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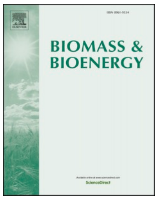

Development, assessment, and efficiency of rice husk ash (RHA) infused by eggshell as a hybrid catalyst towards biodiesel synthesis from iluppai ennai oil

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ABSTRACT

This study addresses the growing demand for sustainable fuel alternatives by developing a solid, eco-friendly catalyst for biodiesel production. Waste eggshells and rice husks were repurposed to create a heterogeneous alkaline catalyst, offering a low-cost and efficient solution. Rice husks were alkali-treated to extract silica, which was mixed with eggshells and calcined at 800 °C to produce calcium silicate in varying ratios (10 %–50 %). Among them, the catalyst containing 30 % eggshell (RHA+30 % EH) exhibited the highest calcium (44.58 %) and silica (51.82 %) content and was selected for transesterification of Lluppai ennai oil into biodiesel. Process parameters ethanol-to-oil ratio, catalyst loading, temperature, and time were optimized, yielding a maximum biodiesel conversion of 94.8 % under ideal conditions: 15:1 ethanol-to-oil molar ratio, 2 wt% catalyst, 150 min at 80 °C. The catalyst was characterized using FT-IR, SEM, XRD, XRF, and XPS, while the biodiesel product was validated via FT-IR, GC, and NMR techniques, meeting ASTM standards. The catalyst retained its efficiency over five reuse cycles, confirming its potential for industrial application as a sustainable, reusable, and effective catalyst for biodiesel synthesis.

1. Introduction

The need for energy is a major factor in the advancement of the world, and the main source of energy is fossil fuels. These fuels have played a major role in the previous several centuries in furthering civilization and forming the modern world [1]. Production, shipping, and electric power have all been significantly impacted by the availability of petroleum and its derivatives, including natural gas, diesel, and petrol [2]. However, the rapid industrialization and population growth have put a great deal of stress onto these limited assets [3].

Utilizing fossil fuels has serious negative effects on the environment, endangering ecosystems and species while also raising the possibility of decline [4]. The burning of oil and petroleum products produces a variety of dangerous air pollutants, including NOx, SOx, and organic molecules (VOCs) [5]. The past few decades have seen a growing need for research into alternatives to petroleum as a result of these ecological and economic difficulties [6]. Biodiesel [7] is one possible alternative, which, when correctly mixed, can partially replace petroleum-based

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diesel [8] or, in some cases, completely replace it [9]. Transesterification of fatty acids, typically those having longer carbon chains, produces biodiesel, a mono-alkyl ester [10]. In this chemical process, an alcohol group reacts with oil to create glycerol and ester, often with the help of an appropriate catalyst [11]. The technique frequently uses methanol because it is cheap, readily available, and speeds up reaction rates [12].

Biodiesel has several benefits, such as being non-toxic, highly biodegradable, and has advantageous properties including a high flash point, 0 % sulfur content, and lower emissions of pollutants [13]. Its manufacturing costs are now more than those of traditional diesel [14], nevertheless. Second-generation raw materials [15] such waste cooking oils [16–18], fish oil [19], wild mustard oil [20], bitter almond oil [21], blends of non-edible oils [22], animal fats, agricultural leftovers, biomass, and other non-edible oils [23] can reduce this expense. Furthermore, putting intensification ideas into practice can lower production costs even further.

Approximately one percent of the surface of the planet is made up by rice, which is an essential food supply for billions of people [24]. The outermost layer of the rice grain, or rice husk, contributes to around 20 % of the weight of paddy produced. Its significant characteristics are a heating value of 16.3 MJ/kg, a volatile matter concentration of 74 %, and an ash content of 12.8 % [25]. According to these characteristics, rice husk may be used as a solid fuel for boilers to produce steam for a variety of industries, which helps save energy [26]. Rice husk ash (RHA), which is produced when rice husk is burnt, is sometimes regarded as agricultural waste [27]. About 200 kg of husk are created for every ton of rice, and 40 kg of RHA gets produced upon the complete combustion. Thus, when burnt, rice husk produces the most ash of any crop by-product [28]. Silica makes up the majority of RHA (87–99 %), with trace levels of inorganic salts [29,30]. Because of the annual production of over 70 million tons of RHA worldwide, environmentally harmful disposal techniques are required. RHA is used in a variety of ways, such as in the manufacturing of concrete [31], as well as as an adsorbent for metal ions like $Pd^{2+}$and Cu^{2+} [32], and organic dyes like malachite green [33]. RHA is a cost-effective raw material for silicate and silica production because of its high silica content [34–36] Furthermore, ZSM-5 zeolite [37] and NaY zeolite [38] have been synthesized using RHA.

One important agricultural waste that may be utilized as fuel is rice husk (RH), and the by-product of its burning, rice husk ash (RHA), is likewise categorized as trash. Approximately 70 million tons of RHA are generated annually worldwide, according to recent reports [39]. The extraction of SiO_2, a cheap resource for creating important catalysts and supports like zeolites and mesoporous silica [40–42] has drawn a lot of interest in RH and its ash. However, the burning temperature can have a significant impact on the physicochemical characteristics of RHA [43]. Even so, not much research has been done on using RHA as a catalytic support for the manufacture of biodiesel. More specifically, nothing is known about how burning temperature affects loading capacity and biodiesel production.

In many country, eggshells and rice husks are readily available waste products. Globally, over 715 million tons of rice paddy are used to produce more than 140 million tons of rice husk annually [44]. Approximately 0.20 tons of rice husk are produced from one ton of paddy on average, and 0.03 tons of rice husk ash (RHA) are produced when the paddy is burnt [45]. While some of these rice husks are recycled into fuel, the majority wind up in landfills [46,47]. The world produced 1.627 trillion eggs in 2022, with Asia producing more than 64 % of the total [48] Approximately 11 percent of an egg's weight, or 5.5 g, is made up of its shell [49]. Eggshells, which are a frequent waste item that eventually ends up in landfills, are made up of both organic and inorganic components. Both eggshell and rice husk waste may be upcycled into concrete matrices, which will promote circularity and aid in the resolution of environmental problems.

Rice husk ash (RHA) is rich in silica, whereas eggshells are high in calcium. Eggshells may be recycled to produce calcium oxide (CaO) and act as a catalyst, increasing the waste's value. A simple heterogeneous catalyst that works well at moderate temperatures (below the boiling point of methanol) and atmospheric pressure is calcium oxide [50]. But when exposed to air at ambient temperature, CaO is very reactive and quickly absorbs carbon dioxide and moisture. It can chemisorb a significant amount of CO_2 and H_2O from the surrounding atmosphere in a matter of minutes [51]. However, the precise composition may differ depending on the species, source, incineration techniques, and burning temperature and duration [52,53]. While regulated burning of rice husks at temperatures over 800 °C produces more reactive RHA [54]. Uncontrolled burning may result in higher carbon content and less reactive crystalline silica. This emphasizes how critical it is to optimize RHA treatment and evaluation [55].

The application of silica from rice husk ash supported by calcium oxide from eggshells as a catalyst for the production of biodiesel, however, has not received much attention [56]. The by-product of grain processing, rice husk, is frequently used to generate electricity by burning, which yields rice husk ash, another consequence. Rice husk ash has the potential to be a cheap catalytic support due to its high silica (SiO_2) concentration [57].

Numerous tree species that produce non-edible items like oilseeds, which have potential for the manufacture of biodiesel, are among the varied variety of forest resources found in India [58]. Jatropha(Jatrophacurcas) [59,60] and karanja oil (Pongamia pinnata) [61] Zare well-researched examples. With an estimated yearly yield of 181 thousand metric tons in India, the *Iluppai ennai* i.e. the mahua (Madhuca indica) tree is also a prospective source of biodiesel [62,63]. Mahua seeds are a good resource for the manufacturing of biodiesel since they contain 35–40 % oil [64]. Mahua oil's affordability and accessibility make it a viable and renewable source. Mahua is a great option for producing biodiesel because of its low cost and high oil output [65].

The goal of this research is to create heterogeneous alkaline catalysts towards the manufacture of biodiesel by mixing residual rice husk ash mixed eggshells using Luppai Ennai oil. This investigation focuses on a number of variables, including temperature variations (50 °C, 60 °C, 70 °C, and 80 °C), catalyst dosages (2 %–10 %), reaction times (60, 90, 120, and 150 min), and Ethanol-to-oil molar proportions (6:1, 9:1, 12:1, and 15:1). When evaluating the efficacy of the RHA+30 % eggshell catalyst, variables such as the molar concentration of ethanol to Luppai Ennai oil, catalyst quantity, temperature, reaction duration, and rotating speed have been taken into consideration. The ideal conditions for reaching a biodiesel conversion rate of 94.8 % are determined via a comprehensive analysis. These consist of a 2 % catalyst weight, a 1:15 concentration proportion of Luppai Ennai oil to ethanol, a 150-min reaction period, and an 80 °C temperature. Fourier transform, X-ray diffraction The catalyst is examined using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and transform infrared spectroscopy. ^{1}H Nuclear Magnetic Resonance, ^{13}C NMR, and Gas Chromatography-MS spectra confirm that the biodiesel generated meets the American Society for Testing and Materials' (ASTM) criteria.

The newly developed rice husk ash-eggshell (RHA-ES) catalyst demonstrates superior performance compared to conventional catalysts through its enhanced activity, exceptional stability, and cost-effectiveness. By combining the high silica content of rice husk ash with the calcium-rich composition of eggshells, this eco-friendly catalyst forms a highly porous and reactive structure that achieves over 94.8 % biodiesel conversion from Lluppai ennai oil under mild conditions matching or exceeding commercial catalysts' performance. Unlike conventional catalysts that degrade rapidly, the RHA-ES composite retains over 94.8 % efficiency after multiple uses and maintains >75 % yield even after five reaction cycles, owing to its stable silica matrix that prevents CaO leaching. Additionally, as it utilizes agricultural waste materials, production costs are reduced by up to 60 % compared to synthetic or commercial SiO_2/CaO catalysts making the RHA–ES composite alternatives, making it both an environmentally sustainable and economically viable solution for biodiesel production and other industrial applications.

Moreover, no prior research has investigated the application of silica-supported CaO catalysts made from rice husk ash for the production of biodiesel. Rice husk ash is a secondary waste product when rice husk, a by-product of grain processing, is burned to generate electricity. Rice husk ash has a high SiO_2 concentration, making it a possible low-cost catalytic support. Therefore, the goal of this work is to create and describe a very effective base catalyst for the transesterification of *lluppai ennai* oil to create fuel-grade biodiesel using two waste components: eggshells and rice husk ash. In order to create a hybrid catalyst that offers a financially feasible way to produce biodiesel and aids in trash disposal.

2. Experimental

2.1. Materials

Raw rice husk, used as the catalyst support, was sourced from a local farm mill in Hyderabad, India. The unused chicken eggshells had been collected from a Hyderabad hostel which is used in making catalyst and the lluppai ennai oil was a non-edible feedstock was acquired from a supermarket in Hyderabad, India, for evaluating the performance and activity of the developed catalyst in the transesterification reaction. The physical properties of the lluppai ennai oil used in this study are listed in Table 1.

Mahua oil with a high acid value (36.24 mg KOH/g) contains excessive free fatty acids (FFAs), moisture, gums, and particulates, all of which can severely hinder base-catalysed transesterification by promoting soap formation and reducing biodiesel yield. Three key pre-treatment steps degumming, filtration, and dehydration are essential: In the First step removes hydratable impurities such as phospholipids ("gums") and metals. An acid (like phosphoric or citric acid) is added to hydrate the gums, followed by water addition and centrifugation or settling to separate them Removing these components prevents them from emulsifying the oil, which improves downstream processing. After degumming, the Mahua oil still contains fine suspended solids and gum aggregates. Filtration (or centrifugation) removes these, ensuring a cleaner feedstock. This not only protects equipment (e.g., reactors, pumps) but also ensures more efficient acid esterification and alkaline transesterification by preventing physical blockages and inefficient mixing. Residual water in the Mahua oil must be removed to prevent soap formation during the alkaline transesterification step water hydrolyses triglycerides and FFAs into more acids and soap. Dehydration involves gently heating the oil (around 60–100 °C). This final step ensures moisture is below critical levels for high-yield biodiesel conversion. Together, these three pre-treatment steps reduce FFA content, moisture, and particulates creating a clean, stable feedstock ready for efficient and reproducible acid esterification (to bring acids 0.43 mg KOH/g) before alkaline transesterification to biodiesel.

Table 1
The physical characteristics of the raw lluppai ennai oil.

