



Research Article

Synthesis and characterization of calcium-based carbon catalyst for biodiesel production from PFAD

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Abstract

This study developed a heterogeneous catalyst (CaO) and activated carbon (AC) support generated from biomass waste (coconut shells) to improve biodiesel synthesis using palm fatty acid distillate (PFAD). Calcium-based carbon catalysts (CaO/CS-ACs) were synthesized from coconut shell biomass through carbonization of the coconut shell, chemical activation with potassium hydroxide (KOH), and calcium incorporation via wet impregnation. The resulting catalysts were characterised using Brunauer-Emmett-Teller (BET) analysis, Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM-EDX), X-ray diffraction (XRD), Fourier Transform Infra-Red (FT-IR), and basicity analysis. Among the synthesized catalysts, namely 10 wt% CaO/CS-AC, 15 wt% CaO/CS-AC, 20 wt% CaO/CS-AC and 25 wt% CaO/CS-AC, the 15 wt% CaO/CS-AC catalyst showed the best catalytic performance. Optimally, the esterification and transesterification reactions yielded a biodiesel production of 96.8% at a 10:1 methanol-to-PFAD molar ratio, with a catalyst dosage of 6 wt%, a temperature of 65 °C, and a 2 hours reaction duration. In addition, it exhibited greater reusability over five reaction cycles than pure CaO, owing to the robustness of the activated carbon and calcium sites. The obtained biodiesel aligns with the standards set by EN 14214, confirming the effectiveness of this waste-derived catalyst approach for sustainable biodiesel synthesis using low-grade feedstock.

Keywords: biodiesel, calcium oxide, activated carbon, palm fatty acid distillate

Introduction

The decline in fossil fuel reserves and a range of environmental issues, such as the greenhouse effect and pollution, have prompted the development of biodiesel [1]. It is greener, renewable, biodegradable, non-toxic, and has high oxygen content, which provides better combustion than diesel. Moreover, it demonstrates excellent lubrication properties, low sulphur and nitrogen content, and can be used directly in the engine without modification [2]. Biodiesel is defined as fatty acid methyl ester (FAME) derived from the synthesis of edible and non-edible vegetable oils as well as animal fats in the presence of alcohol, preferably methanol, using catalysts through the esterification and transesterification processes [3].

research because they address issues associated with homogeneous catalysts, such as low corrosiveness, ease of separation from products, no washing steps, and recyclability [4]. Additionally, they can produce biodiesel in a short period [5]. These catalysts are reliable due to their enhanced activity, selectivity, and flexibility, even with feedstocks containing high FFA [6]. Various types of heterogeneous catalysts used in biodiesel production include hydrotalcite [7], alkaline-earth metal oxides (MgO, BaO, SrO, CaO) [8], zeolites [9], ferric-alginate beads [10, 11], heteropolyacids [12], supported catalysts [13], and ion exchange resins [14]. Several studies suggest that alkaline metal oxides are among the most effective heterogeneous catalysts [15-18].

Heterogeneous catalysts have attracted increasing

CaO, a member of alkaline metal oxides, is a

promising heterogeneous base catalyst characterised by high basic strength, good catalytic activity, low cost, and eco-friendliness [19]. It is commonly used as a catalyst in the trans-esterification of oils or fats to produce biodiesel [20, 21]. Furthermore, it is one of the most efficient solid base catalysts for biodiesel generation due to its low solubility in alcohol, high alkalinity, and low toxicity [22]. Literature [23] reported biodiesel production from synthesized waste *Malleus malleus* shell (CaO) catalyst for the transesterification of waste cooking oil (WCO). Under ideal conditions, using a 7.5 wt% amount of catalyst, MTO of 11.85:1 at 60 °C in 1h 45 min, a high biodiesel yield of 93.81% was achieved. Similarly, [24] synthesized a calcium oxide nano-catalyst for biodiesel production using WCO. At ideal conditions of 8:1 MTO, 1 wt% catalyst concentration, 50 °C reaction temperature, and 1hr 30 min reaction duration, 96% of biodiesel was produced.

