Article

Biodiesel Synthesis from Coconut Oil Using the Ash of *Citrus limetta* Peels as a Renewable Heterogeneous Catalyst

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Abstract: The synthesis of biodiesel can be achieved using either homogeneous or heterogeneous catalysts. Given the non-renewable nature of homogeneous catalysts, heterogeneous catalysts are increasingly preferred for biodiesel production. Agricultural wastes serve as a viable source for these heterogeneous catalysts, contributing to environmental sustainability. This study introduces a novel, eco-friendly, cost-effective, and efficient heterogeneous catalyst that was developed and derived from *Citrus limetta* peels for biodiesel production. The catalyst was thoroughly characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffractograms (XRD), Field Emission Scanning electron microscopy (FESEM), and energy-dispersive X-ray (EDX). Coconut oil, a rich and renewable resource, was used as the feedstock for the biodiesel synthesis. The conversion process was confirmed by ^{1}H NMR, IR spectra, mass spectra, and ^{13}C NMR of the biodiesel. The developed method using the *Citrus limetta* peel-derived catalyst demonstrated a 100% yield. The results show the optimum conditions for biodiesel synthesis are 1 *w/v* (for the catalytical dose), with a 6:1 methanol/oil ratio at 60 °C for 3 h. The synthesized biodiesel exhibited a high cetane value of 54, contributing to improved ignition and reduced engine noise. Its sulfur-free composition, boiling point of 294 °C, high viscosity of 2.5 mm^2/s, acid value of 0.09 mgKOH/g, and flash point of 142 °C enhance its environmental profile. The catalyst can be used for up to five cycles, underscoring its potential as a cost-effective and sustainable approach for biodiesel production.

Keywords: biodiesel; calcined; sweet lime peels; transesterification; heterogeneous acid catalyst; waste biomass

1. Introduction

Every country in this world is putting its best foot forward to provide all the leisure possible to its residents. Various anthropological activities, the continuous rise in population level, and various other factors have taken a toll on the environment. One such factor is fossil fuels; fossil fuels are being reduced at a high pace. The use of fuels such as petrol and diesel is extremely toxic to the environment. As a result, there is a need for alternative and suitable sources of energy that can meet the global demand and should not be toxic to the environment [1,2]. Researchers around the globe are working on alternative sources of energy that can decrease the release of greenhouse gases. The production and use of biodiesel can be taken as a healthy substitute, as compared to traditional sources of energy [2–6].

Biodiesel can be used as an alternative source of petrol or diesel as it is eco-friendly, recyclable, and less poisonous for the environment. Due to the absence of sulfur content, and less releasing of greenhouse gases and particulate matter, biodiesel enhances the engine's life [7–10]. Chemically, biodiesel is known as a fatty acid methyl ester (FAME) and is prepared by the reaction of feedstock i.e., oil dissolved in solvent (generally alcohol), while using acidic or basic catalysts (Figure 1) [11]. Biodiesel has already been prepared by using various homogeneous and heterogeneous catalysts.
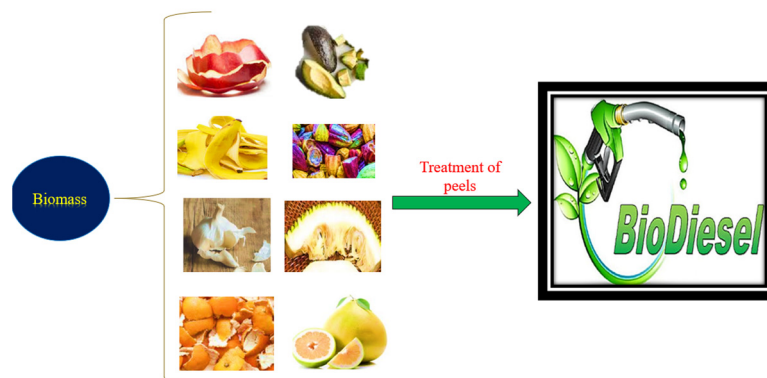
Figure 1. Biodiesel synthesis using different waste biomass in literature.

The homogenous catalysts that are used for the synthesis of biodiesel are KOH, Al_2O_3, NaOH [12,13], etc. When a homogeneous catalyst is used for biodiesel synthesis, the reaction is fast and can reach a high conversion rate quickly. However, it has significant flaws. The catalyst needs to be neutralized and removed as soon as the reaction is finished, since it cannot be retrieved or renewed [14]. Moreover, homogenous catalyst separation from products is a difficult and time-consuming procedure. Consequently, this will require additional equipment, which will increase the capital cost. In the end, this will result in a large amount of wastewater being produced during the purification phase [15,16].

Heterogeneous catalysts have grabbed a lot of attention in recent times. There are lots of heterogeneous catalysts that can be used for the production of biodiesel, for example Zinc oxide (ZnO)-supported silver (Ag) nanoparticles [17], *Ficus carica* leaves [18], and barium cerate [19].

Numerous types of waste cooking oil, vegetable oils, animal waste, etc., can be used as feedstock [20]. The reaction for the synthesis of biodiesel is a transesterification reaction as shown in Figure 2.
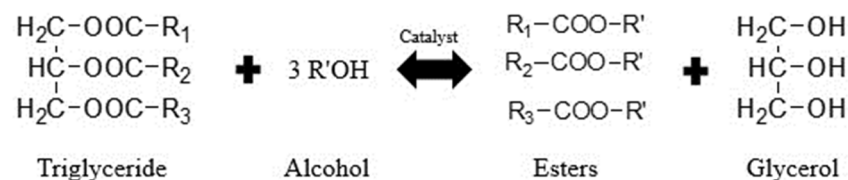

Figure 2. Transesterification reaction for biodiesel synthesis.

Researchers have been working on the synthesis of biodiesel for a very long time. In recent years, various vegetables and fruit peels have been used as heterogeneous catalysts for the production of biodiesel. B. Karmkar et al. in 2018 synthesized biodiesel from castor oil using two catalysts: concentrated sulfuric acid and sulfonated biochar of *Mesua ferrea* Linn seed shells. The biodiesel obtained from concentrated sulfuric acid had a greater yield of 90.83% as compared to sulfonated biochar, with 71.53% [21]. E.K.L. Mares et al. in 2021 synthesized biodiesel using calcined Acai seeds as the catalyst. The biodiesel was obtained with a 92.5% yield using soybean oil [22]. M.G. Nayak et al. synthesized biodiesel using non-edible oil i.e., Argemone Mexicana oil, in 2022. Biodiesel was synthesized with the help of a transesterification reaction, and the resultant product had a yield of 99.03% [23]. G. Yadav et al. (2022) have synthesized biodiesel using sweet lime peels. The treatment of the peels was performed using concentrated sulfuric acid. The reaction of biodiesel turns out to be acid-catalyzed. Oleic acid, along with methanol, reacted with the catalyst (acid-treated sweet lime peels), which helped in the synthesis of a 96% yield of biodiesel [24]. A. Aziz et al. (2023) used a phyto-nanocatalyst obtained from seed (*Citrullus colocynthis*) for the production of biodiesel. Various conditions were set, and the maximum yield of synthesized biodiesel obtained was 95% [25].