Sr. No	Property	Units	Value	ASTM
1.	Kinematic Viscosity at 40 °C	Cst	42.10 ± 0.004	ASTM D445
2.	Acid Value	% w/w	36.24 ± 0.004	AOCS cd 3d-63
3.	Free Fatty acid (FFA)	Wt.%	18.12 ± 3.063	ASTMD**5555**
4.	Specific Gravity	kg/m3	0.901 ± 0.004	ASTM D 4052
5.	Iodine value	Mg KOH/g	75 ± 0.816	AOCS cd 1-**25**
6.	Peroxide value	Wt.%	189.21 ± 0.452	AOCS cd 8-**53**
7.	Color	–	Greenish yellow	–
8.	Flash point	^{0}C	229 ± 0.471	ASTM D 93
9.	Moisture content	Wt.%	0.03 ± 0.004	AOCS cd ca **2c-25**
10.	Calorific value	(kJ/kg)	37.10 ± 0.421	–

2.2. Evaluation of chicken egg shell and rice husk

Using a CHN analyser (LECO CHN 828), the chemical makeup of chicken egg shell and dried rice husk was examined. The analysis's findings are shown in Table 2. The ash, moisture, volatile matter, and fixed carbon contents were measured using proximate and ultimate analyses in accordance with the ASTM D3172-07a standard technique.

2.3. Chemicals

Chemicals used in this investigation included petroleum Ether (60–80 °C), acetone (purity GC ≥ 99.0 %), and analytical-grade ethanol (purity GC ≥ 99.0 %), all of which were obtained from Merck, India. Furthermore, Merck in Mumbai, India, provided the anhydrous sodium sulfate (≥99.0 %) and ethyl acetate (≥99.5 %).

2.4. Catalyst preparation

The extraction of silica from rice husk (RH-SiO_2) was done using a previously published technique [66]. To differentiate between the floating from the sinking rice husks, the husks were first cleansed by soaking in hot water and then let to remain at room temperature for the whole night. The floating husks were thrown away, while the sinking husks which were thought to contain more silica were gathered. 200 g of rice husk was submerged in 200 mL of a 1.5 % NaOH solution in order to extract silica. After boiling, the mixture was allowed to stand for half an hour. After filtering the sample, the filtrate which included the dissolved silica was collected. A 10 % Hcl solution was gradually added to the filtrate in order to precipitate the silica.

$$SiO_2(Ash) + NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na\ _2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O \quad (2)$$

The eggshells undergo several complete washings using deionized water and tap water to get rid of any remaining organic material and debris. In order to remove any residual moisture, the smaller portions were broken up into little bits and then dried in a hot air oven for 24 h at 105 °C. After drying, the shells were crushed using a pestle and mortar, then the powder was filtered using J. Milano's procedure. [67]. According to R. Israa's instructions, the passed powder was then calcined for 4 h at 900 °C in a muffle furnace [68]. Calcium carbonate (CaCO3) found in eggshells was converted to calcium oxide (CaO) by the calcination mechanism. In order to prevent the active CaO catalyst from collecting moisture, it was kept in an airtight container as advised by H. K. Ooi [69]. The phase transformation was shown in Eq. (2) as follows:

Table 2
Estimated and complete examination of rice husk and chicken egg shell.

S. No	Composition	Rice Husk	Egg Shell
Proximate analysis			
1	Moisture (% air dry)	7.20	1.05
2	Volatile matter (% dry basis	58.00	3.18
3	Ash content (% dry basis)	17.54	93.25
4	Fixed carbon (% basis)	17.26	2.52
Ultimate analysis			
1	Carbon (% dry basis)	38.21	–
2	Hydrogen(%dry basis)	5.34	–
3	Oxygen (% dry basis)	0.50	–
4	Sulfur %	0.12	–

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

Wet impregnation was applied to the precursor calcined eggshell at different weight percentages of 10 %, 20 %, 30 %, and 50 %. The catalyst materials were identified as RHA/CaO [70]. In a beaker, these ingredients were combined with 200 mL of distilled water, and the mixture was refluxed for five to 6 h at 70–80 °C while being agitated at 650 rpm. The resultant slurry was filtered, and any remaining moisture was dried for 24 h at 120 °C. The dry substance was subsequently calcined for 4 h at 800 °C in a furnace. Within a desiccator, the last catalyst was kept in a sealed container. In order to produce biodiesel, mahua oil was ethanolzed using the produced RHA/CaO catalyst.

$$SiO_2 + CaO \rightarrow CaSiO_3 \quad (4)$$

2.5. *Catalyst characterization*

Field emission scanning electron microscopy (FESEM), nitrogen adsorption–desorption (NA) analysis, and X-ray diffraction (XRD) were among the analytical methods used to evaluate the physicochemical characteristics of the produced catalysts as well as their effectiveness as catalysts during the production of biodiesel. In order to ascertain the catalyst's crystalline shape, XRD spectroscopy (Rigaku, SmartLab) was utilized to examine its atomic and molecular structure. The catalyst was set in a sample container that was set on a glass plate (40 × 33 × 2 mm) and had a diameter of 10–15 mm and a depth of 1 mm. The sample height was adjusted to fit the diffractometer by placing another glass plate on top. A Siemens Crystalloflex D5000 diffractometer with Cu-Kα radiation ($\lambda = 1.54060$ Å) was used to record XRD patterns while scanning across a 2θ range of 20°–80°.Using a PerkinElmer TGA 4000 system and thermogravimetric analysis (TGA) in a nitrogen environment, the sample's thermal stability was evaluated at temperatures ranging from ambient temperature to 850 °C.

Nitrogen adsorption–desorption analysis (Thermo Scientific) was used to assess the porosity and pore size distribution of the RHA-supported catalyst. A Micrometrics ASAP 2010 analyser was used to quantify the size of the pore, size, and overall pore volume. Utilizing a vacuum pump, a 0.2–0.3 g sample was degassed at 120 °C to eliminate any adsorbed gases before being allowed to cool to ambient temperature. Brunauer-Emmett-Teller (BET) theory was used to compute the particular area of surface and other adsorption of gas data; outcomes were given in m^2/g. Using a Hitachi SU8020 FESEM, the catalyst's surface morphology including the size and form of the particles was investigated. Gold coating was applied to the catalyst to stop charging effects during electron bombardment. The ideal magnification was attained by optimizing electron bombardment using a tungsten filament electron cannon with a 25 kV resolution.

2.6. *Transesterification and characterization for biodiesel production*

The solid catalyst created in this investigation was used to trans esterify ethanol and lluppai ennai oil. In a 100 mL two-neck round-bottom flask, 10 g of lluppai ennai oil and a sufficient amount of ethanol have been added for the reaction. The catalyst is then added to the solution in the necessary amount. A reflux condenser was set up, and the flask was set on a heated plate with a magnetic stirrer spinning at 650 rpm. By increasing the catalyst quantities of 2 %, 6 %, 8 %, and 10 % by weight, as well as the ethanol-to-oil molar ratios (EOMR) of 6:1, 9:1, 12:1, and 15:1, the reaction conditions were adjusted. At 50 °C, 60 °C, 70 °C, and 80 °C, as well as for 60, 90, 120, and 150 min, responses were carried out. Thin Layer Chromatography (TLC) was used to track the process of converting to biodiesel. The mixture was moved to a separating funnel when the reaction was finished. After extracting the biodiesel with petroleum ether (60–80 °C), the liquid was agitated to divide into two layers. The top layer was thrown away, but the lower layer, which was high in biodiesel, had been collected. Five times, this procedure was carried out. After adding anhydrous sodium sulfate, the mixture was allowed overnight to dry to produce biodiesel. A vacuum rotary evaporator (QuickVap, Almicro) was then used to evaporate the residual solvent at 50 °C in order to produce pure biodiesel. Using a particular formula, the amount of biodiesel produced from lluppai ennai oil was determined:

$$\text{Biodiesel yield} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of oil used}} \times 100$$

Gas Chromatography-Mass Spectrometry (GC-MS, Shimadzu QP 2010) was used to determine the fatty acid content of lluppai ennai oil following the conversion of triglycerides to esters. The main esters that were produced during transesterification were also identified by the investigation. Furthermore, the finished biodiesel product's characteristics were evaluated in accordance with the applicable standards, including its density (ASTM D4052), flash point (Cleveland open cup, COC), and kinematic viscosity (ASTM D445) [71]. The saponification value was evaluated using standard titration [72], and the biodiesel's molecular weight was subsequently ascertained [73].

2.7. *Performance of fuel*

The fuel's compatibility for biodiesel uses was assessed using standardized ASTM testing protocols. The fuel was weighed in proportion to water for a certain volume in order to calculate the relative density. To assess the moisture content, which influences heat transfer and reduces the efficiency of combustion in engines with internal combustion (ICEs), observations were taken both before and after dry. The concentration of free fatty acids (FFA) and acid value (AV) were also assessed. Engine damage may result from a high AV, and oxidation during retention may be accelerated and fuel stability reduced by elevated FFA levels. These parameters were measured using phenolphthalein as the titration reagent.

Additionally, the biodiesel's pour and flash points were measured in accordance with ASTM standards. Oxidation stability and ethyl ester content were among the other attributes evaluated using EN testing techniques. Three different experiments' findings were averaged to guarantee dependability.

3. Results and discussion

3.1. *Analysis of XRF*

X-ray fluorescence (XRF) spectroscopy was employed to ascertain the chemical makeup of the RHA and each catalyst. The catalysts' elemental profiles RHA, RHA+10 % CaO, RHA+20 % CaO, RHA+30 % CaO, and RHA+50 % CaO were investigated after they were calcined at 800 °C. It was discovered that the main ingredients in each catalyst were silica, calcium, and potassium. Furthermore, in all samples, trace elements such as manganese, iron, and phosphorus were found at parts per million (ppm) amounts. Table 3 displays every catalyst's complete elemental composition.

The RHA+ 30 % EH catalyst's superior performance stems from its optimal SiO_2-CaO balance (51.82 % Si, 44.58 % Ca), as evidenced in Table 3. This composition uniquely combines three critical advantages:

Table 3
Composition of RHA and the prepared catalyst calcined at 800 °C for 4 h.

Elements Composition	RHA	RHA+10 % ES	RHA+20 % ES	RHA+30 % ES	RHA+50 % ES
Silica	77.25	68.38	56.32	51.82	73.81
Calcium	4.31	25.64	38.39	44.58	24.32
Potassium	10.70	4.50	3.62	2.37	1.257
Phosphorous	3.34	0.69	0.19	–	–
Manganese	0.26	0.41	0.31	0.272	0.15
Iron	0.95	0.170	0.13	0.113	0.07

sufficient silica maintains structural integrity and prevents CaO sintering, maximized calcium content provides abundant active sites for transesterification, and the ideal Si/Ca ratio promotes active $CaSiO_3$ phase formation. While 10 % (25.64 % Ca) and 20 % (38.39 % Ca) formulations are calcium-limited, the 50 % blend (24.32 % Ca, 73.81 % Si) suffers from calcium dilution and poor dispersion a phenomenon recently linked to reduced accessibility of active sites in over-doped systems. The 30 % catalyst's synergy between silica's stabilizing mesoporous framework and calcium's catalytic functionality explains 94.8 % biodiesel yield, outperforming both calcium-deficient and silica-dominated alternatives while resisting deactivation.

The 30 % ES catalyst's exceptional performance arises from its ability to form active calcium silicate ($CaSiO_3$) phases during calcination. At 800 °C, the 44.58 % CaO interacts with 51.82 % SiO_2 to create a stable $CaSiO_3$ matrix, which enhances both basicity and porosity. This phase provides strong Lewis basicity for triglyceride conversion while the silica framework prevents CaO leaching or sintering a common issue in pure CaO catalysts. The 30 % doping level strikes a critical balance: lower CaO (10–20 % ES) limits $CaSiO_3$ formation, while higher doping (50 % ES) disrupts the Si-Ca interaction, favouring inert SiO_2 clusters over active $CaSiO_3$. XRD and XRF studies confirm that RHA+30 % EH yields a homogeneous $CaSiO_3$ composite, explaining its 94.8 % biodiesel yield. Thus, the 30 % catalyst's success lies in its optimized phase composition, not just elemental percentages. Consequently, this specific blend of 51.82 % SiO_2 and 44.58 % CaO not only optimizes catalytic functionality but also improves catalyst stability and reusability, making it a rational and data-backed choice over the other doping levels.

3.2. XRD characterization

Metal oxides in the catalyst were examined for size, shape, and crystallinity using X-ray diffraction (XRD). According to the study, calcium, potassium, and silica were present. Silica and calcium in the manufactured catalyst appear to be efficient catalysts in the transesterification process, which is necessary for the generation of biodiesel, based on the methyl esters generated during the reaction. Both the catalyst's surface composition and crystalline structure were ascertained using XRD. In order to perform the XRD study, Cu Kα radiation was used at a scanning rate of 1°/min over a 2θ range from 15° to 80°.Fig. 1 displays the RHA+30 % EH catalyst's and rice husk ash's (RHA) XRD patterns. Other catalytic XRD patterns, such as RHA+10 % EH, RHA+20 % EH, and RHA+50 % EH, are excluded due to overlapping peaks.