Another study [25] synthesized CaO from snail shells to produce biodiesel from frying oil. The catalyst exhibited good activity in the transesterification process, yielding 87.28% at a catalyst amount of 2.0 wt% and a 6.03:1 MTO ratio in an 8 hours reaction duration at 60 °C reaction conditions. However, pure CaO has a small surface area and can leach into the reaction medium, resulting in product contamination and deactivation [15]. The unendurable calcium diglyceride formed during the transesterification reaction makes the process less reusable. To eliminate these issues, the research aims to improve the CaO performance on a carbon support. Support materials improve the activity and interaction between reactants on the catalyst's surface [26]. Moreover, it provides a stable framework for metal oxide, reducing the leaching of heterogeneous catalysts (CaO) during the transesterification process with alcohol over prolonged periods. Supported materials used in biodiesel production include silica (SiO₂) [27], alumina (Al₂O₃) [28], zeolite [29], and activated carbon (AC) [13]. The application of alumina and silica as catalyst supports at the industrial level retard wider usage due to their expensive nature. Hence, utilizing low-cost support from biomass will decrease the overall cost of biodiesel production. Recently, biomass waste has gained considerable attention among researchers due to its biodegradability, non-toxicity, and sustainable source of porous carbon material [30]. This porous material (activated carbon) derived from biomass can serve as a catalyst support to enhance the surface area and stability of the CaO catalyst [31].

Coconut shells (*Cocos nucifera*) belong to the Arecaceae family and are among Malaysia's primary agricultural waste biomass. Malaysia is the 12th largest

producer of coconuts globally, with about 538,685 metric tonnes of production capacity [32]. These have led to the generation of large quantities of waste shells. Coconut shells have great potential for industrial applications because they are cost-effective, widely available, and derived from renewable resources, with physicochemical compositions of 33.61% cellulose, 36.51% lignin, 29.27% hemicellulose, and 0.61% ash [33]. Because of their high strength, hardness, carbon content, high volatile matter, and low ash content, they are used to produce activated carbon with high quality [34]. Furthermore, turning biomass waste into activated carbon support can lessen waste management problems and biodiesel costs [35]. The use of activated carbon loaded with calcium catalysts has attracted the attention of researchers because these calcium-based carbon catalysts are more stable and capable of retaining physicochemical properties, presenting a promising option for economical biodiesel production [36].

The current study aimed to develop a high-performance, low-cost calcium-based carbon catalyst through the carbonization of coconut shell, employing KOH activation and calcium loaded via wet impregnation for a double-step esterification/transesterification process to generate biodiesel from PFAD. The physicochemical characterizations were carried out on the synthesized catalysts using BET, SEM-EDX, XRD, and FT-IR techniques. The study also investigated the effect of calcium incorporation on catalyst performance in biodiesel production. After identifying the catalyst with the highest activity, the research examined how experimental parameters like catalyst dosage, methanol to PFAD molar ratio, reaction temperature, and time of reaction affected FAME yield (%) through the transesterification of PFAD to FAME. Finally, the ability of the catalyst to be reused was examined.

Materials and Methods

Materials

Coconut shells (CSs) and Palm Fatty Acid Distillate (PFAD) were obtained from the local market and Keck Seng (M) Berhad, Malaysia, respectively. Calcium oxide (CaO), methanol (CH₃OH) (99.99%), potassium hydroxide (KOH) (99%), Isopropyl alcohol, tetrahydrofuran (99.5%), sulphuric acid (H₂SO₄), Hammett indicators (neutral red H- = 6.8, bromothymol blue H- = 7.2, phenolphthalein H- = 9.8, 2,4-dinitroaniline H- = 15, nitroaniline H- = 18.4), and benzoic acid were purchased from united scientific company Malaysia. The components of PFAD were analysed by gas chromatography (GC), revealing free fatty acids (FFA) at 84.1 ± 1.3 wt%, triglycerides at 10.2 ± 0.4 wt%, 1,3 diglycerides at 2.1 ± 0.8 wt%, 1,2 diglycerides at 1.9 ± 0.6 wt%, and monoglycerides at

1.6 ± 0.5 wt%. The physicochemical properties of the produced biodiesel, including iodine value, ester content, viscosity, acid value, pour point, flash point and density, were determined and compared with the specifications of the EN 14214 standard to evaluate its suitability as a diesel fuel substitute.

Activated carbon preparation

The cleaning of the coconut shells was carried out using distilled water, afterwards dried at 100 °C overnight, crushed and ground using a grain grinding machine into a powder, which was then passed via a BL-15B mesh with a 2mm mesh size. Coconut shell biochar was heated using a furnace under N₂ at 600 °C for 2 hours to produce carbonized charcoal. 2g of coconut shell charcoal was mixed and stirred for two hours in a 500 ml 2 M KOH solution for activation. Afterwards, the suspension was filtered, and the recovered solid was repeatedly cleaned using distilled water until the pH was neutral. The final charcoal was dried overnight using an oven at 105 °C. The activated coconut shell charcoal was stored in an air-tight container after being labelled as CS-AC.

