination, Ultrasonic bath, Biodiesel, Heterogeneous catalyst

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Graphical Abstract

Introduction

The depletion of non-renewable energy sources, an extreme inquiry has been created for a long time for elective fills and environmentally responsible energy sources that may emit possible little measures of pollutants [1]. It is imperative to seek out a different non-fossil fuel-based energy system that is ecologically sound, inexpensive, stable, regenerative and emits little amount of pollutants. Biodiesel reduces pollutant emissions because it is cleaner than traditional petroleum derivatives concerning unburnt hydrocarbons (68%), particulate materials (40%), carbon monoxide (44%), sulfur oxide (100%), and polycyclic sweet-smelling hydrocarbons (80–90%) [2]. In the current justification, the biofuel market will increase by 41 billion litres from 2020 to 186 billion litres by 2026, growing at an average rate of 4% per year over the forecast timeline. Biodiesel will account for 87% of total worldwide biofuel demand after the forecast timeframe, decreasing eight percent growth from the current level [3].

Vegetable oil causes problems for engines when it is used directly, for example, low power yield, and the burning product as propanol (which is a poisonous aldehyde). To work on the improvement of vegetable oils, unique choices have been thought of, like micro emulsion with methanol or ethanol, dilution, supercritical fluid, pyrolysis, and transesterification with methanol or ethanol [4, 5]. Waste cooking oil (WCO) can be utilized as a crude raw material for the production of biodiesel instead of using vegetable oil [6]. In the vast majority of lodgings, cafes, and other food ventures, the waste cooking oil is either just released into the waterway or dumped into the land. Cooking oil residue can contaminate water bodies when it is poured into lakes, rivers, or sewers. Since oil is less dense than water, it tends to form wide, thin membranes that impede the oxygenation of water. Up to a million liters of water can become contaminated by just one liter of oil. Sunlight penetration is hindered, photosynthesis is stifled, and the environment is disturbed by floating oil [7]. Marine plants and animal deaths may result from this. When waste oil is disposed away in the garbage, it seeps into groundwater, an essential source of drinking water. Large volumes of water can become contaminated by just one liter of used frying oil. Cooking oil that has been reused repeatedly may accumulate harmful substances in the body, which may result in conditions including heart disease, stroke, and other conditions [8]. Hence, it is possible to effectively make biodiesel using used cooking oil [9]. It has been established that producing biodiesel from WCO is a monetarily viable method [10, 11].

An enzyme-based catalyst provides a more environmentally friendly alternative to the conservative one that has been used to generate biodiesel, but due to their greater price and difficulties in handling, they are really not economically viable for commercial use [12, 13]. Homogenous catalyst is mostly acid-base catalyst which is strong like sulfuric, phosphoric, and hydrochloric acid. KOH, a NaOH-like alkali homogenous catalyst cannot be separated from biodiesel and glycerol [14]. So, the downstream process needs a water wash step to eliminate the catalyst from the products. This makes the process

tedious and more costly. Heterogeneous catalysts are utilized for the transesterification process to solve these problems, and pilot-scale biodiesel production is simple [15, 16]. As of late, nanocatalysts have accomplished uncommon consideration for the production of biodiesel because of their high catalytic proficiency. Nanocatalyst mediums have enormous surface regions, which thus results in intensified action when contrasted with ordinary catalysts [17]. The primary components of nanocatalyst are highly stable, reusability as well as effective surface-to-volume proportion, activity, and higher resistance towards saponification [18, 19]. The tedious downstream processing will be reduced attributable to the heterogeneous catalyst utilized in the transesterification reaction. Several popular heterogeneous catalysts include calcium oxide, magnesium oxide, potassium iodide (KI)/g-aluminium oxide [20], and some waste natural substances rich in potassium and calcium such as egg shells [21], chicken bones [22], cow horn [23], ash from the ostrich bones [24], and so forth [25] showed that it helps to enrich the yield in comparison to homogenous catalyst.

Much research is currently being conducted to intensify the catalytic performance using various methods to increase biodiesel production. However, additional research is still required to find more affordable, efficient, and durable catalysts, feedstock, and alcohols for enhanced and profitable biodiesel synthesis. Even though there are many heterogenous and economical catalysts available there are some disadvantages such as promoting unwanted side reactions, some catalysts exhibit mass transfer limitations particularly when dealing with high-viscosity feedstock like waste cooking oil. The motive of this research work is to overcome the above-mentioned problem and analyze the significance of a heterogeneous-based nendran banana peel catalyst to increase the production of biodiesel without any side reactions through an ultrasound-based transesterification reaction (which enhances the mass transfer reaction) using waste cooking oil and methanol in a 30:15 ratio and also to determine the yield percentage of the biodiesel produced.

Result and discussion

Physico-chemical properties of waste cooking oil

Measurements were made of the oil's density, acid value, moisture content, iodine value, and saponification value after it had been dehydrated. The outcomes are displayed in Table 1. The physicochemical characteristics of waste cooking oil were examined to produce biodiesel. The WCO density at 20 °C shows 0.8384 ± 0.57 g.cm-3. The upsurge in WCO density affects biodiesel conversion. WCO having a high-density value does not lead to complete conversion. The detected moisture content in

Table 1 Physio-chemical properties of Waste Cooking Oil

Properties	Units	Parameters
Density at 20 °C	g/cm^3	0.8384 ± 0.57
Moisture content	%vol	0.014 ± 0.01
Acid value	mg of KOH/g of oil	1.8 ± 0.09
Iodine value	g of I$_2$/g of oil	47.63 ± 1.36
Saponification value	mg of KOH/g of oil	197.01 ± 2.18

WCO was $0.014 \pm 0.01\%$ vol. High moisture levels could buoy up the growth of microorganisms and lead to water buildup. The produced biodiesel's quality and worth were assessed using the following parameters: the acid value of WCO was 1.8 ± 0.09 mg KOH/g, iodine value was 47.63 ± 1.36 g of I2/g of oil. With the use of these physicochemical characteristics, it was possible to assess if waste cooking oil could be used directly or whether further development was necessary to turn it into biodiesel. Table 2 compares the calculated physicochemical features of synthesized biodiesel from waste cooking oil to both European Organization (EN 14214) criteria and the American Society for Testing and Materials (ASTM D6751). Comparing the results with the study made by [26] where sorghum oil had been used to make biodiesel, the physiochemical characteristics of WCO demonstrated the acceptability of biodiesel for diesel engines as well as the potential of synthesized biodiesel as a viable diesel substitute.