The main component was determined to be silica (SiO_2), as seen in Fig. 1. J. Atul reported results that were consistent with the silica sample's broad, strong peak between 10° and 22° 2θ, suggesting that the silica is amorphous [74]. The absence of any impurity peaks is confirmed by the measured peaks matching those of SiO_2 in JCPDS file No. 89–0510. The (220) crystalline planes of KCl are represented as peaks in the potassium XRD patterns at a diffraction angle of 40.51° at 2θ, as seen in Fig. 1 I. Shaymaa observed that these peaks are in good agreement with the typical peaks on the JCPDS Card number 41–1476 [75]. The calcium oxide (CaO) is also visible in the XRD patterns of RHA and the produced catalysts. It displays large peaks at 2θ diffraction angles of 37.2° and 50.0°, which correspond to the standard data (JCPDS file No. 00-037-1497). Moreover, a peak at 29.01° indicates the synthesis of calcium silicate ($CaSiO_3$) in the produced catalyst (PDF#42–547). The synthesis of practically pure $CaSiO_3$ is ascribed to calcination at 800 °C for 4 h. The prominent $CaSiO_3$ peak at 29.01° indicates that the catalyst has a high degree of crystallinity.

3.3. Fourier Transform Infrared Spectroscopy

Fig. 2 shows the FTIR spectra of the produced catalyst samples, calcined egg shell, and calcined rice husk ash (RHA), which vary from 4000 to 500 cm^{-1}.In the CaO sample from the calcined egg shell, the stretching vibrations of the CO_3^{2-} group are represented as bands at 1084 and 790 cm^{-1} in the FTIR spectrum. CO_2 from the atmosphere chemisorbing onto the catalyst surface is responsible for these bands. According to N.H. Khdary, the band at 790 cm^{-1} further validates the existence of the Ca-O bond [76]. When discarded egg shell is calcined at 900 °C in a muffle furnace, a strong peak at 590 cm^{-1} provides evidence for the creation of calcium oxides and further confirms the presence of the Ca-O bond.

The existence of silica is indicated by a broad spectrum in the area of the silica spectra of calcined rice husk ash. The asymmetric stretching of the Si-O-Si bond is responsible for the dominating absorbance peak at 1062 cm^{-1}. The symmetric stretching of the Si-O-Si bond is associated with the peak at 794 cm^{-1}, whereas the bending mode of the Si-O-Si bond is shown at 553 cm^{-1}. According to E. Ruth, these findings support the effective extraction of silica from rice husk [77].

The functional groups in the produced catalysts' spectrum, in contrast, resemble those in the CaO catalyst. OH modes from water molecules physisorbed on the catalyst surface are linked to the bending vibration of OH modes, the deformation of O-H groups, and the C-O and

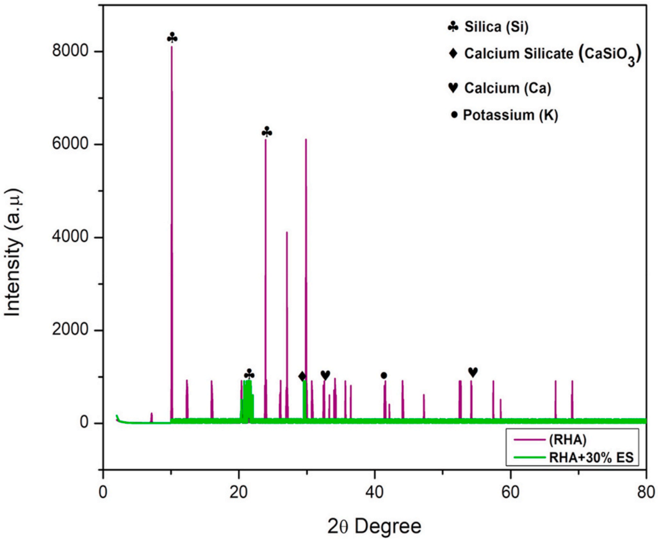


Fig. 1. XRD spectra of RICE Husk Ash and prepared catalyst RHA+30 % EH calcined at 900 °C.

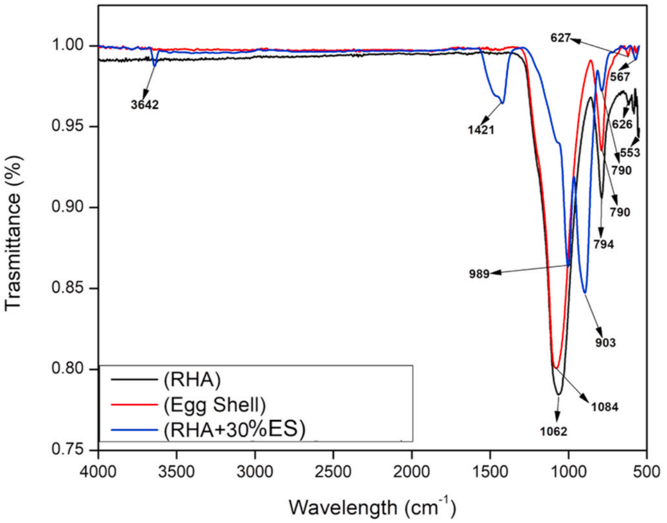


Fig. 2. FTIR spectra of the Rice Husk Ash, Calcined egg shell, and the prepaid catalyst RHA+30 % EH.

Ca-O bonds, respectively, at 3642 cm^{-1}, 903 cm^{-1}, and 567 cm^{-1}. The O-C-O bonds from unknown carbonate groups on the CaO surface exhibit symmetric stretching vibrations, which are represented by the band at 1470 cm^{-1}. An additional band at 879 cm^{-1} is associated with the CO_3^{2-} groups' out-of-plane bending vibration. The absence of the distinctive silica peaks suggests that all of the SiO_2 has interacted with the CaO to create the new phase $CaSiO_3$. The presence of the Si-O-Ca link in the RHA +30 % CaO catalyst is confirmed by the existence of a strong band at 903 cm^{-1}. It appears that a new $CaSiO_3$ phase was produced by a reaction between the whole SiO_2 and CaO. Additionally, the development of a Si-O-Ca bond is indicated by the strong band at 903 cm^{-1} [78].

3.4. Scanning electron microscope (SEM)

The samples were attached to a metal stub and covered with a 40–60 nm coating of platinum, they were analysed using Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM) (FEI Quanta 450). To create high-resolution photographs, SEM imaging was carried out in a vacuum at various magnifications. The pictures were then captured on camera. Scanning electron microscopy (SEM) was used to analyse the surface morphology and the findings are shown in Fig. 3. The activated rice husk's surface was found to be porous and permeable by SEM examination, including rod-like particles, some of which were aggregated. As noted by S. E. Peter the observed flaky surface morphology points to a weakly linked structure with hollow holes, which increases its reactivity and lends it an amorphous nature [79]. The rice husk ash's remaining pores are more visible in the SEM pictures, and surface outcrops suggest that silica is lodged in the outer cells. T. Tenzin characterize this structure as contributing to a highly active, porous material [80].

SEM analysis of the catalyst's surface morphology at a 20 μm resolution showed extremely porous aggregates. SEM pictures comparing catalysts made with different ratios of RHA, RHA+10 % EH, RHA+20 % EH, RHA+30 % EH, and RHA+50 % EH are shown in Fig. 3. The particles' morphologies varied significantly, exhibiting uneven forms and porous surfaces. The sintering and oxide production at high temperatures caused the tiny particles in the RHA+30 % EH to fuse together into bigger aggregates. Particle size and aggregation in the catalyst are quite high, according to the SEM study. CaO was successfully immobilized on the silica surface when it was impregnated into CaO, as evidenced by the catalyst surface displaying the creation of smaller aggregates with discernible tiny impurities [81]. Furthermore, the bigger holes between these agglomerates promote catalytic activity by allowing the catalyst surface to make maximum contact with ethanol and oil ester, which facilitates the transesterification process that yields biodiesel.

3.5. X-ray photoelectron spectroscopy (XPS)

To investigate the basic composition of the produced materials' surfaces, the XPS analytical technique was utilized. In the RHA and RHA+30 % EH catalysts, the elemental compositions and spectra of the different elements are shown in Fig. 8. The catalysts had especially high quantities of Si and Ca, whereas the XPS examination verified the existence of components including O, C, Si, and Ca. With atomic percentages of 51.82 % and 44.58 % in the produced catalysts, respectively, Si and Ca were the most prevalent elements among those discovered. Calcium silicate ($CaSiO_3$) was recognized by the XRD analysis (Fig. 1), and the FT-IR data (Fig. 2) further supported this identification. Moreover, all catalysts had trace levels of iron, manganese, phosphorus, and potassium as shown in the table of XRF.

A peak with a binding energy of 284.12 eV was identified in the C 1s spectrum (Fig. 4) of the XPS analysis of rice husk ash (RHA) [82]. This peak can be attributed to types of carbon: sp2 hybridized carbonate bonds with metals. The O 1s spectra showed that metal oxides or carbonates were present, with the RHA catalyst showing a peak at 530.09 eV [83]. There are C–O groups associated with metal carbonates, most likely in a sp2 hybridized form, according to the C and O XPS spectra. SiO_2, a silicon peak, was found with a binding energy of 103.82 eV [84]. A signal in the C 1s spectra at 284.11 eV for the RHA+30 % EH catalyst was also found by the XPS analysis (Fig. 4), suggesting the existence of sp2 hybridized carbonate bonds between metals. A peak at 530.01 eV was also visible in the O 1s spectra, which further supported the existence of metal oxides or carbonates that resembled the RHA catalyst. The catalyst contains metal carbonates including C–O groups, according to the XPS spectrum. A peak at 103.41 eV of binding energy verified the

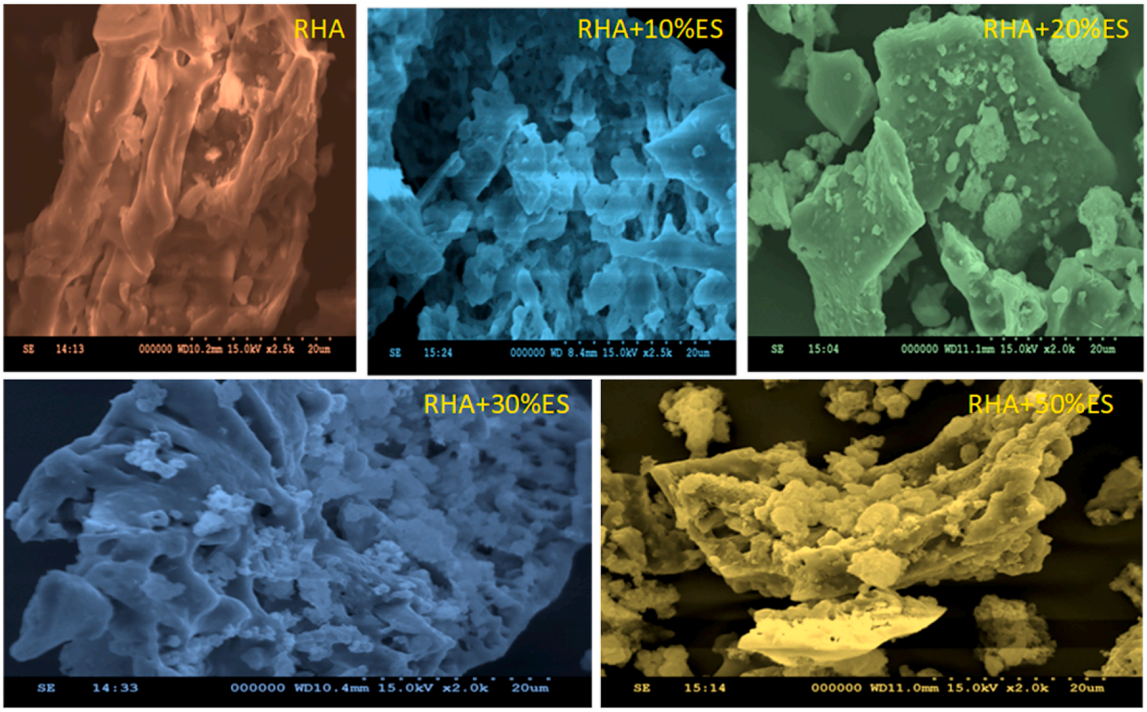


Fig. 3. SEM Image of RHA and all prepared catalyst RHA+10 % EH, RHA+20 % EH, RHA+30 % EH and RHA+50 % EH.