Sweet lime (*Citrus limetta*), a popular citrus fruit for juice, produces significant amounts of peel waste. Peels of fruits such as sweet lime pose a challenge for waste management due to their rapid decomposition. Therefore, the peels can be used in various fields of research, such as sensing, biomedical, and many more [26]. This research paper focuses on the synthesis of biodiesel using *Citrus limetta* peels as a catalyst, using coconut oil for the transesterification reaction. The use of coconut oil not only enhances the sustainability aspect but also leverages its high saturated lipid content (about 91%), ensuring an efficient conversion process by giving it excellent oxidative stability against any bacterial growth and a high cetane number, which is an indication of enhanced combustion (being easy to burn) and an excellent acceleration response (to start the engine when cold), as compared to biodiesel derived from any other vegetable oils. Coconut oil has a lower free fatty acid (FFA) content and has a major compound (~60%), a medium-chain triglyceride (MCTG) of lauric acid, and a C12 carbon chain length, due to which it can be expected to a better raw material for biodiesel formation due to its excellent solvency or solubility (it will not allow the fuel line to deposit a lot of carbon-related impurities, as it can dissolve most of the components) when compared to non-edible oils or used cooking oils that have higher-chain-length triglycerides. Biodiesel is a "diesel-like" fuel, which means it has properties similar to a conventional diesel and hence it can be used in the same way in both land transport and stationary engines, giving at least the same or better efficiency as that of a normal diesel. Other advantages associated with coconut oil are an almost zero sulfur content and no aromatic compound content associated with the biodiesel derived from it, as compared to normal diesel that has a lot of sulfur content and 20–40% aromatic hydrocarbons, which put a lot of carbon content into the environment while burning. Biodiesel derived from coconut has a better lubricity and a similar flash point to that of the actual diesel fuel, so it can be an alternative to actual diesel [27–29].

In this study, calcined sweet lime peels were used as a catalyst for biodiesel synthesis. The key advantage of this study is that it requires waste biomass for the synthesis. The calcination of peel is an eco-friendly process that results in excellent catalytic properties. The catalytical property of Citrus limetta was evaluated through a transesterification reaction for the conversion of biodiesel. This method requires 60 °C for the reaction, with a 100% conversion to biodiesel. The properties of the catalyst were studied using X-ray diffraction (XRD), Field Emission Scanning electron microscope (FESEM), Fourier-transform infrared spectroscopy (FTIR), and electron-dispersive X-ray spectroscopy (EDS). The characterization of the biodiesel was conducted using proton NMR, (^{1}HNMR), carbon NMR (^{13}CNMR), and mass spectroscopy. Research on *Citrus limetta* as a biodiesel catalyst is limited, even though its chemical composition suggests potential.

2. Result and Discussion

2.1. Optimization of Reaction Parameters

2.1.1. Catalyst Amount Effect

Biodiesel was produced by a transesterification reaction using coconut oil and CCLP as catalysts. Optimum conditions were set, as this reaction was performed for 3 h at 60 °C with different amounts of catalyst, ranging from 0.25 to 1.5 g. The methanol and oil molar ratio was set to 6:1. Below, Figure 3 indicates that when the catalyst was low in amount, the conversion (%) achieved was also low, which may be due to less available basic sites. A conversion of 100%, i.e., the maximum, was observed when the catalyst dose was increased (when 1–1.5 g of catalyst was added). This may be due to the presence of a high availability of basic groups present on the catalyst. The rise in catalyst dose increased the FAME until a certain level, but once it reached the optimum level; the yield of FAME remained constant [27].
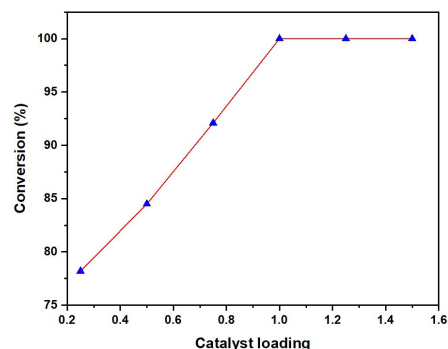
Figure 3. Catalyst dose effect on FAME conversion.

2.1.2. Methanol/Oil Molar Ratio Effect

Various ratios of methanol/oil reactions for biodiesel synthesis were studied. The reaction was set at optimum conditions—1 *w/v*% of CCLP catalyst dose at 60 °C for 3 h. Figure 4 shows a reduced yield, i.e., 75.4%, when the methanol/oil ratio was less, i.e., 3:1, which may be as a result of the reactants and the CCLP catalyst interacting less [28]. Further, a 100% conversion was observed in the 6:1 and 9:1 methanol/oil ratios. When the ratio of methanol and oil is high, the transesterification reaction takes place in the forward direction; in other conditions, reversible transesterification can also take place [29]. Biodiesel is formed via a transesterification reaction which is an equilibrium reaction that can be base-catalyzed. There was a reduction in conversion for 12:1, due to the reverse transesterification reaction. High methanol might have led to the formation of monoglycerides and diglycerides as the product, which ultimately decreased the yield of the FAME [30].
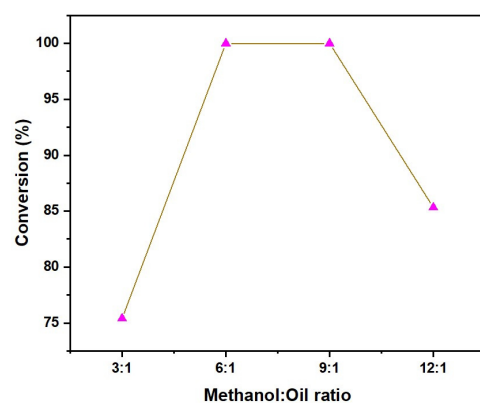

Figure 4. Methanol/oil effect on FAME conversion.