Characterization of Catalyst

The ultrasound-based transesterification reaction was carried out utilizing raw banana peel as a catalyst, but owing to the presence of all other components, the transformation was determined to be insignificant. To get the desired catalytic components and boost the yield conversion of biodiesel, the banana peel was calcinated.

Catalyst characterization through Scanning Electron Microscopy

SEM was used to analyze the morphology of banana peels that had been both raw and calcined. Significant variations in morphologies were observed between raw nendran banana peel and calcined banana peel waste. In Fig. 1(c,d), the raw catalyst, agglomerated and huge-sized particles with small surfaced and rough irregular shapes with holes, cracks, and voids were identified. Due to the above result, we inferred that the conversion to biodiesel was insignificant, and more time was required. However, the catalyst in Fig. 1(a,b), showed many aggregates with mesoporous and microporous characteristics as a result of calcination. The calcined powder crumbled

Table 2 Physio-chemical properties of biodiesel produced from Waste Cooking Oil(WCO)

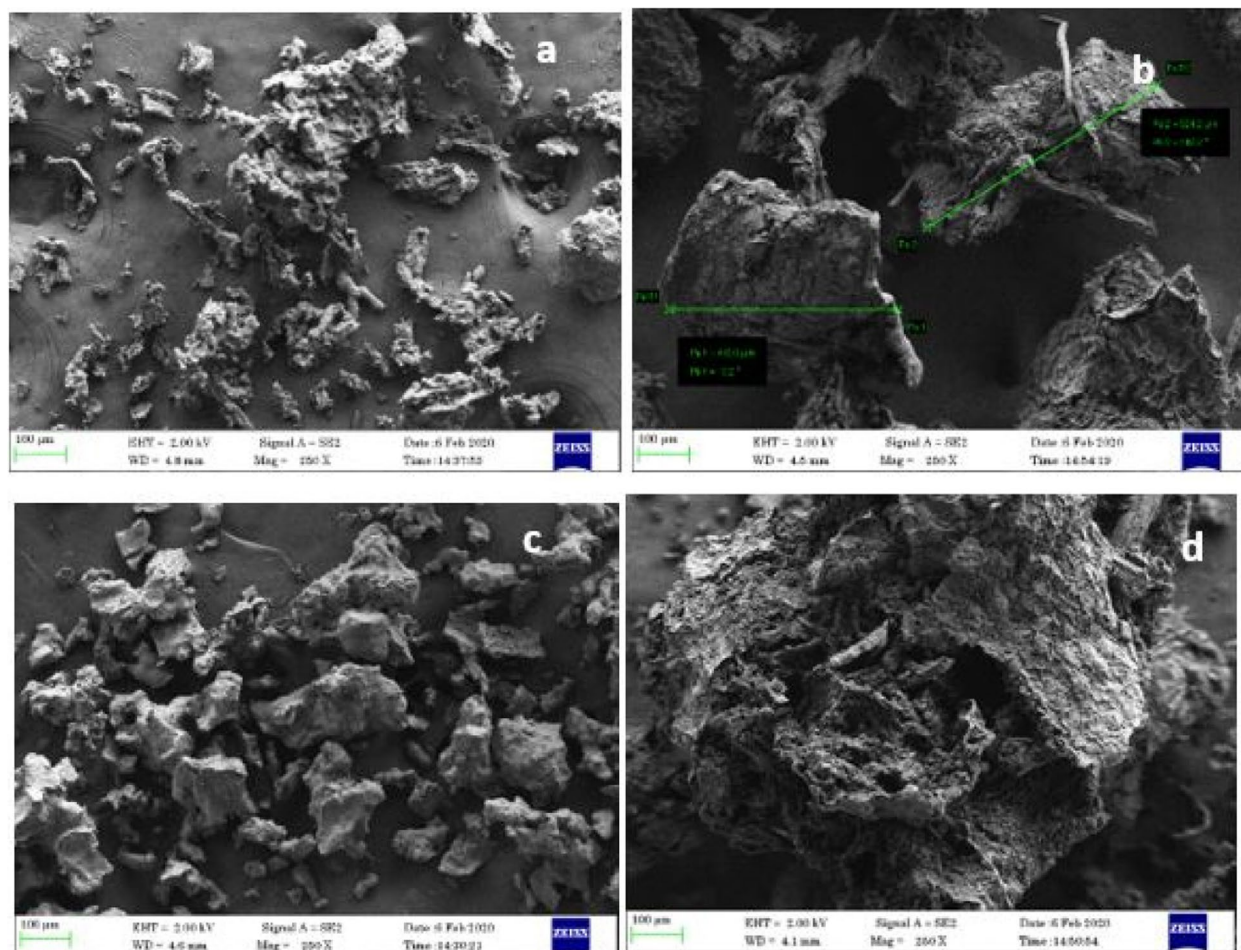| Properties	Units	Values of Biodiesel	Biodiesel EN 14214	Biodiesel ASTM D6751
Density at 30 °C	kg/m^3	0.8714±0.02	0.86–0.90	0.875–0.90
Moisture content	%vol	0.014±0.01	<0.05	0.03
Acid value	mg of NaOH/g of oil	0.51±0.03	<0.5	<0.8
Iodine value	g of I$_2$/g of oil	123±0.99	N/A	N/A
Saponification value	mg of KOH/g of oil	167±2.01	N/A	N/A