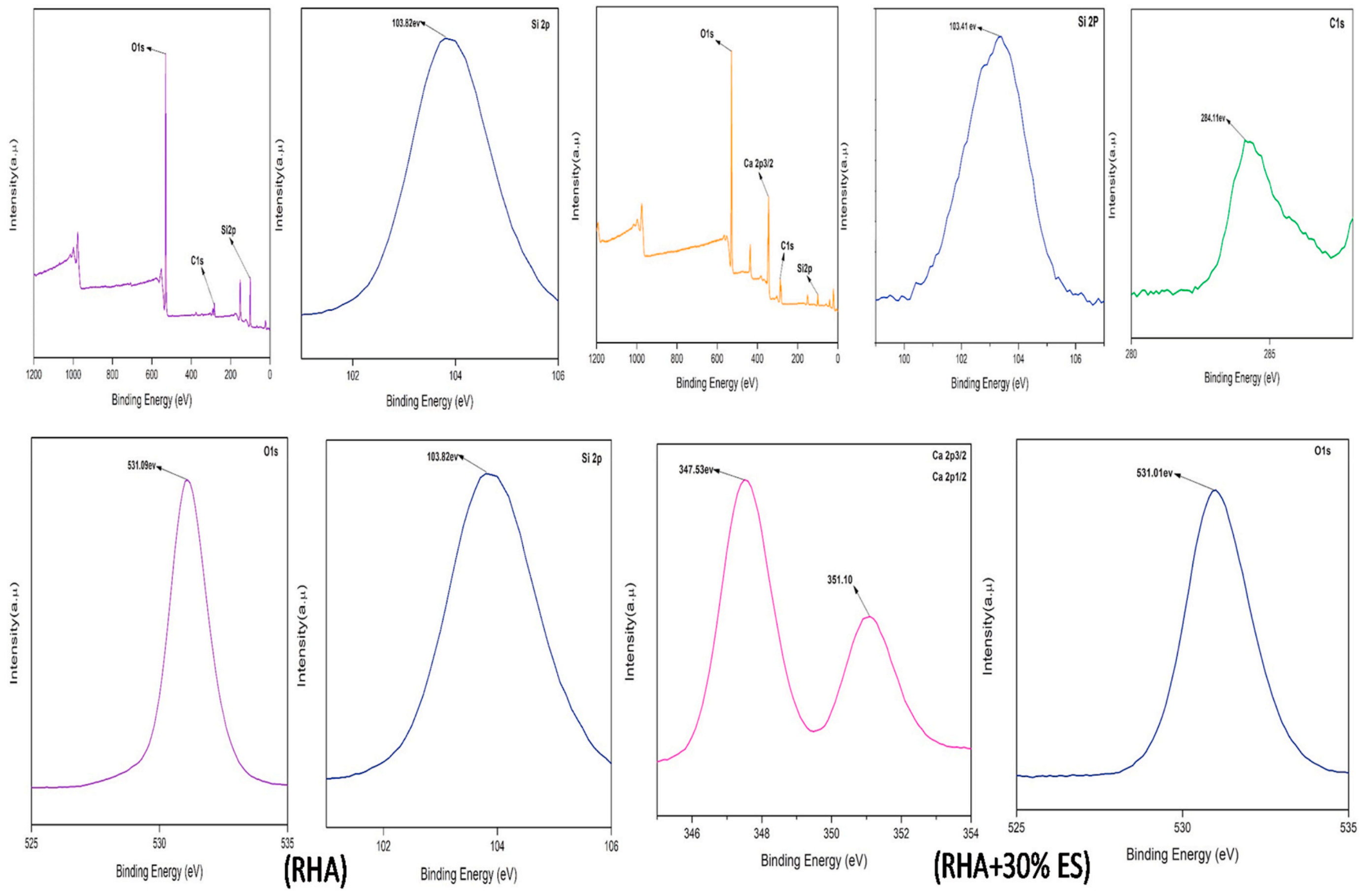


Fig. 4. XPS of the rice husk ash and prepared catalyst RHA+30 %EH.

presence of silicon as SiO_2. The two separate peaks in the Ca 2p XPS spectra, located at 347.53 eV and 351.10 eV, respectively, represent the Ca $2p_3/_2$ and Ca $2p_1/_2$ binding energies in the RHA+30 % EH catalyst. These peaks show that calcium oxide and silicate are present in the catalyst [85,86].

3.6. Brunauer-Emmett-Teller (BET)

The Brunauer-Emmett-Teller (BET) method is a critical analytical technique for determining a material's specific surface area by measuring the physical adsorption of gas molecules onto solid surfaces. In this study, the surface area and textural properties of the catalysts were analysed using a Micromeritics ASAP 2000 after degassing the samples at 105 °C to remove adsorbed contaminants. The RHA+30 % eggshell catalyst exhibited superior catalytic activity, attributed to its optimal textural properties: a high surface area (3.5499 m^2/g), large pore volume (0.005071 cm^3/g), and wide pore diameter (57.135 Å) which is shown in Table 4. These characteristics facilitate enhanced reactant diffusion and greater exposure of active sites compared to other ratios. The 10 % and 20 % eggshell blends showed significantly lower surface areas (0.9435 m^2/g and 1.4516 m^2/g, respectively) and restricted pore volumes, limiting catalytic efficiency. While the 50 % blend had a comparable surface area (~3.50 m^2/g), its reduced pore volume (0.004130 cm^3/g) and narrower pores (48.861 Å) suggest less efficient mass transport. According to BET-based catalyst design principles, the 30 % composition strikes the ideal balance, maximizing active site accessibility and reaction kinetics.

The RHA+30 % eggshell catalyst, calcined at 800 °C, produced the highest biodiesel yield due to its well-developed mesoporous structure. However, at higher calcination temperatures, particle agglomeration can reduce surface area and pore volume, diminishing catalytic performance. Interestingly, while some catalysts with lower surface areas still demonstrated activity, the RHA+30 % eggshell ratios proved most effective, likely due to their optimal porosity and unburned carbon content, which enhance active site availability. Thus, the 30 % eggshell-RHA composite emerges as the superior catalyst, combining high surface area, robust pore architecture, for efficient biodiesel production.

Table 4
BET of All the prepared catalyst.

Sr. No	Prepared catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g),	Pore Diameter (Å)
1.	RHA+10 % EH	0.9453	0.000631	26.692
2.	RHA+20 % EH	1.4516	0.001835	50.572
3.	RHA+30 % EH	3.5499	0.005071	57.135
4	RHA+5 0 % EH	3.5012	0.004130	48.861

4. Procedure factors' effect on transesterification

A number of important variables affect the transesterification process that turns Luppai Ennai oil into biodiesel, such as the kind and quantity of catalyst, the alcohol-to-oil percentage, the reaction temperature, the catalyst mixing rate, and the reaction duration. Cost reduction and increased manufacturing efficiency depend on these factors being optimized effectively. In order to improve the yield and quality of biodiesel, a great deal of research has been done to determine the best ways to modify these variables.

4.1. Impact of ethanol to oil ratio on the production of biodiesel

For the manufacture of biodiesel, 1 mol of alkyl ester requires 3 mol of alcohol and 1 mol of triglycerides [87]. Le Chatelier's principle states that the rate at which products are formed increases with reactant concentration. The rate of biodiesel production increases with increasing alcohol content, and this impact is amplified by a larger alcohol-to-oil molar ratio [88]. But because they often form an emulsion during the saponification reaction in an aqueous media, recovering glycerol and unaffected ethanol can be challenging. Due to variations in density and orientation, the manufacturing of biodiesel is divided into two different phases: a crude glycerol combination makes up the bottom phase, while biodiesel makes up the top phase [89]. Water, soaps, glycerol, alcohol, and non-glycerol organic materials are all included in this combination; the composition varies according to the quality of the feedstock. Post-treatment of crude glycerol usually consists of three steps: (1) neutralization to get rid of salts and soaps, (2) vacuum evaporation to get rid of water and ethanol, and (3) refining to make the glycerol purer. The output of biodiesel is significantly influenced by the molar ratio of alcohol to triglycerides. Usually, extra alcohol is utilized to move the transesterification process in the direction of product synthesis since it is reversible [90]. The quantity of ethyl esters rises when the mass percentage of alcohol to oil increases because it enhances the interaction between ethanol and oil molecules.

Several studies have investigated the impact of different moles of alcohol to oil, including 6:1, 9:1, 12:1, and 15:1 as shown in Fig. 5. For instance, research examined the effects of ethanol-to-oil molar ratios on FAME content at a catalyst concentration of 2 % by weight, a reaction temperature of 80 °C, and a reaction duration of 150 min. Using RHA+30 % EH catalysts, the results indicated that the best molar ratio of 15:1 gave the maximum biodiesel output of 94.8 %, whereas ethanol-to-oil ratios of 6:1, 9:1, and 12:1 resulted in lower FAME concentration. Previous research has looked at utilizing extra ethanol to trans esterify oil. S.M. Farouk, for instance, achieved a maximum biodiesel production of 99.99 % with a high ethanol-to-sunflower oil molar ratio of 15:1, demonstrating a near-complete conversion of triglycerides to methyl esters [91]. According to related research by K.T.T. Amesho, biodiesel output increased from 89.45 % to 97.75 % when the ethanol-to-Jatropha curcas oil ratio was increased from 3:1 to 12:1, and reaction time decreased from 185 min to 65 min [92].

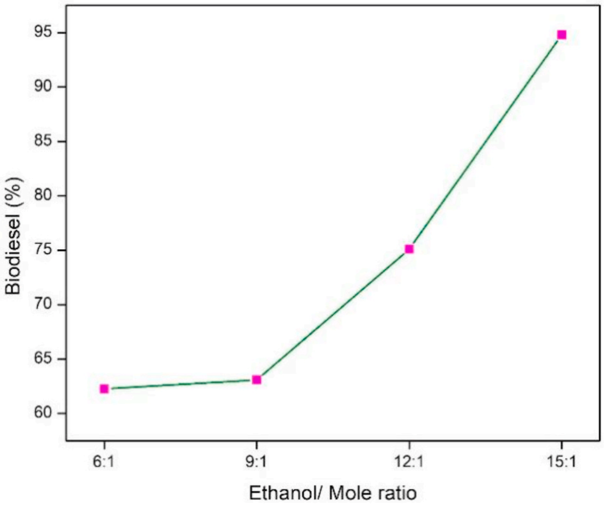


Fig. 5. The impact of the mole ratio of oil to ethanol on the transformation of biodiesel.

4.2. Effect on the reaction temperature on the production of biodiesel

Reaction temperature is a crucial factor in the transesterification process, as it significantly influences the transfer of energy to reactive molecules and impact's reaction kinetics [93,94]. Since transesterification is an endothermic reaction, higher temperatures are necessary to reduce the viscosity of the oils and accelerate the reaction rate, thus improving biodiesel production [95,96]. In this study, the reaction temperature ranged from 50 °C to 80 °C, as illustrated in Fig. 6.

For the transesterification of lluppai ennai oil into biodiesel, the yield increased from 62.25 % to 63.09 % when the temperature was raised from 50 °C to 60 °C. However, a more substantial increase in yield was observed when the temperature was raised from 70 °C to 80 °C, reaching 94.18 %. As shown in Figs. 6 and 80 °C was identified as the optimal temperature. It is essential to maintain the reaction temperature below the boiling point of alcohol to prevent its vaporization and loss. Higher temperatures help lower the viscosity of the oil, leading to a faster reaction rate and shorter reaction time. The results indicate that biodiesel conversion is lower at lower temperatures but increases substantially with higher temperatures.

The increased yield at higher temperatures can be attributed to enhanced chemical reactions that improve mass transfer and miscibility, while reducing the negative effects of the reactants [97]. Although 80 °C is often considered optimal in many studies, other research, such as that by S. Haase [98], according to a number of investigations, the ideal reaction temperatures fall between 70 °C and 140–170 °C. While certain systems may benefit from higher temperatures for catalytic performance in the synthesis of biodiesel, excessive heat can result in fast ethanol vaporization, which can cause considerable ethanol loss and reduce the output of biodiesel [99–101]. It is advised to avoid raising the boiling point of ethanol in order to save money and energy. Moreover, some research indicates that the ideal temperature for producing biodiesel is 60 °C [102]. Therefore, the optimal temperature for biodiesel conversion from Mahua oil using RHA+30 % EH catalysts is 80 °C.

4.3. Impact of reaction duration on the production of biodiesel

An important determinant of the yield of ethyl esters in the manufacture of biodiesel is reaction time. A longer response time often yields a better yield because it enables a more thorough conversion of fatty acids to esters. But, if the catalyst and ethanol are exposed for too long, reverse reactions may occur, which can result in a reduction in yield. As seen in Fig. 7, the yield plateaus after a certain point, while the overall conversion rate rises with reaction time.

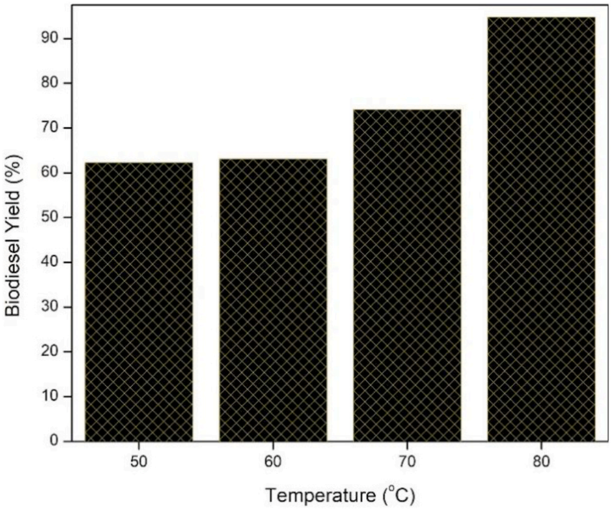


Fig. 6. The impact of temperature on the biodiesel transformation process.