Preparation of catalyst

The wet impregnation-calcination method was carried out to synthesize CaO/CS-AC catalysts. An impregnating solution of CaO, prepared at varying concentrations of 10%, 15%, 20%, and 25%, was incorporated into CS-AC. To prepare a 15 wt% CaO-loaded catalyst, 1.5g calcium powder was mixed with 100 ml of distilled water, and 8.5g of dried CS-AC was incorporated, stirred for 1 hr at 800 rpm. Suspension was then calcined for 3 hours at 650 °C after being dried for 24 hours at 105 °C.

Characterization

N₂ adsorption-desorption isotherms (BET) at -196 °C in liquid N₂, the catalyst's surface area and pore volume were calculated with a Micromeritics ASAP 2020. The morphological features and elemental make-up of the synthesized catalysts were observed via SEM-EDX. XRD was employed to study crystalline features of the catalysts via a Bruker D8 Advance Diffractometer. FTIR analysis was performed with a Perkin Elmer System 2000 to identify surface functional groups of the catalyst within the range of 4000 to 500 cm⁻¹. To evaluate the basic strength, the Hammett indicator method was employed, whereby the catalysts were mixed with methanol solutions containing different Hammett indicators. Hammett indicator titration technique was executed with benzoic acid in a 0.02 mol/L anhydrous methanol solution to assess total basicity.

Investigation of catalytic performance

The experimental investigation was conducted in two

successive stages: esterification and trans esterification of PFAD. Esterification occurred in a three-neck flask. Initially, 60 g of PFAD oil was added at 60 °C. In a 12:1 molar ratio, methanol was introduced along with a 1 wt% H₂SO₄ catalyst. It was stirred for 1 hr at 400 rpm to ensure complete reaction. A separating funnel was used to recover the residual methanol and the H₂SO₄ catalyst [37]. Before transesterification, the FFA of the lower layer was measured. A measured amount of CaO/CS-AC (3-8 wt%) was added to methanol in a ratio of 4:1 to 14:1. Then, 2g of the previously esterified PFAD was introduced into a three-neck bottom flask, heated from 50-80 °C, and stirred at 400 rpm for 1 to 3 hours in a water bath. A heating mantle was used, along with a thermometer, to preserve a stable temperature, while a condenser was employed to recover methanol. The CaO/CS-AC catalyst was filtered out after completing the reaction. To ensure complete separation, the product was left undisturbed in a separatory funnel for 24 hours. Biodiesel is the upper layer, with the bottom layer containing glycerol. Excess methanol was removed from the obtained biodiesel at 70 °C. GC was employed to analyze the FAME yield (biodiesel) and was computed using the following formula.

$$\text{Biodiesel yield (\%)} = \frac{\text{weight of biodiesel} \times \% \text{ FAME}}{\text{weight of oil}} \times 100 \quad (1)$$

whereby % biodiesel is the quantity of biodiesel obtained via GC analysis.

Reusability study of the catalyst

Once the process of transesterification was completed, the used-up catalyst from the reaction medium was extracted, dried in an oven after being cleaned with tetrahydrofuran at 105 °C for 12 hours. The extracted sample was subsequently recycled for the transesterification under the same reaction conditions to assess its catalytic activity over multiple cycles.

Results and Discussion

Characterization: XRD

The XRD patterns of the synthesised CS-AC and CaO/CS-AC catalysts are presented in **Figure 1**. The pristine CS-AC sample displayed broad, low-intensity diffraction peaks centred at 2θ = 24.1° and 43.5°, corresponding to the (002) and (100) planes of amorphous carbon, indicating a predominantly disordered graphitic structure [38, 39]. Upon impregnation with calcium oxide, the CaO/CS-AC composites exhibited peaks at 2θ values of 32.23°, 37.36°, 53.27°, 64.32°, and 67.15° corresponding to (111), (200), (220), (311), and (222), the formation of cubic CaO on the carbon support, aligning with the ICDD standard ICDD 00-037-1497 (JCPDS 37-

1497) [40]. Additional sharp, intense reflections at 2θ values 29.53° , 35.86° , 39.52° , 43.08° , 47.45° , and 48.63° (104), (110), (113), (202), (018), (116) respectively are the CaCO_3 (calcite) XRD diffraction pattern from the interference of CO_2 during the synthesis process, as reported in prior studies [41, 42]. Other minor peaks at 2θ values of 23.0° and 26.4° indicate the presence of amorphous carbon in the composite materials.