Fig. 1 SEM image of Calcinated Nendran Banana peel **a**) 100 μm with width of 4.8 mm **b**) 100 μm with width of 4.5 mm, Raw Nendran Banana peel **c**) 100 μm with width of 4.6 mm **d**) 100 μm with width of 4.1 mm

and had a low particle size with large surfaced particles. Using the calcined powder, the conversion showed an enhanced yield in less time. Large catalytic surface perforations increased the catalytic activity of ash as evidenced by the rise in porosity and folds. The catalyst activation process is heavily influenced by the calcination temperature. Similar changes in the morphology were noticed in the different lignocellulosic sources of a catalyst such as cocoa pod husk ash, wood ash, and banana peel ash. [27], revealed that the cocoa pod husk sample that had been air-burnt demonstrated flattened, smooth, smaller aggregates with significant porosity whereas the calcined powder exhibited spongy and fibrous nature. As a catalyst [28] utilized wood ash biomass and stated that both

calcined and uncalcined biomass had wood ash's porous and spongy nature. The sintering of metal oxides is then thought to be the cause of the appearance of minute mineral clusters and aggregated particles at high calcination temperatures. The sintering of mineral aggregates and aggregated particles gave the banana peel ash sample its properties of being porous, glossy, and spongy [29]. Hence, we determined that the calcined banana peel tends to increase the biodiesel conversion efficiency.

Catalyst characterization through Fourier Transform Infra-Red Spectroscopy

The FTIR peaks of calcined and raw calcined peaks were evident in Fig. 2(A) and Table 3. Lignin, cellulose, and hemicellulose are the key compounds evident in the plant sample. In the raw sample, the appearance of bands from 4000 to 500 cm^{-1} shows lignin, cellulose, and hemicellulose presence. The 2919 cm^{-1} range band indicates the cellulose presence. O–H stretch has appeared in the range of 3295 cm^{-1}. The C-H denoted the spectrum in 2919.23 and 2853.53 cm^{-1}. The spectrum of peaks such as 1308.33, 1147.99, and 1075.18 cm-1 represented the C-O stretching and also indicated the presence of carbonate and K_2CO_3. The halo compounds' presence was indicated in the spectrum of 763.21, 572.65, and 518.13 cm^{-1}. The Nendran banana peels raw sample after calcinating at 700 °C for 4 h has been exhibited in Fig. 2(B) and Table 4. After the calcination, the lignin, and cellulose content appearing in the peel was degraded effectively, resulting in a blue color ash powder. The observed peak rise among 1441.87 and 1351.68 cm^{-1} was related to atmospheric CO_2 adhesion onto metal oxides. The band at 673.16 cm^{-1} was related to the isolated SiO4 vibrations in $CaMgSiO_4$. The Ca-O and K–O stretching was denoted by the range of 565.67 cm^{-1}. The 700.97 cm^{-1} region showed the existence of M–O stretching and also the existence of K_2CO_3. The C-H bending was seen in the spectrum of 879.14 cm^{-1} and 812.12 cm^{-1} respectively. The calcination temperature particularly extracted the alkali oxide such as (K–O, and Ca-O) which is said to be the key active species available in the catalyst responsible for the higher activity. *Ceiba pentandra* oil is used for biodiesel synthesis, and the biomass from the banana peduncle was employed as a heterogeneous catalyst, the research work done by [30] concluded that owing to its basicity, the calcined banana peduncle's catalytic performance affected by the high concentration of mineral oxides present. [31] characterized the biomass and the calcined biomass using FTIR analysis and considered K_2O as the catalytic active species due to effective site generation after calcination. Considering the comparative research made by the previous researchers, the

calcinated nendran banana peel will have a higher conversion efficiency and tend to increase the biodiesel yield.

Catalyst characterization through X-Ray diffraction analysis

According to Fig. 3(A) and 3(B), XRD analysis was utilized to analyze the existence of crystalline components in samples [Tables 5 and 6]. A blend of different compounds such as potassium and calcium in the form of carbonates, oxides, silicates, and sulfides was explained using XRD patterns. It was observed that only a minimum number of peaks were observed in the uncalcined catalyst and it showed the existence of a hemicellulose-cellulose-lignin matrix. After calcinating the Nendran banana peel, the existence of oxides and carbonates showed dominance and a sharp peek denotes the enhanced crystalline nature in high temperatures. Using the Joint Committee on Powder Diffraction Standards (JCPDS) the peaks were compared. In Fig. 4(B) 2Θ values of 26.5, 28.8, 33.1, and 41.2 indicated the peaks of K_2O and K_2CO_3. The Ca-O and $CaCO_3$ presence was indicated by the existence of peaks on 2Θ values of 30.3, 54. The 2Θ peaks on 50.1 denoted the hydroxyapatite presence. In addition to this many other small peaks showed the existence of KCl, K_2SO_4, and K_2MgSiO_4. After the banana peel was calcined at 700 °C, the amount of potassium in it soared. A similar observation was noted by [29] mentioned that 99.73% of potassium was noticed in the calcined banana peel using Napoleon's plume seed oil and another investigation for biodiesel generation from WCO as conducted by [31] using *Musa balbisiana Colla* peel revealed that the mass fraction of potassium present in the calcined catalyst is 83.25%, where the existence of the high amount of potassium showed the strong base site. [32] investigated utilizing a catalyst such as *Tectona grandis* leaves to synthesize biodiesel from WCO, they noticed that the existence of a high amount of calcium and potassium contains very strong basic sites. Comparing the results of the previous studies, this investigation when compared to all other mixtures of the compound, the potassium-rich compounds were observed in a higher ratio.