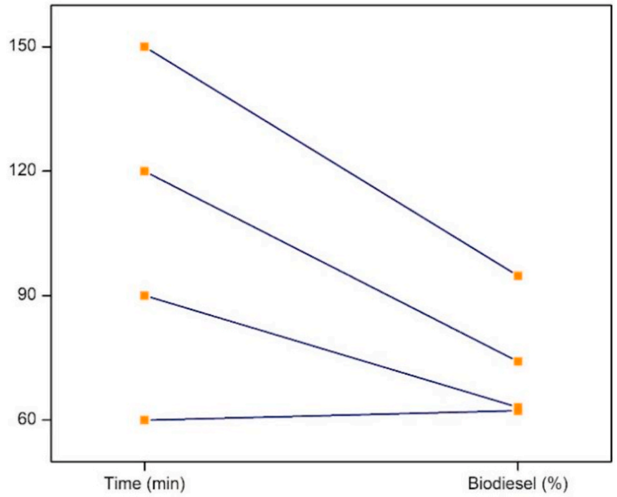


Fig. 7. Effects of reaction time on biodiesel metabolism.

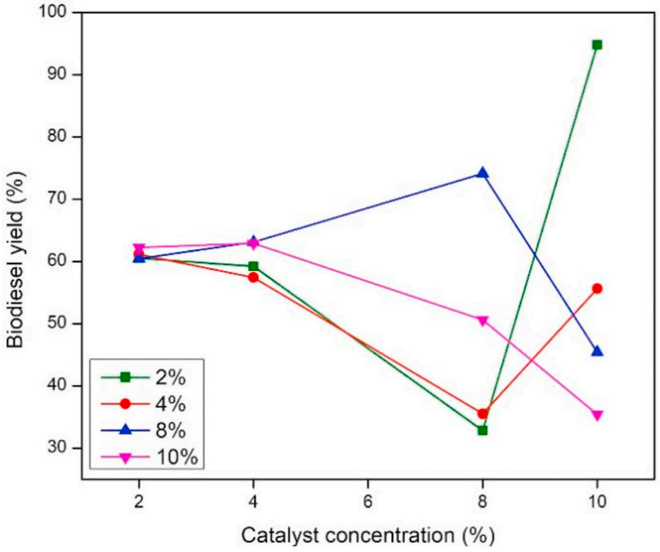


Fig. 8. Impact of adding a catalyst on the synthesis of biodiesel.

This study examined the effect of reaction time on conversion at 60-, 90-, 120-, and 150-min intervals. At 150 min, the maximum output of biodiesel (94.8 %) was obtained (Fig. 7). Furthermore, the reaction was carried out at various temperatures, up to 80 °C, in order to investigate the connection between temperature and reaction time. A chemical reaction may not have sufficient time to finish once it has reached the catalyst surface due to the conveyance process's restricted pace [103]. The yield of biodiesel is not much increased by prolonging the reaction time after equilibrium or the ideal reaction time has been reached [104]. The greatest biodiesel yield is achieved at this ideal moment [105]. Beyond this point, the reaction may continue to consume reactants, perhaps reversing the process. This would slow down the pace of reaction and lower the yield of biodiesel. Furthermore, soap production may be facilitated by longer reaction durations. Numerous studies have identified ideal reaction times depending on the particular process parameters employed in each instance in order to increase energy efficiency, decrease labour, and save time [106,107]. For example, since these variables are related, increasing catalyst loading and prolonging the reaction time might aid in reducing the viscosity of the reactive mixture. On the other hand, ethanol could evaporate if the temperature rises over its boiling point. To maximize these reaction parameters, it is therefore essential to select the catalyst and feedstock with care throughout the transesterification process [108,109].

4.4. Catalyst Concentration's effect on the production of biodiesel

The quantity of catalyst has a significant influence on the synthesis of biodiesel and is essential to the transesterification process. The catalyst's concentration quickens the reaction and greatly increases overall efficiency. A larger amount of catalyst increases the number of active sites, which speeds up the reaction and makes it easier for the system to reach equilibrium more quickly [110]. Further increases in catalyst concentration, however, may have adverse consequences once equilibrium is reached. These impacts may include greater mass transfer resistance, trouble mixing reactants, and slower product desorption because of the mixture's increased viscosity. These issues may hinder the reactants' ability to interact with the catalyst's active sites, which would lower the amount of biodiesel produced [111,112].

As seen in Fig. 8, the yield of biodiesel increases significantly when the catalyst concentration is increased from 2 % to 10 % by weight. After 150 min at 80 °C and 2 wt percent catalyst addition, the reaction achieved equilibrium with 94.8 % biodiesel generation. Higher catalyst doses often enhance biodiesel output and shorten reaction times, according to research. Raising the catalyst concentration from 3 to 7 wt percent considerably shortened the reaction time from 185 min to 65 min, resulting in a greater biodiesel production from Jatropha curcas, which rose from 91.96 % to 97.75 % [113]. Nevertheless, no additional improvement in biodiesel output was seen when the catalyst dose was higher than the ideal 7 wt percent. Likewise, M. Majid discovered that raising the catalyst concentration from 3 wt percent to 9 wt percent increased the biodiesel output from 59.4 % to 92.25 % in the transesterification of used cooking oil [114]. According to A. Kassian, biodiesel yields over 85 % were obtained by increasing the catalyst loading from 3 % to 5 %. A high yield of 91.1 % was achieved with a catalyst loading of 6 % [115]. The yield decreased when the catalyst concentration was raised above 6 %, indicating that in these reaction circumstances, increasing the catalyst loading would not improve the generation of biodiesel. The biodiesel yield increases with increasing catalyst concentration until an ideal point is achieved, according to a pattern that is consistent across several investigations [116–118]. A thick slurry that forms when catalyst concentration surpasses the ideal level might decrease surface area and raise viscosity, interfering with the mixing of catalyst, oil, and ethanol [119,120]. Moreover, reactant aggregation brought on by higher catalyst concentrations might complicate product separation by increasing saponification [121,122]. This might produce a very viscous biodiesel product that is unfit for use as a diesel engine alternative fuel [123].

4.5. Influence of agitation speed or stirring rate

During the transesterification process, the rate of stirring is an important component that ensures efficient reactant interaction [124]. The stirring procedure is essential for increasing contact between the three immiscible phases of the transesterification reaction catalyst, ethanol, and oil and enabling the generation of biodiesel [125]. The biodiesel production is usually poor at lower agitation rates because the reactants are not sufficiently mixed. Reaction durations are shortened and biodiesel yields are increased by increasing the stirring rate, which helps get over mass transfer constraints. Nevertheless, too high a stirring speed may make the reaction mixture more viscous, which may make it more difficult to separate the biodiesel from the glycerol and eventually reduce the yield [126].

The effect of stirring speed on the generation of biodiesel has been the subject of several investigations. R. Akhtar, for instance, found that raising the stirring speed from 100 to 500 rpm increased the yields of biodiesel [127]. Similarly, E.G. Khater discovered that the biodiesel output improved from 93 % to 97.3 % when the agitation speed rose from 300 rpm to 600 rpm [128]. Nevertheless, the yield dropped to 95 % when the stirring speed was increased to 700 rpm. Similarly, I.U. Khan found that raising the stirring speed over 500 rpm resulted in a decrease in biodiesel production, whereas raising the mixing speed to 500 rpm boosted the yield to 94.05 % [129]. L. Zih-Hua proposed that a stirring rate greater than 600 rpm is ideal for producing high-quality biodiesel because it reduces the external diffusion constraints on catalysis [130]. Various studies have determined different ideal stirring rates for the production of biodiesel; these include 550 rpm [131].

4.6. *Evaluation of the Catalyst's reuse and recycling*

The efficacy of heterogeneous catalysts in reactions involving transesterification is greatly increased by their regeneration and reuse capabilities, which makes them perfect for economical and environmentally friendly procedures [132]. The ability to be reused of the RHA+30 % EH catalyst was assessed in this investigation. After the initial transesterification reaction utilizing the newly RHA+30 % EH catalyst, the catalyst was recovered by filtering the reaction mixture using a suction device and What man no. 42 filter paper. Following recovery, the catalyst was rinsed repeatedly with petroleum benzene and then acetone to get rid of any remaining amounts of FAME or glycerol impurities [133]. The catalyst has been placed on a Petri dish and dried for 4 h at 110 °C in the oven. Following drying, the catalyst was employed in the next reaction cycle after having been cooled in a desiccator. The process of regeneration was carried out once again for every cycle. The reusability of the catalyst was evaluated up to the fifth cycle under ideal circumstances, which included a reaction period of 150 min at 80 °C, a catalyst loading of 2 wt percent, and an ethanol-to-oil molar ratio of 15:1 (Fig. 9).

The experimental findings indicate a considerable increase in reaction time and a fall in yield from 94.8 % (with the fresh catalyst) to 77.25 ± 1.42 % after the fifth cycle. According to these findings, the RHA+30 % EH catalyst's activity appears to be steadily decreasing with each cycle, most likely as a result of the catalyst's surface becoming blocked or losing active ingredients. A progressive decline in biodiesel output was also seen by Foroutan et al. [134], Etim et al. [135], and Falowo and Betiku [136] who all reported similar results, suggesting that catalyst effectiveness decreased with repeated usage.

5. Examining biodiesel

FT-IR, ^{1}H NMR, ^{13}C NMR and GC Analysis of the Produced Biodiesel.

5.1. *Biodiesel characterization through ^{1}H and ^{13}C NMR investigations*

To verify the transformation of triglyceride lluppai ennai oil into ester [CH_3-CH_2-O-(C=O)-R], a H^{1}NMR study was performed [137]. Fig. 10 shows the process of turning lluppai ennai oil into biodiesel with a catalyst. The protons of the methyl ester in biodiesel are shown by the peak at 3.65 ppm. The ^{1}H NMR spectra also showed a peak for fatty acid methyl esters between 4.29 and 5.33 ppm, indicating that lluppai ennai oil (triglyceride) was successfully converted into biodiesel [138]. While the lack of a peak at 4.0 ppm, which is linked to the CH_2 group of glycerol, suggests a high output of biodiesel, the 4.29 ppm peak represents the protons (methyl group) from the alcohol (ester) portion. Triglycerides, diglycerides, and monoglycerides' glyceridic protons are responsible for the paired peaks in the 4.0–4.3 ppm region, offering more evidence of the transesterification reaction [139].

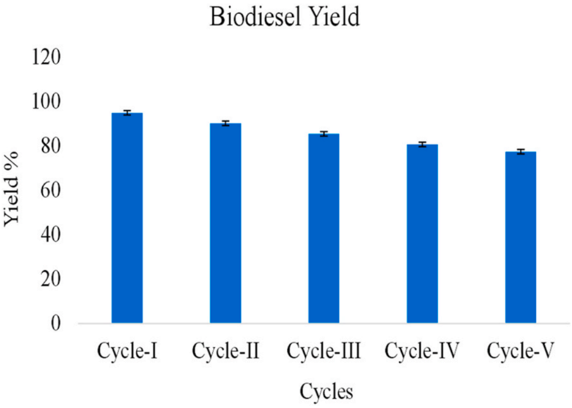


Fig. 9. Reusability of catalysts which consists of RHA+30 % EH.

The ^{13}C NMR spectra of the lluppai ennai biodiesel made with the RHA+30 %EH catalyst is shown in Fig. 11. The signal detected at 173.93 ppm identifies the ester molecules' carbonyl carbon, whereas the olefinic carbons are detected at 129.89 ppm. The oil's full conversion to biodiesel is confirmed by a new peak at 51.15 ppm, which corresponds to the methoxy carbon (-CO-OCH_3) of the methyl esters [140]. This work used ethanol to trans esterify lluppai ennai oil, and ^{13}C NMR was used to examine the biodiesel product, fatty acid ethyl esters (FAEE).

5.2. *FTIR analysis of biodiesel*

Functional groups and related stretching and bending vibrations in the biodiesel sample were identified using the mid-infrared region of the FTIR spectra as shown in Fig. 12. The fingerprint area, or 4000–500 cm^{-1}, is the crucial spectral range for differentiating between oil and FAME [141]. In addition to ester and lactone (C=O) stretching at 1744 cm^{-1}, the FTIR spectra revealed significant asymmetric and symmetric stretching vibrations of the alkyl group at 1461, 2845, and 2928 cm^{-1}, as seen in Fig. 10. Esters are confirmed by the peak at 1744 cm^{-1}, which corresponds to C=O stretching. The stretching of a tertiary alcohol (N-H) group was detected at 1166 cm^{-1}. The –CH_2– rocking vibration of the long-chain methyl esters was also identified as the cause of the peak at 713 cm^{-1} [142]. These results verify that biodiesel is the final result of trans esterifying lluppai ennai oil with eggshell.