2.1.3. Reaction Time Effect

The most favorable conditions were set above, i.e., 1 *w/v*% for the CCLP catalyst dose, 60 °C for 3 h; the methanol to oil ratio was set. The reaction was set for 5 h and was continuously monitored after every hour. Within the first hour, only a 68.66% conversion was obtained. Figure 5 shows that the reaction was completed within 3 h. This finding may be the result of sufficient contact time between the reactants and the CCLP catalyst.
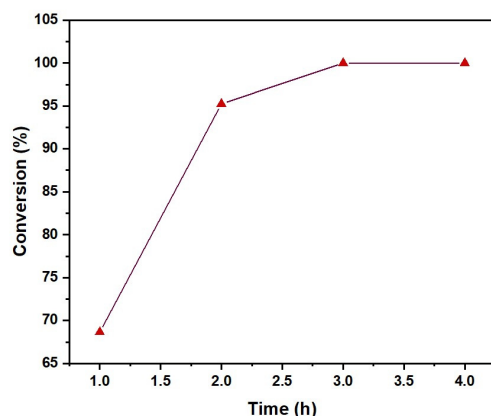
Figure 5. Time effect on FAME conversion.

2.1.4. Heterogeneity Effect

In the past, there were many catalysts which were used for biodiesel synthesis. These catalysts might not be reusable i.e., these catalysts were homogeneous in nature. To determine whether the catalyst may be reused, CCLP was used for the synthesis of biodiesel within optimum conditions, and the same catalyst was used again and again to obtain the product. This process of reusability was checked using TLC, and finally, the percentage conversion was noted, which is depicted below in Figure 6.
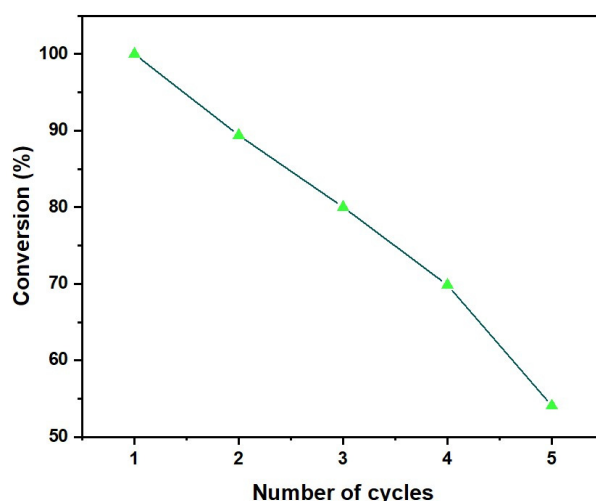

Figure 6. Several cycles affect FAME conversion.

The observed decline in percent conversion across repeated cycles can be due to various factors; it can be due to catalyst loss at the time of transfer. Another reason could be the alteration of catalytic properties upon reuse. Additionally, catalyst leaching may decrease the conversion by reducing the active sites and might lead to the contamination of the glycerol phase [31]. The substantial loss from the catalyst of K and Ca ions is due to leaching over repeated cycles, as revealed in EDS studies. K and calcium were lost due to their susceptibility to leaching.

Figure 7a shows the catalyst's nature. The XRD data of the catalyst show that the catalyst is 65.7% crystalline in nature and 34.3% amorphous in nature. Not much is known in the literature about CCLP catalysts. The predominant species formed after the calcining of the sweet lime peels were oxides and carbonates. The presence of CaO was confirmed at $2\theta = 30, 39, 43,$ and 47 (JCPDS reference code 01-085-0514). Due to leaching, the intensity of the peak at 2θ at $30°$ drastically decreases (Figure 7b).
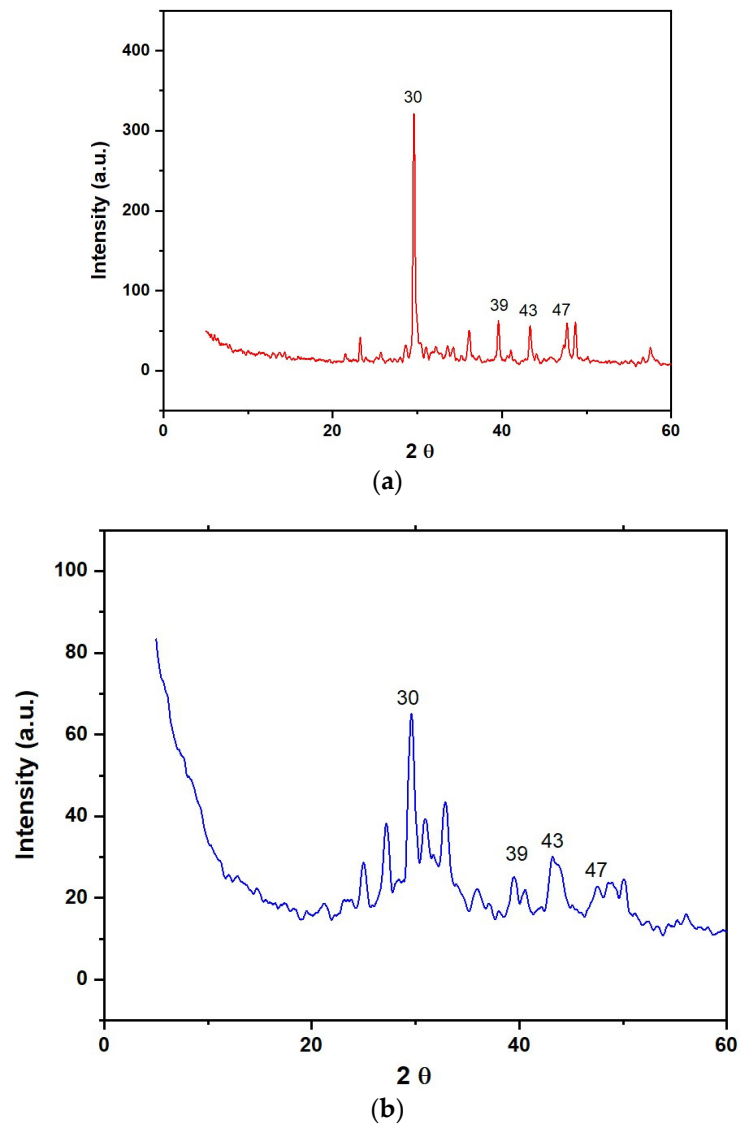
Figure 7. XRD data of (**a**) fresh catalyst and (**b**) catalyst after multiple cycles.