Biodiesel characterization

Using the constant feedstock (Methanol and WCO ratio as 15 ml: 30 ml and catalyst 0.7 g) the reaction was conducted in an ultrasonic bath for 25 min at 65 °C, using the constant reaction parameters biodiesel production was conducted and characterized.

Characterization of biodiesel through nuclear magnetic resonance studies

To assess the catalyst exposed to air, the catalyst not exposed to air was used as a control. Figure 4A, B,
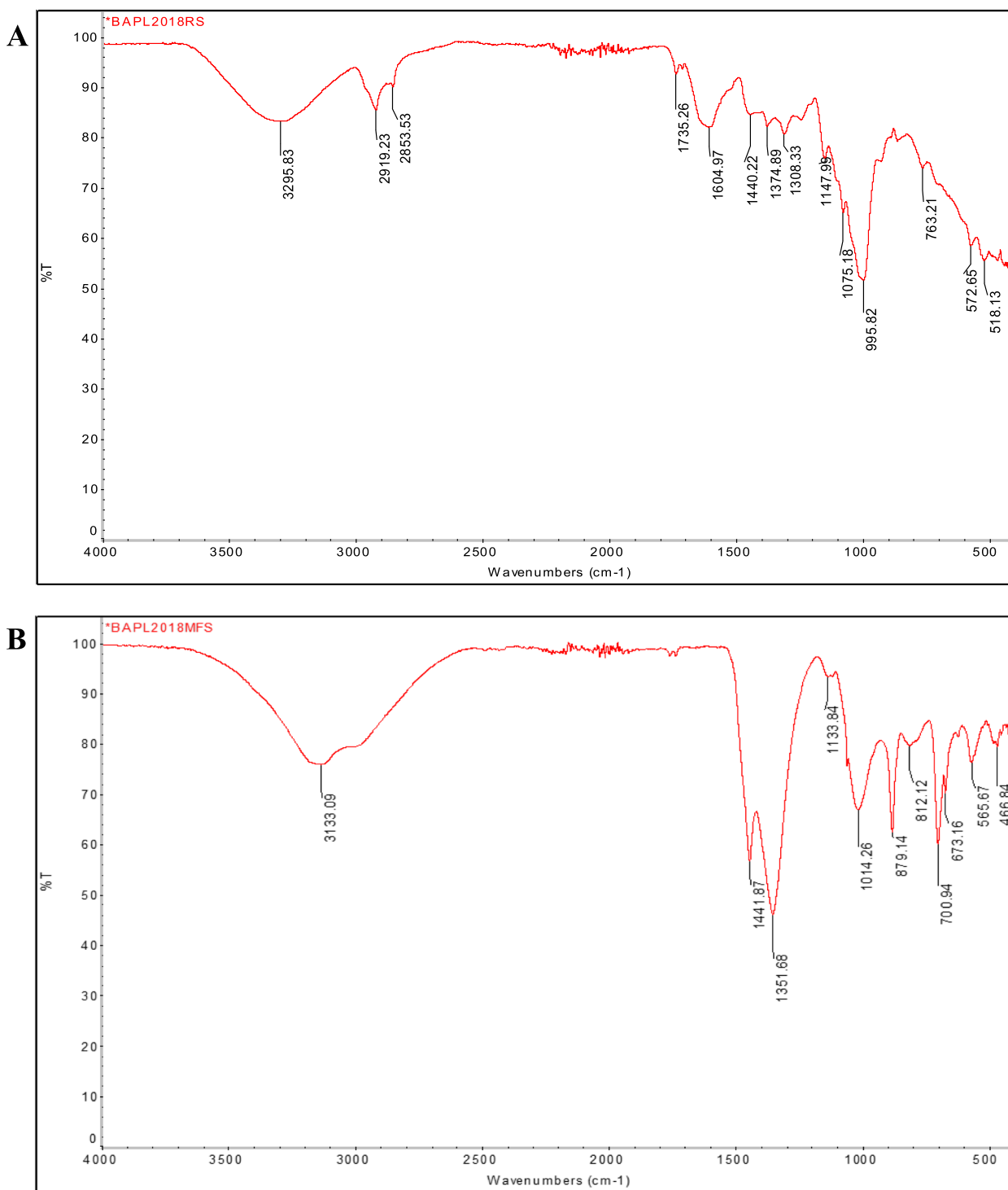
Fig. 2 A FTIR analysis result of raw nendran banana peel powder, **B** FTIR analysis result of calcinated nendran banana peel powder

C, & D showed the WCO was transformed into a methyl ester of fatty acid at the various time intervals of catalyst exposure to air. By substituting the values in Eq. 1, 72.5% of conversion was predicted for the catalyst without exposure to air (NEA), 26.5% was found for catalyst exposure to air for an hour time interval, shorter exposure times (1 h) will make moisture content to observed on the catalyst which acts as a

Table 3 FTIR analysis result of raw nendran banana peel powder

RANGE	ABSORPTION	BOND	FUNCTIONAL GROUP	APPEARANCE
3295.83	3333- 3267	C-H stretching	Alkyne	Strong, sharp
2919.23	3000 – 2840	C- H stretching	Alkane	Medium
2853.53	3000 – 2840	C- H stretching	Alkane	Medium
1735.26	1740- 1720	C = O stretching	Aldehyde	Strong
1604.97	1650- 1580	N–H bending	Amine	Medium
1440.22	1440 – 1395	O–H bending	Carboxylic acid	Medium
1374.89	1420- 1330	O–H bending	Alcohol	Medium
1308.33	1310- 1250	C-O stretching	Aromatic ester	Strong
1147.99	1150- 1084	C-O stretching	Aliphatic ether	Strong
1075.18	1085- 1050	C-O stretching	Primary alcohol	Strong
995.82	1000- 650	C = C bending	Alkene	Strong
763.21	850–550	C–Cl stretching	Halo compound	Strong
572.65	600- 500	C-I stretching	Halo compound	Strong
518.13	690- 515	C- Br stretching	Halo compound	Strong