5.3. *FAME characterisation by GC studies*

Fig. 13 shows the chemical content of the biodiesel made from lluppai ennai oil, which was analysed using the GC method. Saturated, monounsaturated, and polyunsaturated fatty acid esters were among the six kinds that were found by the study (Table 5). Stearic acid (C18:0) at 24.08 % and palmitic acid (C16:0) at 22.54 % were the two main saturated fatty acids. Of the polyunsaturated fatty acids, linoleic acid (C18:2) made up 17.95 % and linolenic acid (C18:3) made up 0.35 percent, while oleic acid (C18:1) made up 33.24 %. Furthermore, 0.587 % of the sample included the saturated fatty acid arachidic acid (C20:0) [143,144].

5.4. *Characteristics and features of biodiesel*

To assess the quality of biodiesel, certain criteria must be met. Table 6 outlines the properties of biodiesel produced from lluppai ennai oil, along with the relevant ASTM D6751 standards. One of the key properties of biodiesel is its viscosity, which reflects its internal resistance or friction to flow at a given temperature.

This property is crucial because excessive viscosity can negatively impact the performance of fuel injection systems in engines. When biodiesel is too viscous, it becomes difficult to pump and flow through injector nozzles, pipelines, and orifices, leading to poor atomization and the formation of larger droplets during fuel injection. According to Table 5, the viscosity of lluppai ennai oil -derived biodiesel at 40 °C is 4.15 cSt, which falls within the acceptable range set by U.S. standards. Furthermore, viscosity measurements taken at different temperatures show that Mahua biodiesel has a viscosity of 4.12 cSt, in accordance with ASTM methods [145]. This relatively high viscosity may be due to

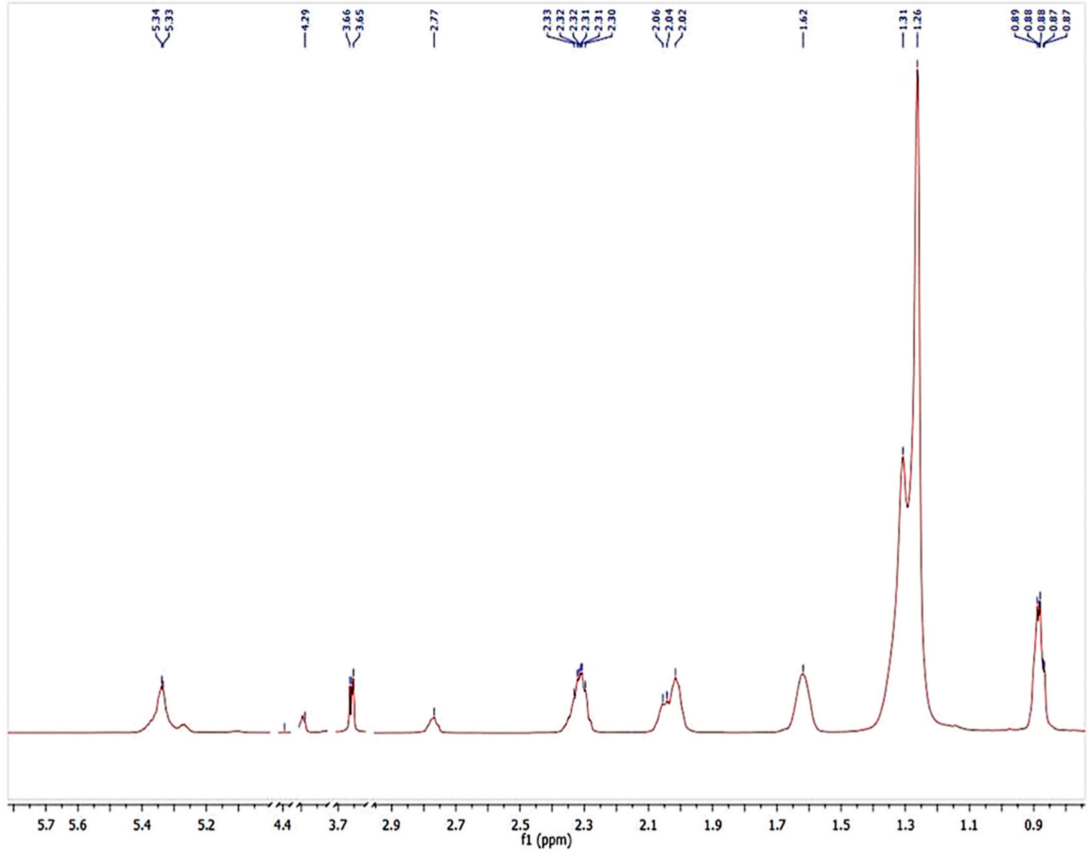


Fig. 10. ^{1}H NMR of lluppai ennai biodiesel generated from a RHA+30 % EH catalyst.

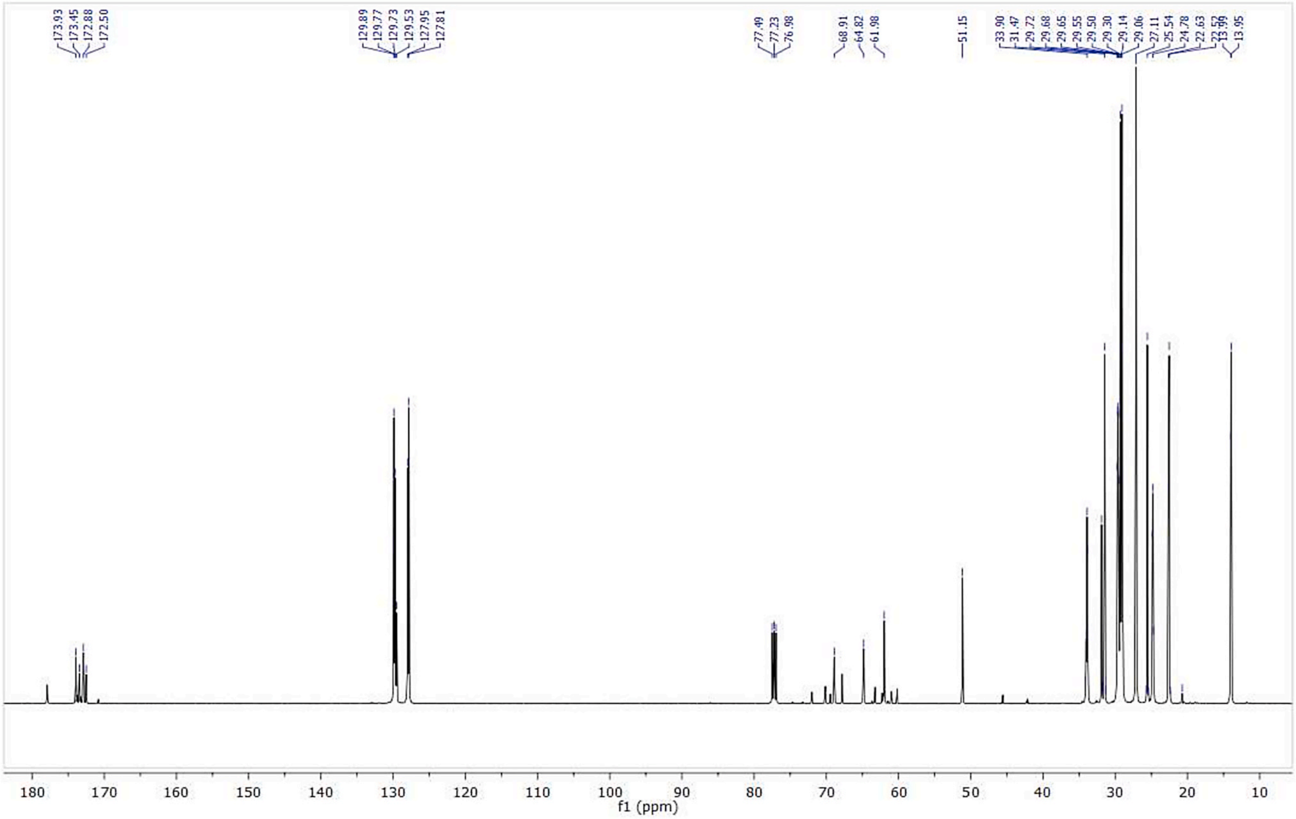


Fig. 11. ^{13}C NMR of lluppai ennai biodiesel generated from a RHA+30 % EH catalyst.

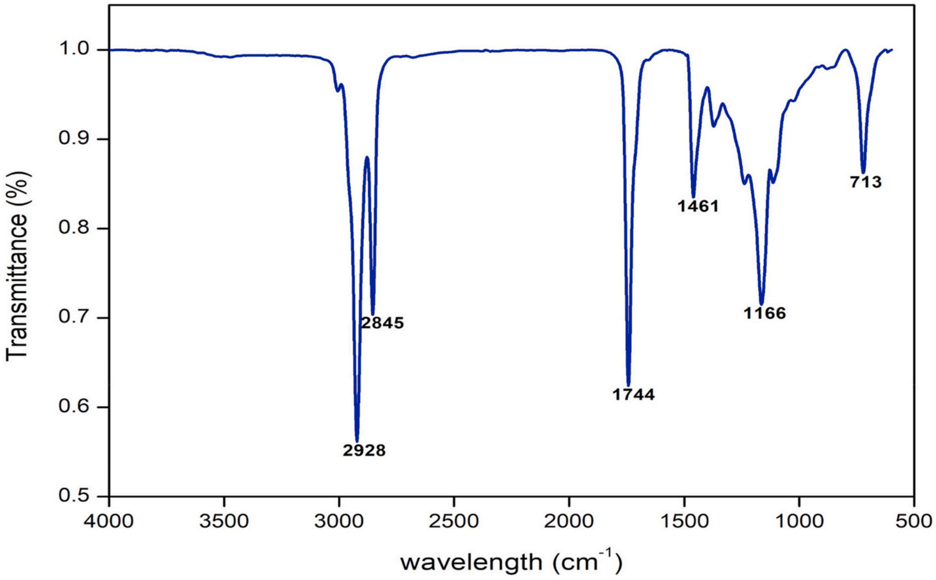


Fig. 12. FT-IR analysis lluppai ennai biodiesel with catalyst-based RHA+30 % EH.

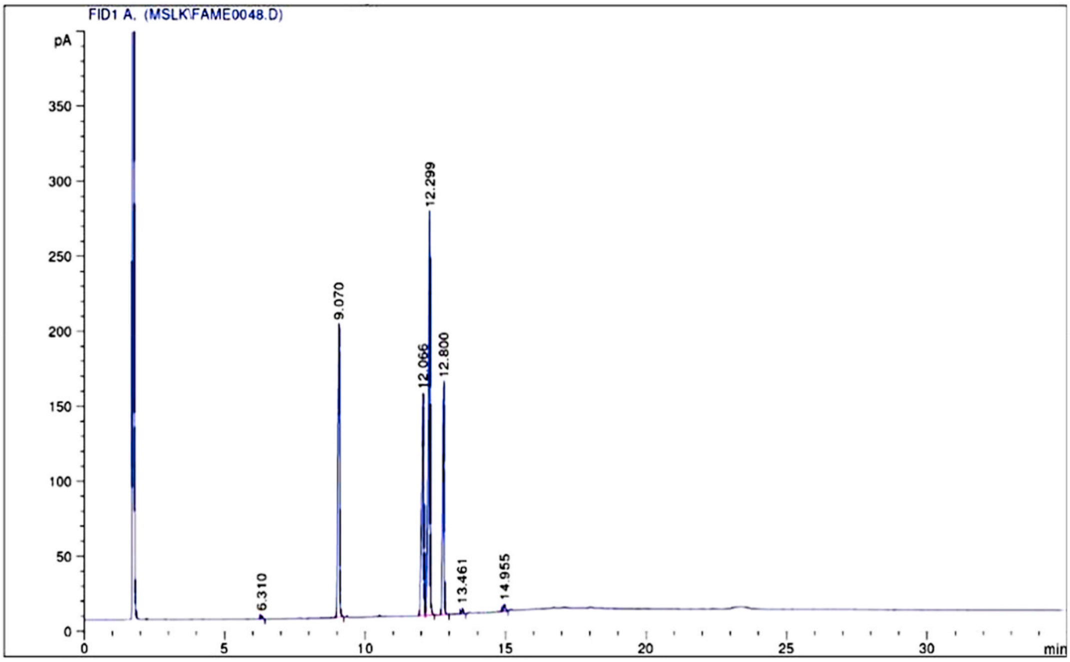


Fig. 13. GC profile of lluppai ennai biodiesel prepared from RHA+30 % EH.

the high degree of unsaturation in lluppai ennai oil biodiesel, as the viscosity of biodiesel generally increases when its degree of unsaturation decreases. Viscosity plays an important role in fuel injection and spray atomization. As noted by W. D. Gam, an increase in viscosity can hinder fuel flow, particularly at low temperatures. Due to its complex chemical structure and larger molecular mass, biodiesel typically has a viscosity that is 10–15 times higher than that of fossil diesel [146]. At low temperatures, biodiesel can solidify and become more viscous, which can compromise the integrity of pump drive systems [147]. According to ASTM D445 standards, the recommended viscosity range for biodiesel is 1.9–6.0 cst [148].