The peak intensity varied with CaO loading. Lower loadings (10 wt%) produced weak CaO peaks, indicating smaller crystallites, a highly dispersed phase and limited basic site density [43]. Clear CaO crystalline peaks were observed at 15 wt%, suggesting well-developed crystals, good dispersion and a high number of exposed active sites. At 20 wt%, the CO_3^{2-} peaks became sharper and reduced CaO peaks, with a tendency toward larger crystallite agglomeration and reduced adequate surface exposure, aligning with N_2 adsorption–desorption isotherm findings. In contrast, at higher loading (25 wt%), the peaks are more intense and sharper, implying partial aggregation and increased crystallinity due to overlapping CaO domains [44]. The increasing peak intensity with calcium loading confirms the successful incorporation and crystallisation of CaO within the carbon matrix. Notably, the 15 wt% CaO/CS-AC sample exhibited well-defined CaO peaks without significant baseline distortion, suggesting optimal dispersion of CaO particles on the carbon surface, which presents good catalytic activity [45].

Morphological and elemental analysis (SEM/ EDX)

The surface morphology of the synthesized CS-AC

and CaO/CS-AC catalysts was examined using SEM at an accelerating voltage of 20 kV with a magnification of $2000\times$, and a scale bar of $10\ \mu\text{m}$ was used as displayed in **Figure 2**. The corresponding elemental composition was analysed by EDX (**Table 1**). The SEM micrograph of the CS-AC appears rough and porous, as seen in **Figure 2(a)**. This porosity provides a large surface area to anchor the basic site (CaO), prevent leaching, and thereby accelerate the reaction rate [15]. Compared with the CaO/CS-AC samples, **Figure 2(b-e)**, the 10 wt% CaO/CS-AC catalyst retained a relatively porous architecture with visible micropore channels, suggesting that low loading did not occlude the carbon pores. At 15 wt%, this morphological pattern exhibits homogeneous CaO dispersion and strong metal-support interaction, which enhances both catalytic activity and accessibility [46, 47]. In contrast, at 20 wt% CaO/CS-AC catalyst, the surface topography became progressively denser and more granular, filling the pore walls and forming a rougher, more textured morphology.

However, further increasing the loading to 25 wt% CaO (**Figure 2e**) resulted in agglomerated CaO clusters, evidenced by larger, block-like particles that partially covered the porous framework. Such agglomeration reduces the effective surface area and limits reactant diffusion, corroborating the decreased catalytic performance observed at higher loading levels as confirmed by N_2 adsorption–desorption isotherm and XRD analysis [15]. The SEM analysis confirms that 15 wt% CaO/CS-AC presents the most balanced surface morphology, retaining porous structure while ensuring efficient CaO dispersion.

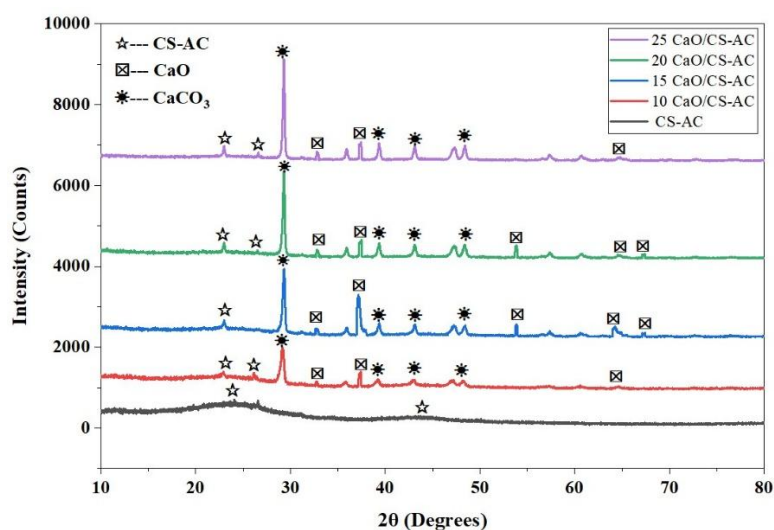


Figure 1. XRD pattern of the synthesized CS-AC, CaO/CS-ACs catalyst showing characteristic diffraction peaks of crystalline CaO