Table 4 FTIR analysis result of calcinated nendran banana peel powder

RANGE	ABSORPTION	BOND	FUNCTIONAL GROUP	APPEARANCE
3133.09	2500–3300	O–H stretch	Carboxylic acid	Strong and broad
1441.87	1450	C-H bending	Alkane	Medium
1351.68	1370- 1335	S = O stretching	Sulfonamide	Strong
1133.84	1150- 1085	C- O stretching	Aliphatic ether	Strong
1014.26	1400 – 1000	C-F stretching, Si -O—Si bonds	Fluoro compound	Strong
879.14	880 ± 20	C-H bending	1,2,4 tri substituted	Strong
812.12	810 ± 20	C-H bending	1,4 di substituted	Strong
700.94	745–690	M–O stretching	Oxide derivative	-
673.16	690—515	Si–O vibration	Oxide derivative	Strong
565.67	600- 500	K–O, Ca-O stretching	Oxide derivative	Strong
466.84	1000- 400	-	Fingerprint region	-

contaminant on the catalyst surface. Contaminants can interfere with catalytic activity and result in decreased biodiesel yield. This leads to catalyst sites or functionalities being negatively affected, leading to a decrease in biodiesel yield. 42.27% was identified for catalyst exposure to air at a 2 h time interval and 40.16% was predicted for catalyst exposure to air at the time interval of 3 h as given in Table 7. The extended exposure of the catalyst to air (2 h and 3 h) will lead to the surface transformation of the catalyst. This surface reaction will recover the oxygen species in the contaminants and lead to improvement in the biodiesel yield. Longer exposure times allow for recovery or reactivation of these sites. The existence of the β-carbonyl proton signal was indicated by the strong methylene proton signal that was seen in the 1.23 ppm and 1.5 ppm in Fig. 4(A). The multiplet peak in Fig. 4(B) at 4—4.2 ppm

indicated the glyceridic proton in addition to the hydrocarbon proton peaks. The peak at 2.23–2.28 ppm in Fig. 4(C) corresponds to the alpha-methylene proton (α-CH$_2$) which results in the presence of the methyl ester group in the produced biodiesel. The peak at 5.2–5.3 ppm in Fig. 4(D) showed the existence of olefinic hydrogens and 3.6 ppm showed methoxy proton intense peak presence. According to the research by [33], the presence of the methyl ester group, as indicated by the ^{1}H NMR peak, was the reason for the high conversion efficiency of biodiesel. The achieved yield shows 97% efficient biodiesel conversion [31] research work comparing the biodiesel conversion without catalysts and with catalysts. Based on the previously reported findings, we can infer that the biodiesel synthesized from WCO had a better conversion rate since it included the methyl ester group.

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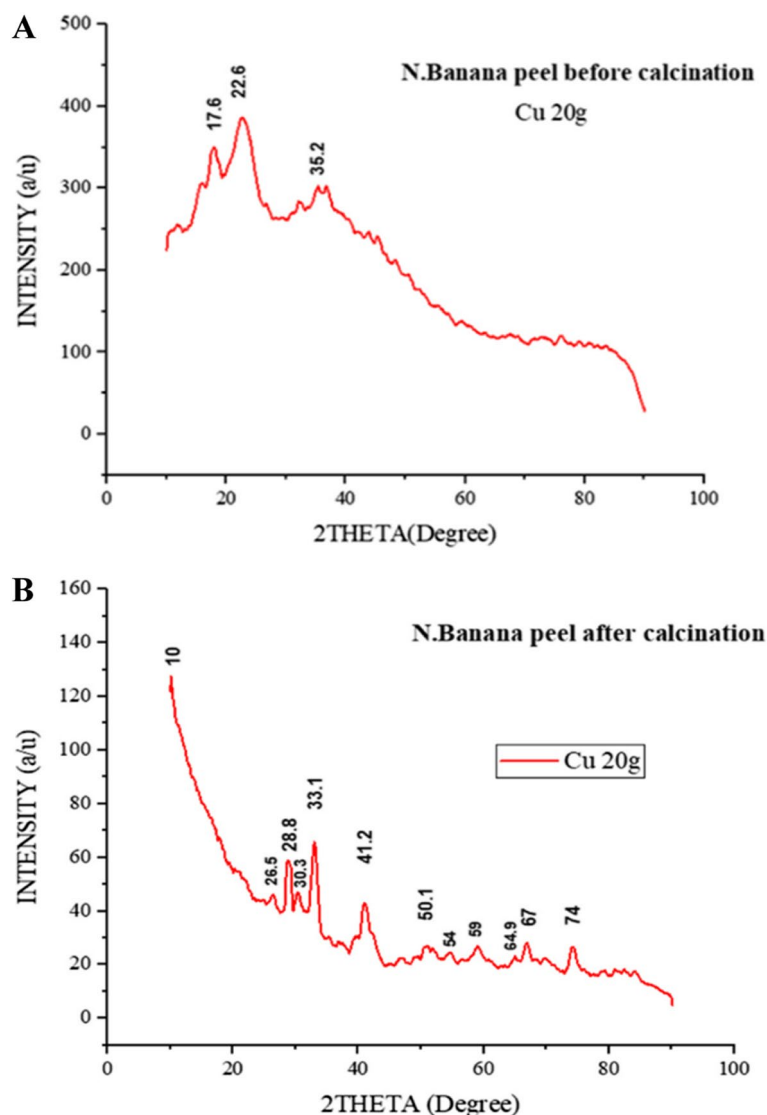**Fig. 3 A** XRD analysis result of raw nendran banana peel, **(B)**: XRD analysis result of calcinated nendran banana peel