The surface morphology was studied using FESEM. Through FESEM (Figure 8), the surface of the catalyst appears porous and rough, having a lot of spaces, and looks like a rectangular fiber-like structure.
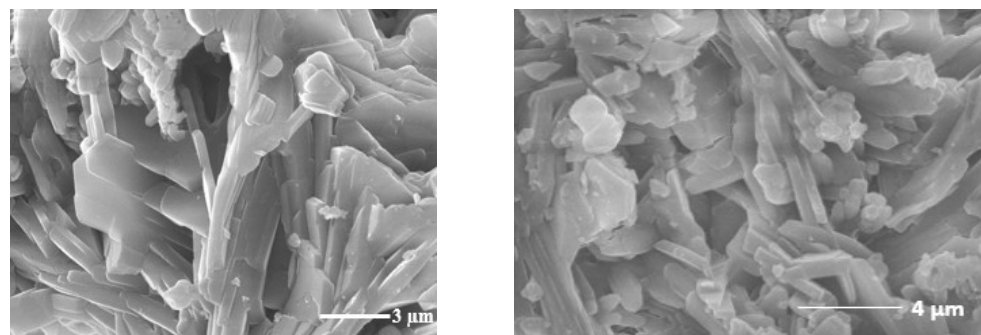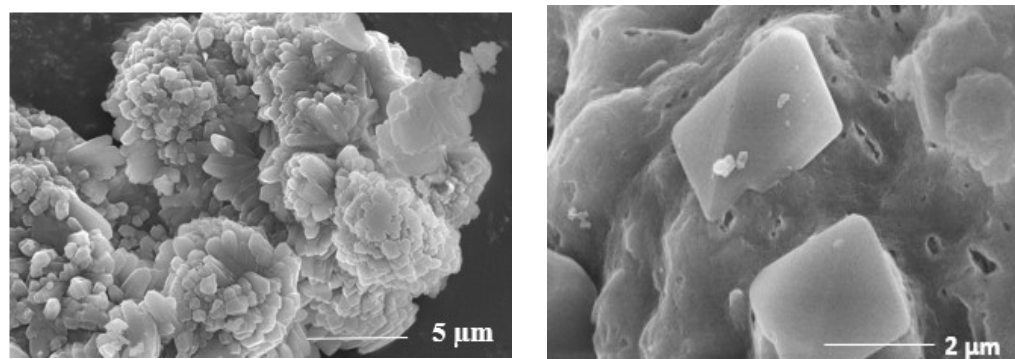

Figure 8. *Cont*.

Figure 8. FESEM data of CCLP.

The elements present in the catalyst are calcium (36.54%), oxygen (31.41%), potassium (6.45%), and phosphorous (1.47%) as depicted in Figure 9.
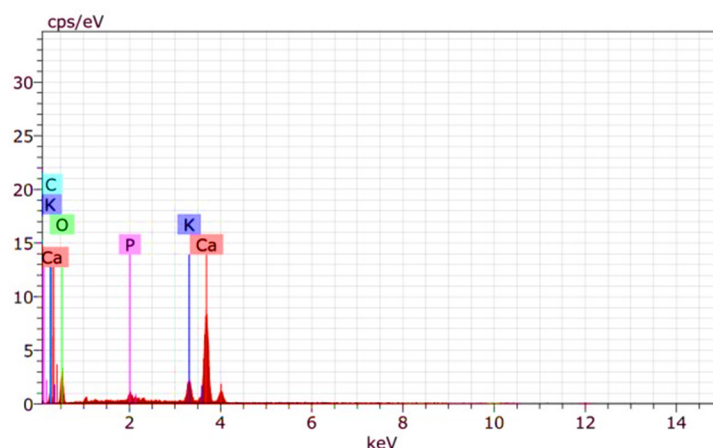

Figure 9. EDS of the catalyst.

Biodiesel formation was confirmed by various spectral data like IR, Mass, ^{1}H NMR, and ^{13}C NMR. The FTIR spectrum of the biodiesel is shown in Figure 10c. The intense bands around 2923 and 2855 cm^{-1} show the C-H bond stretching, and a strong peak around 1114 cm^{-1} was observed due to C-O stretch. A strong methyl ester C=O stretching band at 1742 cm^{-1} depicts the presence of an ester bond, i.e., biodiesel formation. Figure 10a depicts the fresh catalyst, which shows the presence of C-H stretching at 2914 cm^{-1}. A strong peak around 1386 cm^{-1} confirms the K_2CO_3 presence, and it reduces in Figure 10b, which depicts the reduction in functional groups after multiple uses of the catalyst are reported, due to the leaching of the catalyst. The disappearance of C-H stretching and C=O stretching shows the absence of an ester bond.

Biodiesel was synthesized from coconut oil. Coconut oil has lauric acid, which participates in biodiesel synthesis [32]. Lauric acid's chemical name is dodecanoic acid ($C_{12}H_{24}O_2$). Lauric acid, when reacting with methanol, will form the methyl ester of lauric acid or methyl laurate, with the molecular formula $C_{13}H_{26}O_2$. Below, Figures 11 and 12 depict the molecular structure and mass spectra of the methyl ester of lauric acid with a molecular weight 214. Mass data are taken in ESI (−ve mode). The molecular ion peak, which is not visible in the data, might be due to the unstable nature of the ESI (−ve mode). A fragment around 199.2 depicts the $CH_3(CH_2)_{10}COO^-$ ion (M-CH$_3$$^+$). A peak around 183.2 depicts the $CH_3(CH_2)_{10}CO^-$ fragment (M-OCH$_3$$^+$).
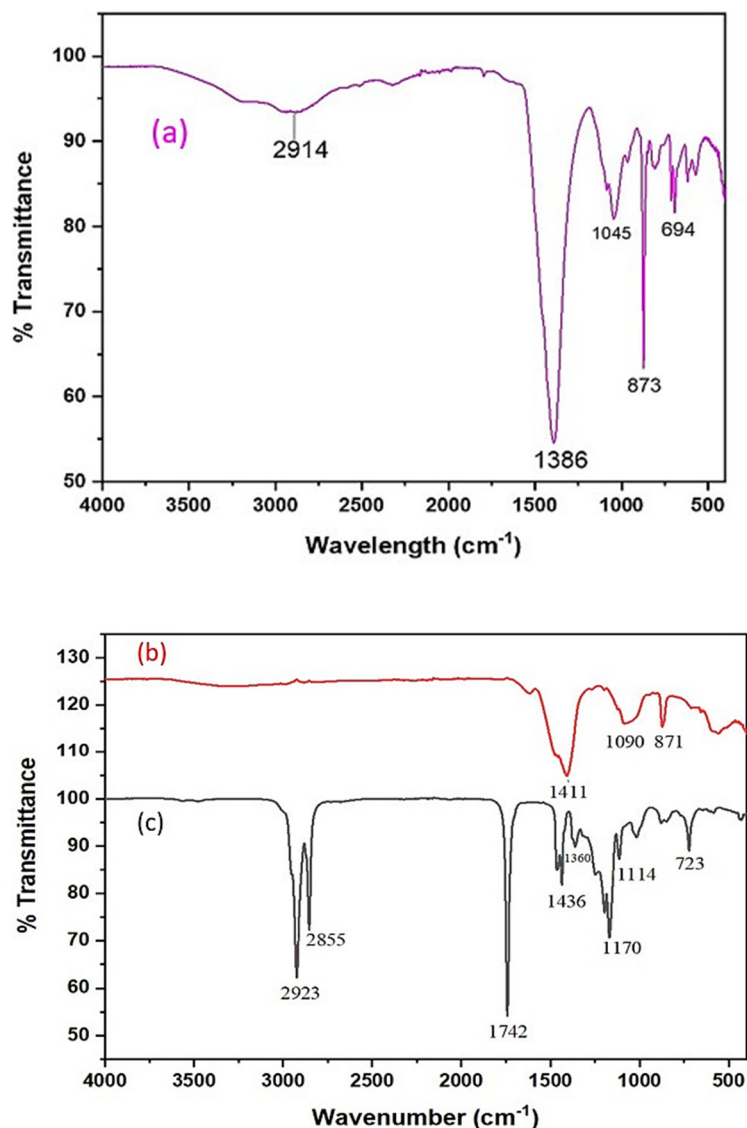
Figure 10. IR data of (**a**) fresh catalyst, (**b**) catalyst after leaching, and (**c**) synthesized biodiesel.
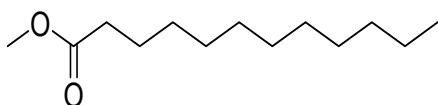