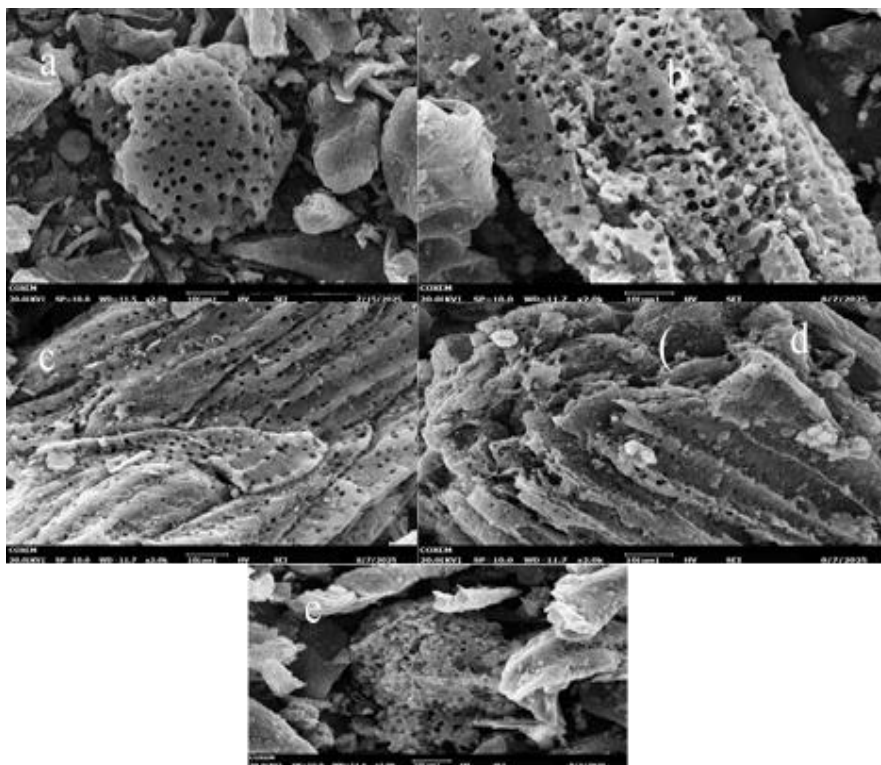


Figure 2. SEM micrographs of porous structure CS-AC (a) and (b-e) CaO/CS-AC catalysts illustrating dispersi on of CaO particles on the support surface

Table 1. EDX analysis of CS-AC and CaO/CS-AC Catalysts

Samples	Elemental Contents (wt.%)						
	Ca	C	O	K	Si	Na	Mg
CS-AC	-	67.64	26.14	5.36	0.20	0.12	0.54
10CaO/CS-AC	2.44	72.14	19.78	4.25	0.32	0.52	0.55
15CaO/CS-AC	7.18	60.62	26.54	4.72	0.37	0.58	-
20CaO/CS-AC	21.01	48.54	28.81	1.24	0.25	-	0.15
25CaO/CS-AC	31.88	30.02	35.57	0.94	1.44	-	0.16

The EDX compositional data (**Table 1**) further substantiate the morphological observations. The unmodified CS-AC exhibited elemental composition of carbon (C) and oxygen (O), with trace elements such as magnesium (Mg), sodium (Na), silicon (Si), and potassium (K) originating from the parent coconut shell biomass. Following CaO impregnation, the elemental data show a steady increase in Ca content from 2.44 wt% at 10 wt% CaO/CS-AC to 31.88 wt% at 25 wt% CaO/AC, accompanied by a corresponding decrease in carbon concentration, confirming the successful deposition of CaO. The oxygen content also increased with the increasing CaO loading, indicating the enhanced formation of Ca–O bonds and the presence of basic oxide functionalities, which are critical for transesterification activity [1]. The 15 wt% CaO/CS-AC catalyst displayed an optimal Ca/O ratio,

reflecting efficient anchoring of CaO particles without excessive accumulation. Similar compositional trends have been reported in other biomass-derived CaO-supported catalysts [22, 48].

Collectively, the SEM–EDX findings confirm that the impregnation and calcination procedures effectively introduced CaO onto the CS-AC support, resulting in a robust and porous catalyst with a uniform particle distribution. The microstructural and compositional evidence validates the suitability of the 15 wt% CaO/CS-AC catalyst for achieving high basicity and stability in PFAD biodiesel synthesis.