Characterization of Biodiesel through Gas Chromatography-Mass Spectrometry

FAME refers to fatty acid methyl esters, which are made when lipids and methanol are trans-esterified. Biodiesel is the combination of FAME. The transesterification reaction generates a substantial amount of FAME, illustrative of the high yield of biodiesel. To analyze the fat conversion into FAME the GCMS was carried out. The FAME was generated using waste cooking oil in different phases majorly consisting of methyl hexadecanoic (58.50%) in the zeroth hour of exposure, Octadecenoic Acid Methyl Ester (84.42%) in the first hour of exposure, Hexadecanoic acid (62.10%) in the second hour of exposure, and Methyl oleate (79.42%) in the third hour of exposure. An increased conversion rate of waste cooking oil to biodiesel was greatly attributed to the shorter chain methyl ester during transesterification reaction and high catalytic activity. The peaks in the graph indicated the presence of methyl ester, which is said to be the component that gives the product its high quality. Similar observations were done by [34] FAME evaluation of biodiesel synthesis from soyabean oil contains Methyl oleate (64.03%), Methyl palmitoleate (20.19%), which indicated that the results obtained were 98% from ^{1}H NMR spectrum. Using the proportion of fatty acid methyl ester analysis such as 9,12-Octadecadienoic acid (Z, Z)-, methyl ester (48.379%), 9-Octadecenoic acid (Z)-, methyl ester

Table 5 XRD analysis result of raw nendran banana peel

2Ө	K-Constant	β-beta FWMH	Λ X-ray wavelength Å	Intensity in %	D-(size) Å
10.364380	0.8467	0.705600	1.54	10.63	8.52827
17.476430	0.8467	0.705600	1.54	68.96	5.07042
19.849830	0.2822	0.235200	1.54	33.83	4.46919
28.696420	0.2117	0.176400	1.54	100.00	3.10837
30.988330	0.2117	0.176400	1.54	76.02	2.88350
32.300010	0.7056	0.588000	1.54	81.85	2.76934
35.233830	0.8467	0.705600	1.54	29.16	2.54517
45.374820	0.8467	0.705600	1.54	56.75	1.99713
52.017590	0.2117	0.176400	1.54	83.23	1.75663
67.614480	0.2117	0.176400	1.54	27.99	1.38443
69.046800	0.2117	0.176400	1.54	45.39	1.35917
82.293600	0.8467	0.705600	1.54	35.09	1.17068

Table 6 XRD analysis result of calcinated nendran banana peel

2Ө	K-Constant	β-beta FWMH	λ-X-ray wavelength Å	Intensity in %	D-(size) Å
12.649930	0.2822	0.235200	1.54	9.82	6.99208
19.390000	0.2822	0.235200	1.54	6.13	4.57413
19.821500	0.3528	0.294000	1.54	2.03	4.47552
20.741460	0.4234	0.352800	1.54	6.08	4.27904
26.853870	0.2117	0.176400	1.54	9.11	3.31732
28.907770	0.2822	0.235200	1.54	100.00	3.08612
30.176770	0.4234	0.352800	1.54	8.84	2.95917
33.222500	0.4234	0.352800	1.54	29.34	2.69452
39.464480	0.7056	0.588000	1.54	4.91	2.28152
41.048710	0.8467	0.705600	1.54	12.95	2.19705
46.864690	0.2117	0.176400	1.54	17.24	1.93705
66.886380	0.8467	0.705600	1.54	2.37	1.39772
74.261150	0.8467	0.705600	1.54	4.60	1.27610
75.490620	0.4234	0.352800	1.54	7.87	1.25834
76.393750	0.4234	0.352800	1.54	3.98	1.24570
77.572040	0.2117	0.176400	1.54	8.66	1.22970

(30.559%), [31] noticed the effective conversion of biodiesel from used cooking oil. A specific fatty acid ethyl ester mixture is present in the biodiesel produced from waste cooking oil [35] which accounts for 94.05 weight percent of biodiesel synthesis. Methyl palmitate (65.85 wt %), methyl linoleate (20.65 wt %), and methyl oleate (5.5 wt %) are the primary methyl ester compositions accountable for the manufacturing of biodiesel depicted by the chromatogram. Relying on a comparison of the results with the prior discovery and the generated peaks of the methyl esters, we can affirm the existence of the biodiesel.

Conclusion

The increasing demand for an alternative renewable fuel inspired scholars and shareholders all over the world to carefully contemplate biodiesel, which is a promising renewable energy. Biodiesel is less polluting and more environmentally friendly, which makes it a more appealing source of energy. In this study, the biodiesel production was carried out by nendran banana peel using ultrasound assisted transesterification. Catalyst characterization of FTIR, and XRD shows the existence of K_2O, K_2CO_3, K_2SO_4, CaO, and $CaCO_3$ as dominant components present in them. NMR analysis was used to

Fig. 4 ^{1}H NMR spectra of biodiesel, when the catalyst is **A**) no exposed to air (NEA), **B**) exposed to air for 1 h **C**) exposure to air for 2 h **D**) exposure to air for 3 h