Figure 11. Lauric acid is present in coconut oil.

The ^{1}H NMR data of the biodiesel formed are depicted in Figure 13. The effective synthesis of FAME is demonstrated by the existence of a signal at 3.67 ppm in the ^{1}H NMR spectra, which is attributed to methoxy protons. The ^{1}H NMR (500 MHz, CDCl$_3$) shows δ = 3.63 (s, 3H), 2.27 (t, J = 10 Hz, 2H), 1.27–1.23 (m, 18H), and 0.85 (t, J = 7 Hz, 3H). For further confirmation, ^{13}C NMR data were collected (Figure 14). A strong signal at 50.35 ppm indicates the presence of a methoxy group, which confirms biodiesel formation. The ^{13}C NMR (500 MHz, CDCl$_3$) gives 173.25, 50.35, 33.10, 30.93, 28.70, 28.67, 28.62, 28.47, 28.37, 28.35, 28.28, 23.96, and 21.69.
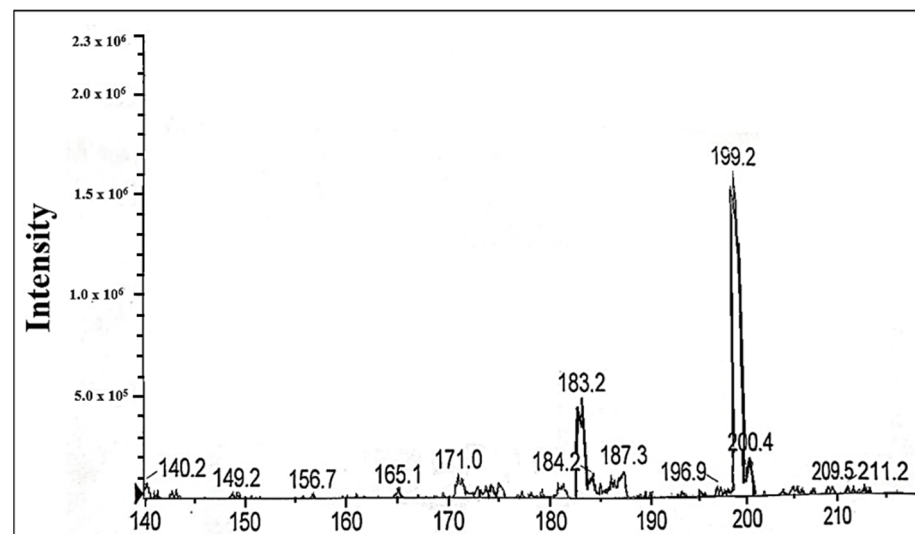
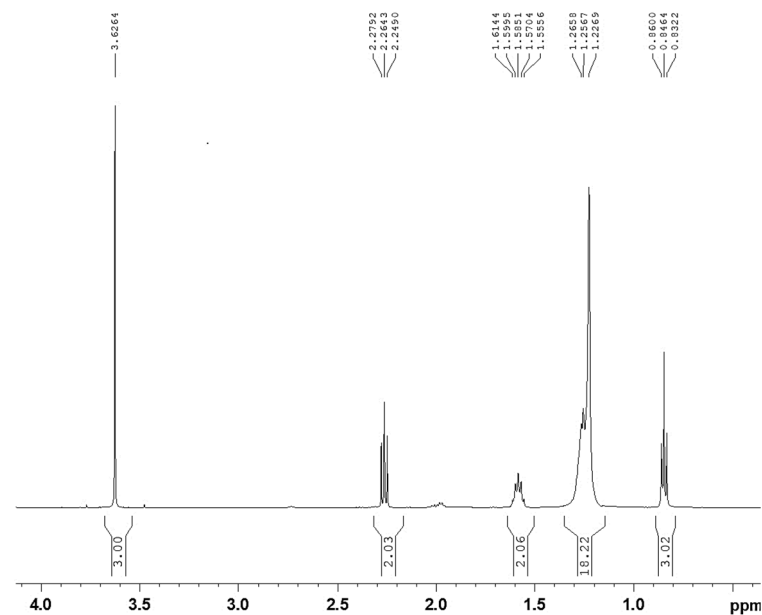**Figure 12.** Mass spectra of synthesized biodiesel.

Figure 13. ^{1}H NMR data of biodiesel.

Various properties of biodiesel were studied, as reported in Table 1. The cetane number was calculated using Bunyakiat et al. [33].

Table 1. Properties of synthesized biodiesel.