Since density affects an engine's atomization and burning procedures, it is a crucial factor in determining the quality of fuel. The European standard allows for a range of 860–900 kg/m^3, but ASTM standards call for biodiesel to have a density of between 860 and 894 kg/m^3. Because they are less volatile, higher density fuels can have worse vaporization after injection of fuel, which can cause partial combustion and carbon particles to accumulate in the combustion chamber. The biodiesel made from lluppai ennai oil has a density of 0.89 kg/m^3, which is within the acceptable limit. This is because a larger level of unsaturation results in an increased density of biofuel. Fuel behaviour is strongly influenced by fuel density, which is the weight per unit volume. Overall fuel efficiency is impacted by the thicker surface layers that high-energy oils, such as biodiesel, create [149]. Mass-to-volume conversions as well as measurements of flow and viscosity are required to determine relative density. Additionally, the relative density of biodiesel indicates how uniform it is in storage tanks [150].

Whenever a fuel comes in contact to an ignition source, its flashpoint is the lowest possible temperature at which it produces sufficient water vapour to ignite and produce a short flash. The flash is referred to as the

Table 5

The fatty acid content of lluppai ennai oil prepaid with catalyst RHA+30 % EH.

Fatty acids	Molecular formula	Saturated/ unsaturated	Content (%)	Molecular weight (g/ mol)
Palmitic acid (C16:0)	$C_{16}H_{32}O_2$	Saturated	22.5416	256.40
Stearic acid (C18:0)	$C_{18}H_{36}O_2$	Saturated	24.0841	284.48
Oleic acid (C18:1)	$C_{18}H_{34}O_2$	Monounsaturated	33.2460	282.46
Linoleic acid (C18:2)	$C_{18}H_{32}O_2$	Polyunsaturated	17.9574	280.45
Linolenic acid (C18:3)	$C_{18}H_{30}O_2$	Polyunsaturated	0.3570	278.43
Arachidic acid (C20:0)	$C_{20}H_{40}O_2$	Saturated	0.5874	312.53

Table 6

Characteristics of biodiesel generated from lluppai ennai Biodiesel with the catalyst RHA+30 % EH compared to ASTM standards.

Property	Unit	Lluppai ennai Biodiesel	ASTM standards	ASTM Range
Density at 40^{o}c	g/cm3	0.89 ± 0.004	D4052	0.86-0.90
Kinematic viscosity at 40 °C	cSt	4.15 ± 0.043	D445	1.9 to 6.0
Acid value	mg/ KOH/g	0.43 ± 0.008	D 664	0.8 max
FFA	Wt.%	0.21 ± 0.012	D5555	0.42 max
Flash point	^{0}C	180 ± 0.816	D93	100 to 170
Pour point	^{0}C	2 ± 0.471	D97	−15 to 16
Cloud point	^{0}C	4 ± 0.471	D2500	−3 to 12

fire point if it lasts longer than 5 s lluppai ennai biodiesel has a flashpoint of 180 °C, which is within the permissible limit. Fuel volatility and flashpoint are inversely correlated; fuels with greater flashpoints often exhibit lower volatility. Biodiesel has to have a flashpoint higher than the minimum needed for diesel fuel in order to be transported, handled, and stored safely [151]. Compared to the original vegetable oils, biodiesel derived from Fatty Acid Methyl Esters (FAME) often has a lower flashpoint [152]. As stated by Mejía, ASTM D93 sets the flashpoint norms at 93 °C and 120 °C.

How much free fatty acids (FFAs) are in biodiesel is indicated by its acid value. In a biodiesel sample, it is the amount of potassium hydroxide needed to neutralize the free acids. A result of less than 0.5 mg KOH/g is considered safe for handling. In engines, a high acid value can cause rubber parts to deteriorate, leading to problems like clogged filters. It was discovered that Mahua biodiesel had an acid value of 0.43 mg KOH/g, which is inside the acceptable range.

Proper engine functioning and fuel flow depend on biodiesel's low temperature characteristics. Poor engine efficiency, fuel hunger, problems starting, and possible damage from insufficient lubrication can result from even a partial solidification of the gasoline [153]. When fuel is cold, wax crystallizes, giving it a hazy or cloudy appearance. This temperature is known as the cloud point [154]. It was discovered that the lluppai ennai biodiesel's cloud point was 4 °C, which is within an acceptable range. When enough wax crystallizes to cause the gasoline to solidify and stop flowing, it is known as the pour point. Using the ASTM D2500 and D97 techniques, the pour point is estimated. Conventional diesel often has a lower pour point and cloud point than biodiesel [155]. lluppai ennai biodiesel's pour point, which is likewise within the permissible range, was determined to be 2 °C.

6. The benefits and drawbacks of adopting RHA as an environmentally conscious substitute

A renewable and adaptable substance, rice husk silica (RHA) offers several benefits. RHS is an ecologically acceptable alternative that lowers waste and promotes sustainability by offering a renewable source of silica as a by-product of rice milling [156]. RHA, which has a silica concentration of 85 %–95 %, is used in a number of sectors, including as storage of energy, agriculture, & architecture. Several studies have demonstrated that RHA works well as a reinforcing ingredient in composites, enhancing the mechanical qualities of materials like cement and polymers, including tensile and flexural durability and impact resistance [157]. Because of its remarkable purity, considerable purification is not necessary, saving time and money. Other benefits of RHA include a wide surface area, superior mechanical qualities, heat resistance, and biocompatibility, all of which increase the range of possible uses for this material.

RHA functions as a fertilizer with a gradual release that enhances soil moisture preservation, reduces soil compaction, and promotes crop development, making it an eco-friendly substitute for chemical fertilizers in farming. It has excellent promise as a material for environmentally friendly energy storage devices because of its porous structure, which also increases the dependability of cycles in electrochemical reactions and increases energy storage capability [158]. Additionally, compared to traditional materials, RHA-based goods have less embodied energy and ecological impact, which lessens their negative environmental effects.

The use of RHA as an alternative to conventional silica sources has several drawbacks despite its many advantages. Variability in its attributes, influenced by things like rice type, location, and farming practices, can alter the concentration of silica and limit its usage in applications that need consistent and accurate qualities [159]. The requirement for large harvesting and processing amenities, economic feasibility, and variations in the availability of rice husks may make scaling up RHA manufacturing difficult. RHA might demand specific processing techniques because to its substantial amount of silica and other impurities, and modifications to its hydrophilic surface may be necessary to increase its suitability with other materials [160].

Environmental issues and increased production costs are caused by costly extraction procedures such calcination, acid leaching, and pretreatment. Additionally, a few of the environmental benefits may be lessened if contaminants are released when rice husks are burned to produce power.

RHA is nevertheless a practical and sustainable substitute for traditional silica sources for a variety of uses, notwithstanding these difficulties. In order to overcome these constraints and improve RHA production and use in sustainable innovations, further research and development is required.

7. The financial and ecological consequences of using RHA

7.1. The economic viability and flexibility of RHA manufacturing

When evaluating the feasibility of producing rice husk ash (RHA), accessibility and commercial viability are crucial considerations. Variables include the extraction process chosen; the cost of raw materials, labour, and equipment all affect the cost of production of RHA. Techno-economic evaluations indicate that the generation of rice husk ash (RHA) is comparable in terms of expenses, with an average cost of around $100 per ton. RHA's potential for usage in sectors like rubber and polymer strengthening is demonstrated by the fact that prices can vary from $62 to $102 per ton, depending on manufacturing size. Additionally, because of its scalability, the combustion approach is ideal for producing RHA on a big scale, satisfying the growing need.

Additional advantages of integrating RHA extraction into already-existing rice mills include less waste and increased possibility for profit. For example, the cost-effectiveness ($0.17/kg) and notable waste reduction of the acid-leaching process have been evaluated. Furthermore, the potential of the alkali fusion method to reduce manufacturing costs while maintaining the necessary silica manufacturing performance has been studied. Furthermore, at the manufacturing cost of $234.3 per ton of silica, the Microwave-Assisted Extraction (MAE) technology has demonstrated economic feasibility. The opportunity for extensive industrial application is demonstrated by its ability to scale up to 3.5 million tons yearly.

Additional scalable techniques including sol-gel and acid-leaching have additionally shown promise for producing RHA on a wide scale. The competitiveness of traditional silica supplies, manufacturing costs, and consumer demand all affect how economically viable various methods are. RHA is a growingly popular substitute for conventional silica sources as worries about its sustainability and environmental impact grow. RHA is positioned as a competitive and environmentally friendly alternative to traditional silica supplies because to the cost-effectiveness and scalability of advanced extraction procedures including leaching with acids and alkali fusion, which have been demonstrated to be $0.16/kg.

Research indicates that RHA production can be an advantageous and economical substitute for conventional silica, despite the fact that a number of factors affect its economic viability. RHA manufacturing is also scalable and flexible, which makes it ideal for industrial application. Variables including the extraction technique, the accessibility of raw materials, and the need for silica in a given location all affect how scalable the process is. Further investigation is required to assess the scalability of distinct separation processes for a range of applications in industry and to enhance production strategies.

7.2. The sustainability of RHA consumption and manufacturing

Rice husk ash (RHA) is a renewable substitute for conventional silica sources that offers environmental benefits, despite considerable difficulties in its manufacturing and use. On the plus side, RHA serves to solve environmental issues related to the handling of rice husk trash. Usually thrown away or burnt, rice husks a residue of milling rice because trash build up and air pollution. RHA helps to lessen the environmental effect of these activities by turning this waste into a valuable product, hence reducing the demand for waste.

Nevertheless, the collection and processing of RHA can use a lot of energy and water, which might have a negative impact on the environment. Concerns with the release of greenhouse gases and the decreasing quantity of water resources may arise from the high energy and water demands of some extraction techniques. Furthermore, if not used properly, substances like strong acids or alkalis used in the extraction process might pose hazards to both people and the surrounding ecosystem.

Green manufacturing methods that limit the use of chemicals, energy and water consumption, waste, and emissions are essential to lowering these adverse effects. According to life cycle studies, the manufacture of RHA, particularly by acid leaching, might reduce the release of greenhouse gases and energy consumption in comparison to traditional silica production, hence lessening its environmental effect. RHA presents a viable, sustainable substitute for silica supplies and disposal; nonetheless, in order to guarantee that its production and use are ecologically appropriate, it is crucial to carefully assess and control its environmental effects.

8. Challenges and future outlook

In the fields of environmental research, chemical transformations, and biofuel production, biomass has attracted a lot of attention. Of all the biomass resources, rice trash is one that shows the most promise for the agriculture sector. The process of turning rice trash into useful goods contributes significantly to solving urgent energy and environmental issues in addition to increasing the economic worth of agricultural by-products [161]. Even with the advancements, commercializing the conversion of rice trash still faces several obstacles.

A variety of prior treatment methods are typically needed for the effective use of rice waste materials. These include physical procedures like grinding, breaking, ultrasound examinations, and a microwave treatment, as well as chemical approaches like acid/alkali treatments and catalytic hydrothermal extraction with catalysts or digestive enzymes. Increasing surface area, improving homogeneity, and decreasing particle size are the main objectives of physical techniques. Chemical processes including oxidation, hydrothermal processing, and acid-base treatments, on the other hand, are essential for decomposing organic materials in rice debris and reducing complicated organic compounds to forms that are easier to handle [162]. Although chemical pre-treatments make rice trash more accessible, they are often energy-intensive, water-intensive, and generate a lot of effluent. This makes more post-treatment procedures necessary, which raises expenses and strains the environment. Furthermore, there are dangers to equipment and safety due to the high temperature and pressure conditions needed for these operations. With the promise of gentler and more affordable conditions, there is increasing interest in creating novel pre-treatment techniques, such as the use of regenerated high-performance catalysts or biochemical processes, to reduce energy, water, and ecological expenses.

A lot of research has been done on turning rice trash into useful compounds. But the extreme conditions required by the present biofuel production methods such as high temperatures, high pressures, catalyst involvement, and anaerobic environments make the process energy-intensive. Furthermore, the production rates of gaseous and liquid biofuels frequently do not meet their ideal potential [163]. Enhanced catalyst research and the combination of several processing processes are essential for more effective biofuel generation from rice trash under milder circumstances. For instance, combining the pyrolysis of rice trash to create liquid fuels at comparatively low temperatures with the catalytic reforming of gaseous fuels to get high hydrogen density would offer a workable option. In order to promote catalytic reactions, rice trash is frequently immediately reacted with liquid acids such as HCL and H_2SO_4 in chemical conversion procedures. Unfortunately, these produce effluent, which is problematic for the environment. Because of their excellent accessibility and operation, ionic liquid catalysts have considerable promise in this process, despite their incomplete understanding. They must be made more reusable and less expensive in order to reach their full potential.