Table 7 Biodiesel conversion percentage obtained from 1H NMR analysis

Time of exposure to air	δ (ppm)	Peak shape	Peak area	Formula	Biodiesel production percentage
Zeroth hour	3.595 ppm	Triplet	1.96	$100 \times 2A_{ME} / 3A\alpha\text{-CH2}$	$72.5 \pm 2.14\%$
	2.241 ppm	Singlet	1.80		
First hour	3.624 ppm	Quartet	0.84		$26.5 \pm 0.96\%$
	2.265 ppm	Doublet	1.08		
Second hour	3.614 ppm	Singlet	3.45		$42.27 \pm 1.23\%$
	2.286 ppm	Quartet	5.44		
Third hour	3.633 ppm	Doublet	3.97		$40.16 \pm 1.87\%$
	2.299 ppm	Pentet	6.59		

determine the conversion efficiency of the biodiesel that was produced, and the results demonstrate that the catalyst without air exposure gave a higher yield percentage than the catalyst with air exposure. Also, the nendran banana peel catalyst has the advantage of slightly high withstandable stability even after extended exposure to air, when compared to the existing heterogeneous catalyst. According to these findings, the nendran banana peel ranks among the most effective heterogeneous catalysts for biodiesel synthesis due to its enhanced mass transfer reaction and negligible unwanted side reactions. However, research is still required to increase the stability of catalysts for a longer period.

Materials and methodology
Materials
The waste cooking oil (WCO) was gathered from the hostel kitchen in Bannari Amman Institute of Technology, Sathyamangalam, Tamil Nadu, (11.4970° N, 77.2771° E) and the Nendran banana peel (NBP) sample was collected from a nearby market at Sathyamangalam (11.5034° N, 77.2444° E). The collected WCO was kept in a hot air oven at 100 °C to remove the moisture until it reached a constant weight during the consecutive measurement. Potassium Hydroxide (KOH), 2-proponal, Potassium iodide (KI), Thiosulphate ($Na_2S_2O_3$), Hydrochloric acid (HCl) are purchased from Sigma Aldrich.

Physicochemical characteristics of waste cooking oil
The physicochemical characteristics of waste cooking oil were analysed using the accepted method, the American Society for Testing and Materials (ASTM D6751) and European Organization (EN 14214) standards. The moisture content of the oil is lost when the sample is heated at 105 ± 1 °C and weighed using a weighing balance. This method's focus is on measuring the amount of moisture in samples of used cooking oil. An analytical balance was used for weighing an oil sample in order to begin with the estimation of oil density. After that, the sample was put inside a gas pycnometer's cylindrical cell, which used an adsorbate gas (a high-purity helium gas) to determine the oil density in accordance with the Boyle and Mariotte law. The acid value can be used to figure out the quantity of acidic substances in biodiesel. Heating the 50 ml of 2-propanol solution almost to boiling point and adding a few drops of phenolphthalein, the mixture was combined with a 10 ml of oil sample and titrated against 0.1 M KOH at a steady 40 °C until a permanent light pink color was obtained. The consumption of KOH during the titration is measured to find the acid value [36]. The saponification value is to identify the oils and fats average relative chain length existing as triglycerides in the source. The oil sample weighed 0.002 kg and was placed in a volumetric flask. After that, 25 ml of 1.0N alcoholic KOH was pipetted into the mixture and let to drain for roughly a minute. This combination was given a 45-min gentle boil. and after adding 1 ml of phenolphthalein indicator, allowed to cool. 0.5N hydrochloric acid (HCl) was added to the solution and titrated until the pink hue vanished. The iodine value is used to assess how effectively diesel fuel is made from waste cooking oil. Wijs solution (25 ml) was added to 15 ml of carbon tetrachloride and 0.001 kg of oil sample. The solution was kept for stirring. 150 ml of distilled water was added to the solution followed by 20 ml of a 10% potassium iodide (KI). 0.1N thiosulphate ($Na_2S_2O_3$) solution was used to titrate the mixture until the yellow color nearly vanished. After adding 1.5 ml of starch indicator solution, the titration was carried out repeatedly until the blue color vanished [37]. It is related to oxidative potential representing fats or oil's capacity to oxidize in addition to polymerizing and generating engine deposits [38].

Catalyst preparation and characterization
The collected nendran peel was washed in deionized water and dried in the sunlight for 5 days. After the peel was completely dried, using the mixer the peel was powdered and stored in an air-tight container then the peel powder was kept in the muffle furnace for calcination reaction at 700 °C for 4 h as exhibited in Fig. 5 [30]. The

Fig. 5 Nendran banana peel powder **a**) before calcination **b**) after calcination at 700 °C

catalyst characterization was studied to analyze the surface area, and morphology, then to identify elements present in them.

Scanning Electron Microscope (SEM) analysis

The topography of a heterogeneous catalyst was examined using a Scanning Electron Microscope (SEM) (JEOL Model JSM—6390LV, Germany). Palladium was applied to the samples using a sputter coater, and they were then magnified between 500 and 3000X.

Fourier Transform Infrared Spectroscopy (FTIR) analysis

By generating an infrared absorption spectrum, the Fourier Transform Infrared Spectrometer (FTIR) (Thermo Nicolet, Avatar 370, USA) analyses the chemical bonds of molecules [39]. By preparing pellets of the sample (2 mg) with KBr (200 mg) in the region of 4000 cm^{-1} to 400 cm^{-1} with a magnification of 4 cm^{-1} and 25 scans per sample, an FTIR examination was performed. The spectra give sample profiles, or specific molecular fingerprints, that can be used to test them for various components [40].

X-ray powder diffraction (XRD) analysis

The degree of structural order in raw and calcinated banana peel was measured using an X-ray Diffractometer (XRD) (Bruker AXS D8 Advance, Germany) with Cu-Kα (1.54056 Å) radiation. The applied potential and current of 35 kV and 40 mA respectively. The X-ray diffractograms were scanned at 2°/min in the 2θ range of 3°–80° with a step size of 0.01°. One of the most popular uses for XRD analysis involves the determination of materials based on their diffraction pattern. XRD gives information about how the actual structure differs from the ideal one due to internal tensions and flaws, in addition to phase identification [41].