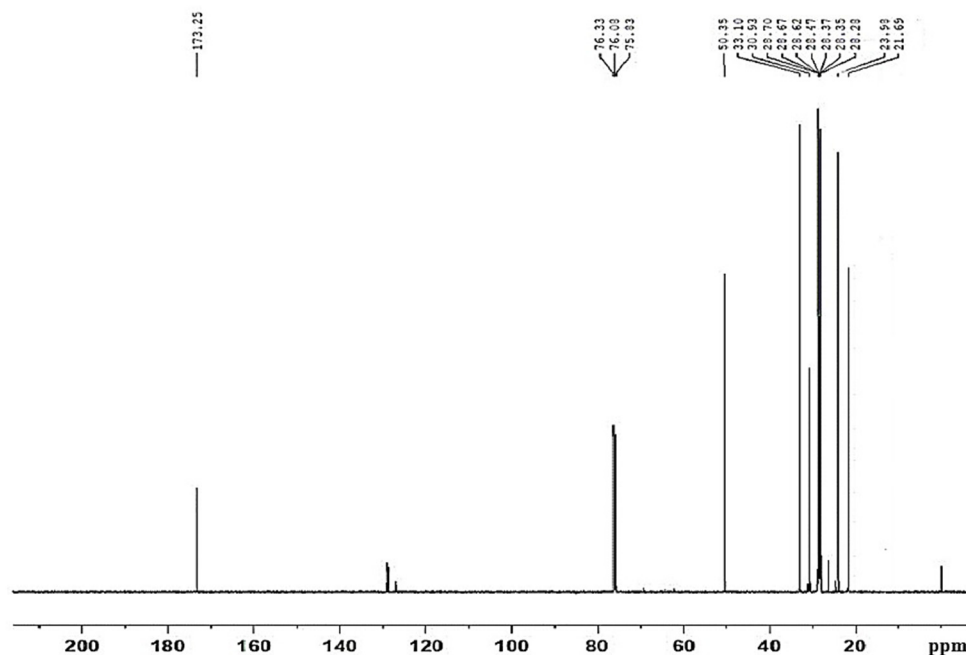| Properties	Biodiesel	ASTM D 6751 [34]
Density (g)	0.87	0.86–0.90
Viscosity (mm^2/s)	2.5	1.9–6.0
Flashpoint (°C)	142	93 min
Cetane number	54	Above 46
Heating value (MJ/kg)	43.1	-
Boiling point (°C)	294	-
Oxidation stability	3 h	3 h
Acid value (mg KOH^{-1} g)	0.09	<0.80

Figure 14. ^{13}C NMR data of synthesized biodiesel.

3. Experimental

3.1. Materials and Methodology

The *Citrus limetta* peels were procured from local juice shops in Mohali, Punjab, India. The coconut oil was purchased from the local grocery shop. The chemicals used in this research were bought from Loba Chemie Pvt. Ltd. (Mumbai, Maharashtra, India) and were used without purification. The FTIR analysis was performed using an FTIR spectrophotometer, the Perkin Elmer, PE 1600 spectrophotometer (Waltham, MA, USA), with a wavelength range between 400–4000 cm^{-1}. Further, the XRD, i.e., X-ray diffractogram, of the calcined *Citrus limetta* peels (CCLPs) was recorded using a Bruker (Billerica, MA, USA) D8 Advance diffractometer. The mass spectrometry was studied with the help of an Agilent (Santa Clara, CA, USA) G6530AA (LC-HRMS-Q-TOF) mass spectrometer. The catalyst morphology was studied with the help of FESEM (Hitachi, SU8010 Series, Tokyo, Japan), and the EDS analysis was conducted using a Bruker X Flash 7 T. The proton and carbon NMR were studied using a Bruker Advance Neo 500 MHz FT-NMR spectrometer, Fällanden, Switzerland (Model: Avance-II 500 MHz).

3.2. Catalyst Preparation

Citrus limetta peels were washed multiple times with distilled water. These peels were washed and then oven-dried for 12 h at 80 °C. These peels were crushed, and powdered sweet lime peels were obtained. Now, these peels were kept for calcination in a muffle furnace for 4 h at 700 °C. Brown powdered sweet lime peels had now turned into white powder. The catalyst prepared was called calcined *Citrus limetta* peels (CCLPs) [30,32,35]. There are various organic groups and metal ions present in the catalyst as stated in Figure 15.

Figure 15. Metals present in CCLP.

3.3. Procedure for the Synthesis of Biodiesel

The solution of methanol and oil is immiscible; therefore, an agitation speed of 500 rpm (revolutions per minute) was maintained to guarantee adequate mixing. A 100 mL two-necked round-bottom (R.B.) flask containing 50 mL of coconut oil was heated to 100 °C to eliminate any remaining moisture that may have been absorbed. The methanol to coconut oil molar ratio that must be reached, as well as the CCLP catalyst's loading (1 *w/v*%), were added once the temperature had cooled to 60 °C. The reaction was heated at 60 °C for about 3 h (Figure 16).
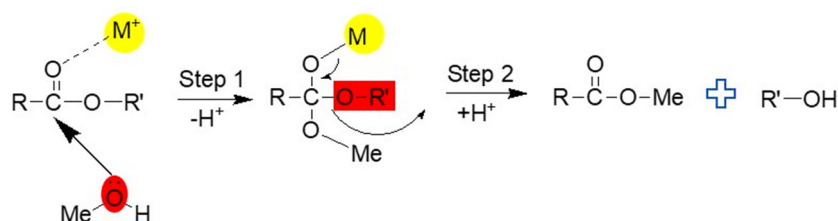

Figure 16. Metal interaction with triglyceride.

The reaction mixture was cooled to room temperature, and on standing in the separatory funnel for 2–3 h, 3 layers were observed. The reaction liquid could be divided into 3 layers: catalyst (bottom), middle-layer glycerin, and FAME (top). The upper layer was poured into different flasks, and the unreacted methanol was removed using a rotary evaporator, to give biodiesel. The residual lower layer, from where the catalyst was removed, was extracted 2–3 times with ethyl acetate, and the mixture was dried over anhydrous sodium sulfate to produce more biodiesel, after the evaporation of the ethyl acetate on a rotary evaporator.

$$\text{Yield of biodiesel} = \frac{\text{Weight of FAME}}{\text{Weight of Lauric Acid}} * 100 \tag{1}$$

3.4. Plausible Mechanism

Step 1: Interaction of metal (from CCLP) with triglyceride which is present in coconut oil (Figure 16).

Step 2: Catalyst acting like an enzyme, holding both of the substrates together (Figure 17).

During Step 1 of the reaction, triglyceride will react with methanol in the presence of CCLP as a catalyst. The catalyst has many metal ions, i.e., it is electrophilic in nature, so it will try to form bonds with nucleophilic species like the oxygen (divalent) of lauric acid, as well as the oxygen of methanol. Since oxygen is electronegative in nature and metal is electropositive in nature, it will lead to an interaction between them which further results in the breakage of the double bond between carbon and oxygen. As carbon becomes more electropositive, it will bind with the OCH_3 group of the methanol. In Step 2, the methyl ester of lauric acid is formed by the formation of a double bond between carbonyl groups and the elimination of O-R'. As a result, biodiesel will be produced, with glycerol emerging as a byproduct.
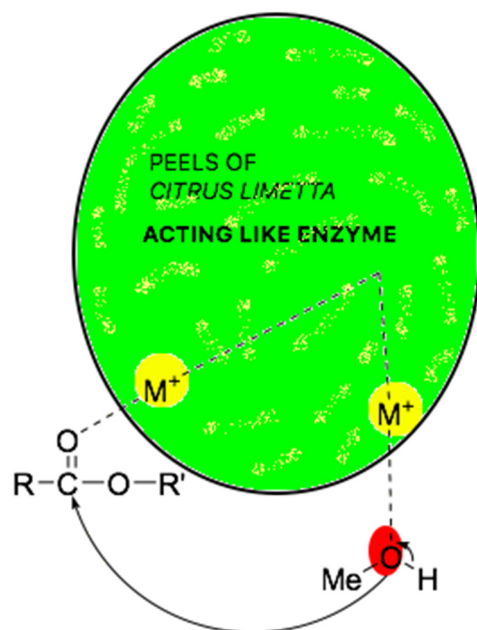
Figure 17. The enzymatic action of the catalyst.