Analysis of surface area and pore volume

N₂ adsorption–desorption isotherm of CaO/CS-AC catalysts displays Type IV isotherms with H4

hysteresis loops, indicating a mesoporous structure with slit-shaped pores, in accordance with the IUPAC classification, as shown in **Figure 3**. The initial sharp uptake at low relative pressure ($P/P_0 < 0.1$) corresponds to a monolayer, indicating the presence of micropores, followed by the gradual increase at intermediate pressures, which is multilayer adsorption. The hysteresis loop is associated with capillary condensation in mesopores. This is highly desirable for biodiesel production, confirming that the CaO/CS-AC catalysts possess a hierarchical pore structure (micro–mesoporous) [49]. The surface area along with its pore volume are shown in **Table 2**. There was a notable decrease in surface area from $307.87(\text{m}^2/\text{g})$ to $306.81(\text{m}^2/\text{g})$ and pore volume from $0.17\text{cm}^3/\text{g}$ to $0.16\text{cm}^3/\text{g}$ for 10 to 15 CaO/CS-ACs, respectively. However, at higher CaO loading, the

surface area and the pore volume decrease further. This decrease indicates that the catalyst support is occupied by a Ca compound, blocking the pore channels and reducing pore volume, thereby confirming the effective impregnation of CaO into the pore channels [50].

At lower loading (10 wt%), the catalyst showed a high surface area and well-developed mesoporous structure, facilitating effective diffusion of triglyceride molecules; however, the limited basic sites restricted catalytic activity. While excessive CaO loading of 20 and 25 wt% resulted in pore blockage and reduced surface accessibility despite higher basicity, which hindered reactant diffusion and lowered catalytic efficiency.