Transesterification reaction and biodiesel production

The catalyst is taken from the muffle furnace, and after that, it is exposed to air in various time intervals such as 1 h, 2 h, and 3 h, and some amount of catalyst is maintained without exposure to air that is no exposure to air (NEA). Transesterification reaction was carried out utilizing both exposed and unexposed catalysts. During ultrasound-assisted transesterification, ultrasonic waves create cavitation bubbles in the reaction mixture. When these bubbles collapse, they generate high temperatures and pressure locally. This leads to improved mixing and mass transfer between the reactants, promoting faster and more complete transesterification. When compared to the direct method of biodiesel production, the enhanced mixing and mass transfer achieved through ultrasonic waves reduce the reaction

time required for transesterification. This can contribute to higher productivity and efficiency in biodiesel production. This reaction took place in a three-necked round bottom flask. The ultrasound-based transesterification procedure was carried out using 30 ml of feedstock (waste cooking oil) and 15 ml of methanol with the addition of 0.7 g of catalyst. The methanol to oil ratio utilized in our study is 2:1. The stoichiometric molar ratio required for transesterification is typically 3:1 (3 mol of methanol for 1 mol of triglycerides). The 2:1 ratio is used to ensure excess methanol is present, promoting the complete conversion of triglycerides to biodiesel. The catalyst is essential for initiating and accelerating the transesterification reaction. The chosen amount of catalysts has been found to be sufficient for achieving a high level of catalytic activity and efficient conversion of triglycerides in the waste cooking oil to biodiesel. Upon addition of a catalyst will lead to a decrease in the produced biodiesel quality. The specific amount of catalyst (0.7 g) is also to minimize the excess cost of the reaction. The production was completed in the ultrasonic bath at 65 °C for 25 min. The collected biodiesel sample was poured using the Whatman 42 filter paper in the separating funnel to obtain the desired product. After 24 h, a clear phase separation was visible. The solid catalyst remained in the filter paper and the liquid portion was collected in the funnel separately. The top layer obtained was biodiesel and the bottom layer was glycerol. The difference among the biodiesel was noted for every catalyst sample and the characterization of biodiesel obtained for the catalyst samples was studied. Similar to this, the ester content of the biodiesel generated from WCO was examined using the ^{1}H NMR equation.

Biodiesel characterization
Biodiesel Yield calculation

$$\% \, Biodiesel \, Conversion \, Yield \; = \; 100 \; \times \; 2AME/3A \propto -CH2 \tag{1}$$

Where,

% Conversion = % of Fatty acid methyl ester (FAME) in biodiesel

AME = Peak area at 3.7 ppm corresponding to FAME of the methyl group in NMR micrograph,

Aα-CH$_2$ = Peak area at 2.3 ppm corresponding to FAME of the α-methylene group in NMR micrograph.

Combining the characterization methods and the aforesaid formula, the estimated rate of triglyceride and alcohol conversion to fatty acid methyl ester in the biodiesel produced. Biodiesel yield manufacturing is directly correlated with the conversion rate [42].

Nuclear Magnetic Resonance (NMR) analysis

Organic molecules were studied utilizing nuclear magnetic resonance (NMR) spectroscopy (Bruker AMX 400 NMR), recording the 1H (operating at 400.13 MHz). Each peak's surrounding area showed the numerous protons available in a certain environment [43].

Gas chromatography-mass spectrometry (GC–MS) analysis

The Elite-5MS (5% biphenyl 95% dimethylpolysiloxane, 30 m 0.25 mm ID 250 m df) was loaded into a fused silica column for the Clarus 680 GC analysis, and the contents were segregated using Helium as the carrier gas with a steady flow of 1 ml/min. 260 °C was the injector temperature for the chromatographic cycle. The sample preparation is made by mixing 1:5 ratio of biodiesel with hexane and filtering using a 0.2 μm pore size syringe filter to avoid particulate matter stuck during the analysis. When the 1L of extract sample was added to the apparatus, the furnace's temperature was set to the following: After reaching 60 °C for 2 min, 300 °C was reached at a rate of 10 °C min^{-1}, and 300 °C was maintained for 6 min. Parameters for the mass detector included 240 °C transfer line and ion source temperatures, 70 eV electron collision in the ionization mode, 0.2 s scan time, and 0.1-s scan interval. The fragments were between 40 and 600 Da. The acquired band intensity and the number of bands indicated the quantity of analytes and compounds in the mixture, respectively when the component spectra were referenced to the library's GC–MS NIST (2008) database of known component spectra.

Abbreviations

WCO	Waste Cooking Oil
NBA	Nendran Banana Peel
NEA	No Exposure to air
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
HCl	Hydrochloric acid
KI	Potassium iodide
$Na_2S_2O_3$	Thiosulphate
ASTM	American Society for Testing and Materials
EN	European Organization
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray diffraction
FAME	Fatty acid methyl ester
NMR	Nuclear Magnetic Resonance Spectroscopy
GCMS	Gas Chromatography-Mass Spectroscopy
NIST	National Institute of Standards and Technology" library
α-CH_2	alpha-methylene proton
JCPDS	Joint Committee on Powder Diffraction Standards
Ca-O	Calcium Oxide
K-O	Potassium Oxide
K_2CO_3	Potassium Carbonate
$CaCO_3$	Calcium Carbonate
$CaMgSiO_4$	Calcium Magnesium Silicate
K_2SO_4	Potassium Sulphate
SiO_4	Silicate

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