4. Conclusions

The biodiesel was synthesized using the heterogeneous catalyst calcined *Citrus limetta* peels (CCLPs). The catalyst used in the reaction is a waste material that is available throughout all the seasons. This transesterification reaction was completed within 3 h, i.e., it is time-saving, conversion takes place at an easily achievable temperature (60 °C), and the yield is 100%. The chemicals used in the reaction were basic, and this process can be commercialized. The calcined catalyst has a porous and rough structure which gives a high catalytical activity, and it is heterogenous. The synthesized biodiesel exhibited no sulfur content and a high cetane value of 54, leading to significantly improved engine performance, demonstrating the effectiveness of CCLP as compared to the other paper reported in Table 2. However, the biodiesel's viscosity and acid value require further evaluation for optimum engine performance and long-term stability. In the future, various waste biomasses can be used for the synthesis of biodiesel, which will be not only environmentally friendly but will also give a greater yield of biodiesel.

Table 2. CCLP comparison with other heterogeneous catalysts obtained from waste biomass.

Feedstock Oil	Catalyst	Catalyst Loading (wt%)	Methanol: Oil	Time (Hours)	Temperature (°C)	Conversion (%)	References
Waste cooking oil	Zeolites	1.5	9:1	2	60	93	[36]
Camelina sativa oil	Waste shell	1	12:1	3	65	Lobster shell—90% Eggshell—97.2%	[37]
Waste cooking oil	Citrus limetta peels	5	20:1	3	70	96	[24]
Coconut oil	CCLP	1	6:1	3	60	100	Present Work

Author Contributions: P.K.: Writing, Conceptualization, Methodology, Formal Analysis, and Investigation. G.K.: Conceptualization, Supervision, Review and Editing, Investigation. I.H.: Conceptualization, Supervision, Methodology, Data Curation, Review and Editing. All authors have read and agreed to the published version of the manuscript.

References

1. Arumugam, A.; Ponnusami, V. Biodiesel production from *Calophyllum inophyllum* oil a potential non-edible feedstock: An overview. *Renew. Energy* **2019**, *131*, 459–471. [CrossRef]
2. Sandouqa, A.; Al-Hamamre, Z.; Asfar, J. Preparation and performance investigation of a lignin-based solid acid catalyst manufactured from olive cake for biodiesel production. *Renew. Energy* **2019**, *132*, 667–682. [CrossRef]
3. Sánchez-Cantú, M.; Téllez, M.M.; Pérez-Díaz, L.M.; Zeferino-Díaz, R.; Hilario-Martínez, J.C.; Sandoval-Ramírez, J. Biodiesel production under mild reaction conditions assisted by high shear mixing. *Renew. Energy* **2019**, *130*, 174–181. [CrossRef]
4. Eldiehy, K.S.H.; Bardhan, P.; Borah, D.; Gohain, M.; Rather, M.A.; Deka, D.; Mandal, M. A comprehensive review on microalgal biomass production and processing for biodiesel production. *Fuel* **2022**, *324*, 124773. [CrossRef]
5. Ghosh, N.; Halder, G. Current progress and perspective of heterogeneous nanocatalytic transesterification towards biodiesel production from edible and inedible feedstock: A review. *Energy Convers. Manag.* **2022**, *270*, 116292. [CrossRef]
6. Zhao, C.; Chen, H.; Wu, X.; Shan, R. Exploiting the Waste Biomass of Durian Shell as a Heterogeneous Catalyst for Biodiesel Production at Room Temperature. *Int. J. Environ. Res. Public Health* **2023**, *20*, 1760. [CrossRef]
7. Dehkhoda, A.M.; West, A.H.; Ellis, N. Biochar based solid acid catalyst for biodiesel production. *Appl. Catal. A Gen.* **2010**, *382*, 197–204. [CrossRef]
8. Monteiro, M.R.; Ambrozin, A.R.P.; Lião, L.M.; Ferreira, A.G. Critical review on analytical methods for biodiesel characterization. *Talanta* **2008**, *77*, 593–605. [CrossRef]
9. Monteiro, M.R.; Ambrozin, A.R.P.; da Silva Santos, M.; Boffo, E.F.; Pereira-Filho, E.R.; Lião, L.M.; Ferreira, A.G. Evaluation of biodiesel–diesel blends quality using 1H NMR and chemometrics. *Talanta* **2009**, *78*, 660–664. [CrossRef]
10. Gonzaga, F.B.; Sobral, S.P. A new method for determining the acid number of biodiesel based on coulometric titration. *Talanta* **2012**, *97*, 199–203. [CrossRef]
11. Hamza, M.; Ayoub, M.; Shamsuddin, R.B.; Mukhtar, A.; Saqib, S.; Zahid, I.; Ameen, M.; Ullah, S.; Al-Sehemi, A.G.; Ibrahim, M. A review on the waste biomass derived catalysts for biodiesel production. *Environ. Technol. Innov.* **2021**, *21*, 101200. [CrossRef]
12. Shinde, K.; Kaliaguine, S. A Comparative Study of Ultrasound Biodiesel Production Using Different Homogeneous Catalysts. *ChemEngineering* **2019**, *3*, 18. [CrossRef]
13. Sree, J.V.; Chowdary, B.A.; Kumar, K.S.; Anbazhagan, M.P.; Subramanian, S. Optimization of the biodiesel production from waste cooking oil using homogeneous catalyst and heterogeneous catalysts. *Mater. Today Proc.* **2021**, *46*, 4900–4908. [CrossRef]
14. Wang, J.; Mu, M.; Liu, Y. Recycled cement. *Constr. Build. Mater.* **2018**, *190*, 1124–1132. [CrossRef]
15. Marinković, D.M.; Stanković, M.V.; Veličković, A.V.; Avramović, J.M.; Miladinović, M.R.; Stamenković, O.O.; Veljković, V.B.; Jovanović, D.M. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. *Renew. Sustain. Energy Rev.* **2016**, *56*, 1387–1408. [CrossRef]
16. Ling, J.S.J.; Tan, Y.H.; Mubarak, N.M.; Kansedo, J.; Saptoro, A.; Nolasco-Hipolito, C. A review of heterogeneous calcium oxide based catalyst from waste for biodiesel synthesis. *SN Appl. Sci.* **2019**, *1*, 810. [CrossRef]
17. Laskar, I.B.; Rokhum, L.; Gupta, R.; Chatterjee, S. Zinc oxide supported silver nanoparticles as a heterogeneous catalyst for production of biodiesel from palm oil. *Environ. Prog. Sustain. Energy* **2020**, *39*, e13369. [CrossRef]
18. Kamel, D.A.; Farag, H.A.; Amin, N.K.; Zatout, A.A.; Fouad, Y.O. Utilization of Ficus carica leaves as a heterogeneous catalyst for production of biodiesel from waste cooking oil. *Environ. Sci. Pollut. Res.* **2019**, *26*, 32804–32814. [CrossRef] [PubMed]
19. Sahani, S.; Roy, T.; Sharma, Y.C. Clean and efficient production of biodiesel using barium cerate as a heterogeneous catalyst for the biodiesel production; kinetics and thermodynamic study. *J. Clean. Prod.* **2019**, *237*, 117699. [CrossRef]
20. Jayaraju, R.M.; Gaddam, K.; Ravindiran, G.; Palani, S.; Paulraj, M.P.; Achuthan, A.; Saravanan, P.; Muniasamy, S.K. Biochar from waste biomass as a biocatalyst for biodiesel production: An overview. *Appl. Nanosci.* **2022**, *12*, 3665–3676. [CrossRef]
21. Karmakar, B.; Dhawane, S.H.; Halder, G. Optimization of biodiesel production from castor oil by Taguchi design. *J. Environ. Chem. Eng.* **2018**, *6*, 2684–2695. [CrossRef]
22. Mares, E.K.L.; Gonçalves, M.A.; da Luz, P.T.S.; da Rocha Filho, G.N.; Zamian, J.R.; da Conceição, L.R.V. Acai seed ash as a novel basic heterogeneous catalyst for biodiesel synthesis: Optimization of the biodiesel production process. *Fuel* **2021**, *299*, 120887. [CrossRef]