To increase productivity, lower costs, and enhance scalability, the emphasis should be on improving rice husk ash (RHA) techniques for extraction. The need for more research is highlighted by the limits of the many approaches that have been established. Variations in the extracted silica's purity and grade might affect how well it works in different applications. Further investigation is necessary to assess RHA's long-term stability and endurance in various usage, as well as the capacity for expansion of its manufacturing procedures. The environmental effects of RHA production and use must also be controlled by giving renewable energy sources top priority and putting effective waste management techniques into place.

Moreover, comprehensive safety and toxicity analyses are essential to comprehending RHA's long-term effects on the environment and human well-being. Every step of the chain of supply, from manufacture to shipment and storage, must have its financial feasibility evaluated in order to verify the economic sustainability of RHA development. In conclusion, RHA has a lot of potential as an affordable and sustainable substance, but its widespread use across different industries will depend on how well it handles issues like process standardization, increasing production efficiency, investigating new uses, and controlling environmental effects. The key to realizing RHA's maximum potential as a popular, sustainable substitute is ongoing investigation and creativity.

High activity and long-term durability are crucial in real-world applications, particularly for complex processes like catalytic transforming, where many reactions occur simultaneously and catalyst deactivation is a common issue. A better comprehension of coke formation mechanisms and transformation routes is necessary to increase catalytic activity and stability. Nevertheless, our comprehension of the fundamental processes is still restricted because of the intricacy of these reaction circumstances. Future studies should concentrate on examining these reactions in situ as doing so will yield information that will direct the creation of high-performance catalysts appropriate for widespread use. The sustainable synthesis of valuable chemicals and fuels from rice trash is achievable with improvements in pre-treatment technologies, a better comprehension of reaction processes, and the development of more efficient catalysts. This will have significant positive effects on society in the near future.

9. Comparison with previous studies

Several studies have investigated the synthesis of silica-impregnated CaO catalysts for the manufacture of biodiesel, and some of them have produced biodiesel yields over 85 %. Table 7 lists many techniques for creating CaO/silica catalysts from diverse sources. For instance, A. Farook, used the sol-gel technique to create silica from sodium silicate by impregnating it with calcium nitrate tetrahydrate in an aqueous solution [164]. After stirring, drying, and calcining the mixture, the CaO/silica catalyst was created. Using TEOS and calcium nitrate tetrahydrate, M. Majid, employed a similar method, immediately synthesizing the CaO/silica catalyst by sol-gel and then calcining it [165]. Similar to this N. Hong, used commercial CaO and TEOS as the source of silica, obtaining the catalyst by a co-condensation and calcination procedure [166].

However, the majority of the chemicals utilized in this research were commercial ones, which raises the cost of producing biodiesel and restricts the process's scalability. Recent studies have concentrated on employing waste materials as heterogeneous catalysts to lessen this. For example, Z. Helwani, used discarded fruit bunches as the silica source and leftover chicken eggshells as the CaO source to create a silica-impregnated CaO catalyst [167]. They used calcination and NaOH precipitation to produce silica, which was then impregnated with eggshell powder and calcined again. The same authors produced the CaO/silica catalyst in another investigation using peat clay as a source of silica. With a yield of more than 90 %, both catalysts demonstrated exceptional biodiesel production.

The two-step calcination procedure used in both trials, despite the high biodiesel yields, raises operating costs and diminishes the method's applicability. In comparison, the process employed in this work only calls for one calcination step and is simpler and more environmentally friendly. Furthermore, the manufacture of RHA supported catalysts using leftover Chicken egg shell has not been studied. According to our research, this innovative approach may significantly enhance the procedures used to produce biodiesel by producing heterogeneous catalysts from waste materials. Its eco-friendly qualities, affordability, adaptability, and compatibility with sustainable development, provides a sustainable alternative that reduces environmental effect and addresses waste management issues.

Table 7
Summary of silica/CaO Catalyst Synthesis from Various Sources for Biodiesel Production.

Source of catalyst	Preparation catalyst	Remark	Biodiesel yield (%)	Ref.
Rice husk and waste goat bones.	Ion-exchange, wet impregnation, calcination process	Waste materials	94	[168]
Peat clay and waste egg shell Waste materials	Calcination, precipitation and second calcination process	Waste materials	91	[169]
Empty fruit bunch and waste eggshell Waste materials	Calcination, precipitation and second calcination process	Waste materials	96	[170]
Tetraethylortho silicate(TEOS) and commercial CaO	Co-condensation and calcination process	Commercial chemical	95.4	[171]
Tetraethylortho silicate(TEOS) and calcium nitrate tetrahydrate	Sol-gel and calcination process	Commercial chemical	85.6	[172]
Sodium silicate and calcium nitrate tetrahydrate	Sol-gel,wet impregnation and calcination process	Commercial chemical	94.15	[173]
Rice husk and chicken egg shell	calcination process and, wet impregnation	Waste material	94.8	This study

10. Performance decline and deactivation mechanisms of RHA-ES catalyst

10.1. Catalyst deactivation mechanisms of RHA-ES catalyst by LECO CHN analyser

The performance decline and deactivation mechanisms of a heterogeneous catalyst derived from rice husk ash (RHA-Si) and eggshell (CaO) were investigated over five reuse cycles using a LECO CHN analyser which is shown in Table 8. Initial catalytic performance showed a low carbon deposition (0.369 %) and high biodiesel yield (94.8 %), but subsequent cycles revealed progressive deactivation, with carbon content peaking at 25.9 % in Cycle 3 and yields declining to 77.25 % by Cycle 5. This degradation was attributed to coking, active site leaching, and pore blockage, with fluctuations in carbon content (e.g., 13.0 % in Cycle 4) suggesting partial regeneration or non-uniform coke deposition [174]. While the catalyst retained moderate activity (>75 % yield after five cycles), the findings underscore the need for improved stabilization methods, such as surface modification or dopants, to mitigate deactivation in sustainable biodiesel production [175].

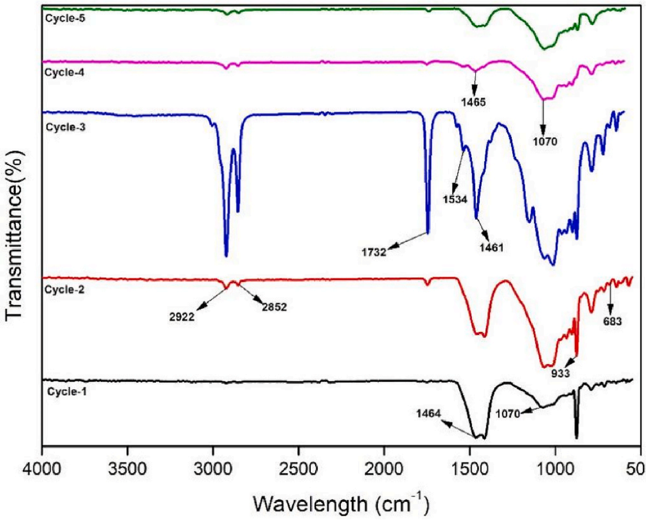
10.2. Catalyst deactivation mechanisms of RHA-ES catalyst by FT-IR

The RHA/CaO catalyst exhibited progressive deactivation through three distinct mechanisms across five reaction cycles. Initial performance (Cycle 1) showed optimal activity (94.8 % yield) with intact structural features (Si-O-Si at 1070 cm^{-1}, Ca-O at 1464 cm^{-1}) and minimal carbon deposition (0.369 %). The onset of deactivation became evident in Cycle 2 through emerging C-H stretches (2922/2852 cm^{-1}) and initial coke formation (933/683 cm^{-1}), correlating with reduced yield (90.1 %) and increased carbon content (7.38 %) [176]. Cycle 3 represented the critical deactivation phase, where advanced coking (1573/1536 cm^{-1} polyaromatic structures) and framework distortion led to severe pore blockage (25.9 % carbon) and yield decline to 85.3 %. Interestingly, Cycles 4–5 demonstrated competing phenomena: partial

Table 8
Analysis of Carbon content by CHN analyser (LECO CHN 828).

No of Cycles	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Cycle-1	0.369	0.0354	−0.809
Cycle-2	7.38	0.235	−0.864
Cycle-3	25.9	2.49	−0.831
Cycle-4	13.0	1.16	−0.909
Cycle-5	4.45	0.257	−0.493

thermal regeneration (carbon reduction to 4.45 %, transmittance recovery) through in-situ coke removal [177], countered by irreversible structural fatigue (broadened Si-O-Si/Ca-O vibrations) that ultimately limited performance to 77.3 % yield. This multiphase deactivation profile - from surface fouling to structural collapse - highlights the need for strategic interventions like dopant incorporation (Mg/Zr) and controlled thermal regeneration to extend catalyst lifespan while maintaining sustainable production metrics [178]. The study underscores that while carbon deposition initiates deactivation, structural integrity ultimately determines the catalyst's operational lifetime in biodiesel applications.



11. Circular bio economy

The use of a circular bio economy strategy to the transesterification of oils into biodiesel has been the subject of a few studies, including the one conducted by P. Andreo-Martínez [179]. This method emphasizes avoiding waste, lowering reliance on limited resources, producing biodiesel in a sustainable and resource-efficient manner, and promoting a regenerative system. The following fundamental ideas should be the focus of future research: Renewable, non-food feedstock's: One way to lessen rivalry with food production is to give priority to renewable feedstock's that are not generated from food crops. This involves using trash or by-products as raw materials to make biodiesel. Sewage as a Source Gathering and transformation of waste cooking oils, animal fats, and other lipid-rich waste products into biodiesel deserves greater emphasis in order to improve the circular bioeconomy's efficacy in transesterification processes. This method enhances resource usage while decreasing waste. Closed-loop applications Systems: Recycling or reusing by-products should be promoted via circular bioeconomy technologies. Glycerol, a typical by-product of transesterification, for instance, can be treated to extract valuable molecules or used again for chemical manufacturing, production of energy, or feed for animals. System Collaboration: To reduce waste and maximize resource utilization, the circular bioeconomy method should integrate multiple steps inside the biodiesel manufacturing chain. The Life Cycle Evaluation: To analyse the economic, social, and environmental effects of transesterification, future research should include life cycle evaluations. Advances in biomass conversion to biofuels and their effects on the environment using life cycle assessment (LCA) were evaluated A. E. anak Erison [180]. Future studies should evaluate the environmental performance of transesterification processes, with an emphasis on lowering greenhouse gas emissions, lowering energy consumption, and increasing resource efficiency, as system bounds in LCA studies might differ.

12. Conclusion

The goal of this study is to generate calcium silicate, a novel alkaline catalyst, by mixing leftover chicken eggshells with rice husk ash (RHA) and calcining the mixture for 4 h at 800 °C. The catalyst combination that resulted showed a significant number of alkaline components, particularly silica and calcium. The synthesized RHA+30 % eggshell (EH) catalyst had a high degree of crystallinity and was mostly composed of silica and calcium-based compounds, with silica accounting for 51.82 % and calcium for 44.58 % of the catalyst mass, respectively, both of which made substantial contributions to the catalytic process. Once the physical and chemical characteristics of several ratios were assessed, the RHA+30 % EH combination was selected for transesterification-based biodiesel synthesis. It was found that a catalyst concentration equal to 2 wt percent, an 80 °C temperature, a 150-min reaction duration, and a 15:1 ethanol-to-oil proportion were the ideal parameters for transforming into Luppai Ennai oil. A noteworthy 94.8 percent by weight biodiesel production was obtained with these settings, indicating how well the RHA+30 % EH catalyst conducted the method of transesterification. The generated biodiesel was analysed using gas chromatography, Fourier Transform Infrared Spectroscopy (FTIR), and H^1-NMR to ensure that it met standard fuel requirements. Additionally, the catalyst demonstrated exceptional reusability, maintaining the production of biodiesel of over 77 % following five separate cycles. The study's findings are in accordance with other investigations, therefore reaffirming the viability and scalability of producing biodiesel utilizing waste-derived heterogeneous alkaline catalysts. The growing need for reasonably priced and ecologically friendly energy solutions is mostly satisfied by this approach, which makes use of plentiful, inexpensive, and secure resources.

Prospective investigations have to concentrate on improving the purity of silica, developing nanoparticle technology, honing extraction techniques, and integrating green chemistry concepts. We may better serve the varied demands of different businesses and take important steps in the direction of an environmentally friendly energy future by making the most of RHA.

CRediT authorship contribution statement

Amit Kumar Rajak: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Devi Lal Mahato:** Visualization. **Shivani Dalal:** Formal analysis. **Syeda Fatima Zeenath:** Data curation. **Abdurahman Hajinur Hirad:** Formal analysis. **Ramyakrishna Pothu:** Software, Formal analysis. **Masimukku Srinivaas:** Validation. **Senthilkumar Nangan:** Writing – review & editing, Visualization. **Rajender Boddula:** Writing – review & editing, Supervision, Resources, Methodology, Investigation.

Data availability statement

Data is contained within the article.

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