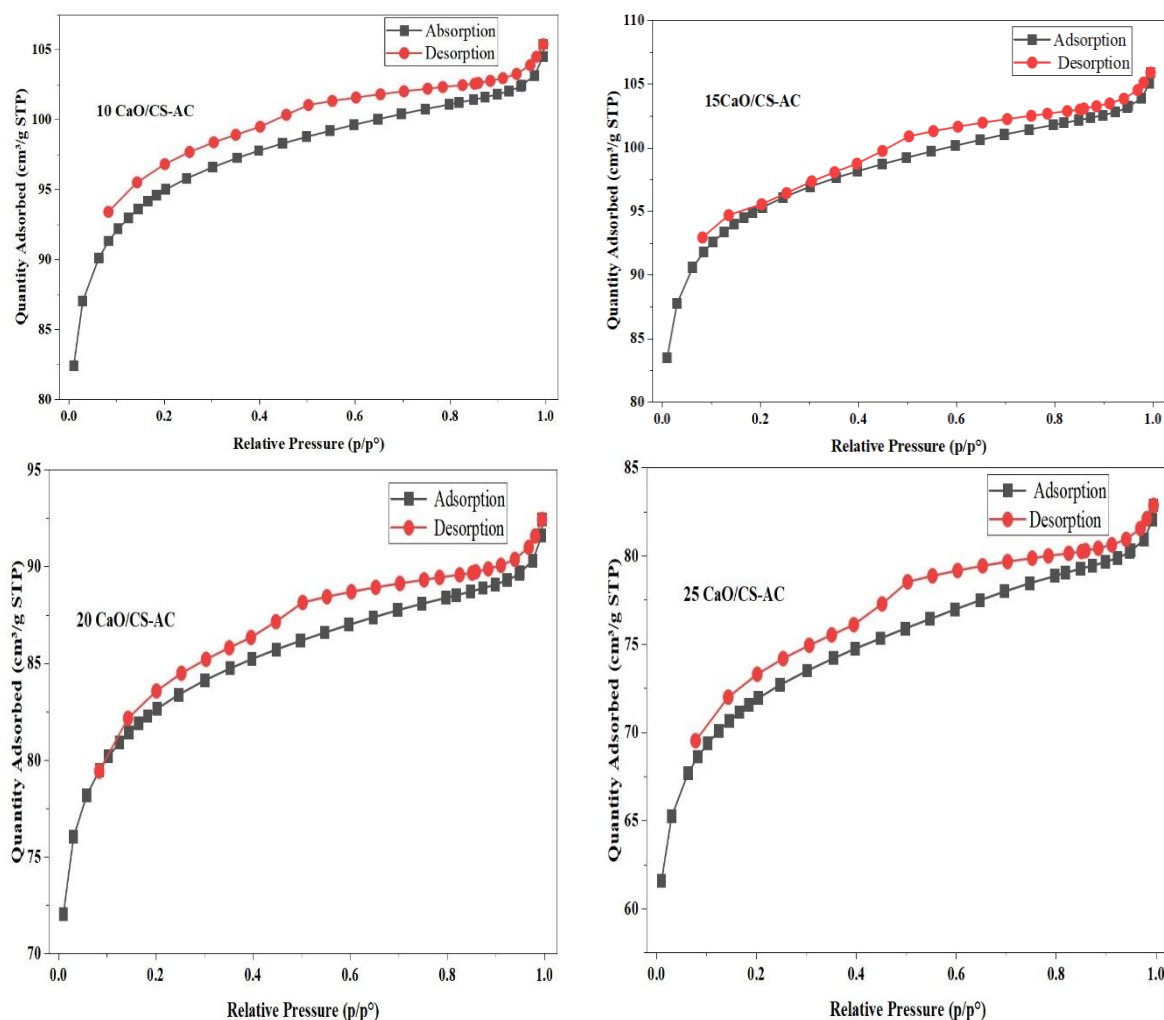


Figure 3. N_2 adsorption-desorption isotherms of CaO/CS-ACs catalysts exhibiting a Type IV isotherm with a hysteresis loop, indicating mesoporous characteristics

Table 2. Properties of the samples

Catalyst	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
10CaO/CS-AC	307.87	0.17
15CaO/CS-AC	306.81	0.16
20CaO/CS-AC	267.71	0.14
25CaO/CS-AC	233.32	0.12

An optimum balance was achieved at 15 wt%, where sufficient surface area and pore structure were retained alongside adequate and strong basic sites. This synergy between textural properties and surface basicity resulted in the highest biodiesel yield. Therefore, the catalytic performance is governed by structural accessibility and active site availability, confirming that both N₂ adsorption–desorption isotherm surface characteristics and basicity play crucial roles in determining the efficiency of biodiesel production.

Basicity

The basic strength and the total basicity of CS-AC and CaO/CS-AC catalysts are presented in **Table 3**. The obtained result shows that CS-AC has a low basic strength and is neutral due to its synthesis process [15]. The basic strength and overall basicity of the produced catalysts considerably improved as CS-AC was loaded with CaO from 10 wt% to 15 wt%, i.e., the basic strength is $7.2 < H_- < 9.8$ and $15.0 < H_- < 18.4$, and the total basicity is 2.6 to 10.2 mmol/g, respectively. Specifically, the synthesised catalyst with a 15 wt% CaO loading exhibited much higher basicity due to the complete decomposition of the Ca phase; at lower loadings, insufficient CaO results in low basicity values. The presence of the Ca compound on the surface catalyst was primarily responsible for the increased total basicity. However, increasing CaO from 20 to 25wt.% led to a decrease in total basicity to 8.0 and 4.5 mmol/g, respectively, due to excessive Ca, which hindered complete coverage of the AC phase [39, 49].

Fourier transform infrared (FTIR)

The FTIR spectrum of CS-AC is shown in **Figure 4**. The FTIR profile appears at 3347 cm⁻¹, indicating the presence stretching vibration of an O-H group associated with water molecule absorption, while the vibration peaks at ~2000 to 2653 cm⁻¹ are associated with aliphatic groups (C-H) [49]. Other vibrational bands located at 1701, 1562 and 1162 cm⁻¹ are assigned to C=O, C=C, and C-O corresponding to carboxylic acid groups, aromatic carbon structure and stretching vibration of ester groups, respectively [32]. The CS-AC derived from coconut shell displays functional groups comparable to those reported in existing literature which enhance surface polarity and better metal anchoring sites [39].

The FTIR spectrum of the CaO/CS-AC samples exhibits peaks at 3323, 3372 and 3308 cm⁻¹ interrelated to the hydroxyl group as displaced in **Figure 5**, with slight shifts in peaks position due to the interaction of the metal oxide and the support surface. The sharp stretching bands associated with CaCO₃ result from CO₂ interaction during preparation process are located at 1393 to 1404. This is further confirmed by XRD analysis [51]. Weak bands are observed around ~2509 cm⁻¹ are linked to C-H stretching vibrations and the band at 1796 cm⁻¹ in all the synthesised catalysts are carboxyl groups C=O [15]. Moreover, sharp bands at 872 and 712 cm⁻¹ are indicative of Ca-O-Ca and Ca-O bonds, respectively, confirming the existence of active calcium on the carbon support [41].