23. Nayak, M.G.; Vyas, A.P. Parametric study and optimization of microwave assisted biodiesel synthesis from Argemone Mexicana oil using response surface methodology. *Chem. Eng. Process.-Process Intensif.* **2022**, *170*, 108665. [CrossRef]

24. Yadav, G.; Ahmaruzzaman, M. Citrus limetta Peel-Derived Catalyst for Sustainable Production of Biodiesel. *ACS Omega* **2022**, *7*, 28534–28544. [CrossRef] [PubMed]

25. Aziz, A.; Ahmad, M.; Zafar, M.; Gaafar, A.-R.Z.; Hodhod, M.S.; Sultana, S.; Athar, M.; Ozdemir, F.A.; Makhkamov, T.; Yuldashev, A.; et al. Novel Copper Oxide Phyto-Nanocatalyst Utilized for the Synthesis of Sustainable Biodiesel from Citrullus colocynthis Seed Oil. *Processes* **2023**, *11*, 1857. [CrossRef]

26. Thakur, A.; Devi, P.; Saini, S.; Jain, R.; Sinha, R.K.; Kumar, P. Citrus limetta Organic Waste Recycled Carbon Nanolights: Photoelectro Catalytic, Sensing, and Biomedical Applications. *ACS Sustain. Chem. Eng.* **2019**, *7*, 502–512. [CrossRef]

27. Hossain, M.A.; Chowdhury, S.M.; Rekhu, Y.; Faraz, K.S.; Islam, M.U. Biodiesel from Coconut Oil: A RenewableAlternative Fuel for Diesel Engine. *World Acad. Sci. Eng. Technol.* **2012**, *68*, 1289–1293.

28. Lugo-Méndez, H.; Sánchez-Domínguez, M.; Sales-Cruz, M.; Olivares-Hernández, R.; Lugo-Leyte, R.; Torres-Aldaco, A. Synthesis of biodiesel from coconut oil and characterization of its blends. *Fuel* **2021**, *295*, 120595. [CrossRef]

29. Ng, Y.J.; Tham, P.E.; Khoo, K.S.; Cheng, C.K.; Chew, K.W.; Show, P.L. A comprehensive review on the techniques for coconut oil extraction and its application. *Bioprocess Biosyst. Eng.* **2021**, *44*, 1807–1818. [CrossRef]

30. Betiku, E.; Ajala, S.O. Modeling and optimization of Thevetia peruviana (yellow oleander) oil biodiesel synthesis via Musa paradisiacal (plantain) peels as heterogeneous base catalyst: A case of artificial neural network vs. response surface methodology. *Ind. Crops Prod.* **2014**, *53*, 314–322. [CrossRef]

31. Sádaba, I.; Granados, M.L.; Riisager, A.; Taarning, E. Deactivation of solid catalysts in liquid media: The case of leaching of active sites in biomass conversion reactions. *Green Chem.* **2015**, *17*, 4133–4145. [CrossRef]

32. Betiku, E.; Akintunde, A.M.; Ojumu, T.V. Banana peels as a biobase catalyst for fatty acid methyl esters production using Napoleon's plume (*Bauhinia monandra*) seed oil: A process parameters optimization study. *Energy* **2016**, *103*, 797–806. [CrossRef]

33. Bunyakiat, K.; Makmee, S.; Sawangkeaw, R.; Ngamprasertsith, S. Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol. *Energy Fuels* **2006**, *20*, 812–817. [CrossRef]

34. *ASTM D 6751*; Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuel. ASTM International: West Conshohocken, PA, USA, 2023.

35. Gohain, M.; Devi, A.; Deka, D. *Musa balbisiana* Colla peel as highly effective renewable heterogeneous base catalyst for biodiesel production. *Ind. Crops Prod.* **2017**, *109*, 8–18. [CrossRef]

36. Saad, M.; Siyo, B.; Alrakkad, H. Preparation and characterization of biodiesel from waste cooking oils using heterogeneous Catalyst(Cat.TS-7) based on natural zeolite. *Heliyon* **2023**, *9*, e15836. [CrossRef]

37. Hangun-Balkir, Y. Green Biodiesel Synthesis Using Waste Shells as Sustainable Catalysts with *Camelina sativa* Oil. *J. Chem.* **2016**, *2016*, 6715232. [CrossRef]