Table 3. Basicity analysis of samples

Catalyst	Basic Strength (H ₋)	Total Basicity (mmol/g)
CS-AC	$6.8 < H_- < 7.2$	-
10CaO/CS-AC	$7.2 < H_- < 9.8$	2.6
15CaO/CS-AC	$15.0 < H_- < 18.4$	10.2
20CaO/CS-AC	$15.0 < H_- < 18.4$	8.0
25CaO/CS-AC	$9.8 < H_- < 15.0$	4.5

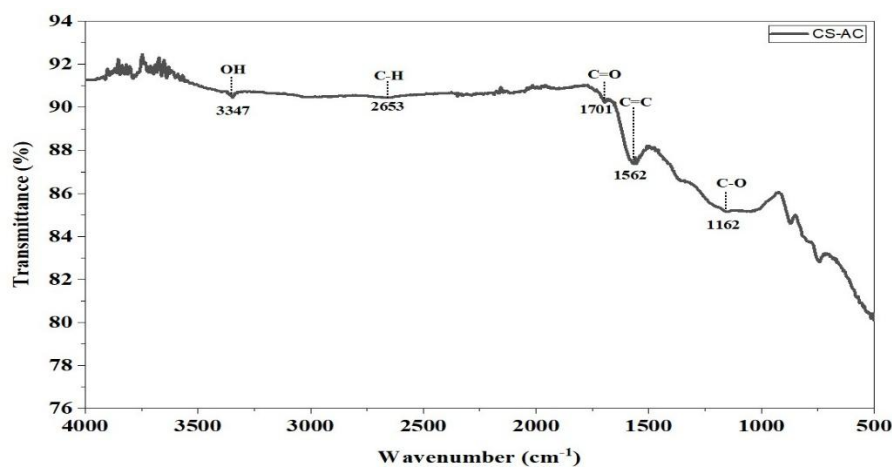


Figure 4. FTIR spectrum of synthesized CS-AC, shows characteristic peaks oxygen functional groups

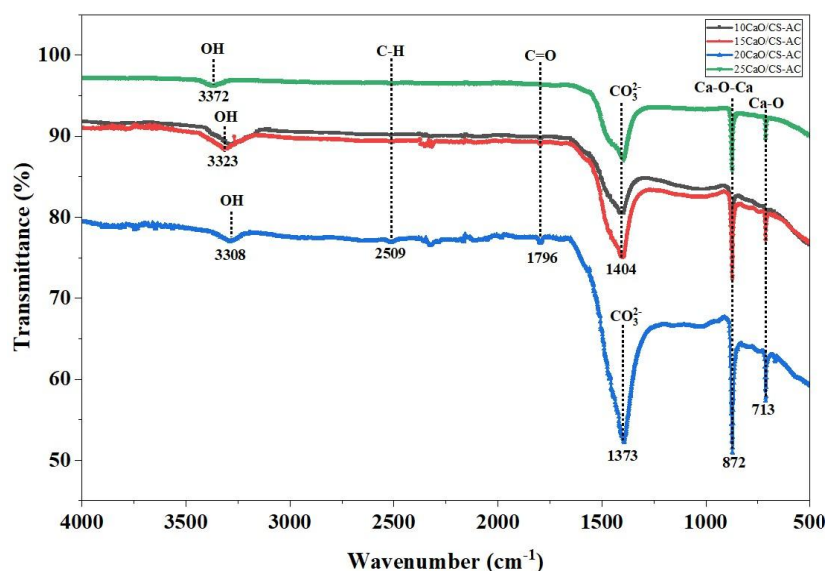


Figure 5. FTIR spectra of synthesized CaO/CS-ACs catalyst indicate the presence of surface functional groups of Ca–O bonding associated with the active catalytic species

This analysis confirms the successful incorporation of CaO onto the CS-AC support, as proved by the presence of Ca–O and CO_3^{2-} bands. Oxygenated functional groups on the CaO/CS-ACs catalyst are reduced indicates surface coverage by CaO species. The presence of strong basic sites and carbonate species plays a crucial role in enhancing the catalytic activity for biodiesel production [52].

PFAD esterification

In the reaction involving esterification, a series of experiments was conducted due to a high level of FFA content in PFAD. After the reactions, the acid value was investigated through the titration using the American Oil Chemists' Society method. A sample of

0.1 grams of PFAD was combined with 10 ml of isopropanol, with the addition of a few drops of phenolphthalein indicator. The mixture was shaken properly to guarantee homogeneous mixing and titrated with a 0.1 N KOH solution. Titration continued till the solution turned a light pink colour, marking the endpoint. This process drastically decreased the acid value to 2.0 mg KOH/g, which is in accordance with the ASTM standard value of 4 mg KOH/g for transesterification reactions [53, 54].

The amount of KOH utilized was measured and utilized to ascertain the acidity of the PFAD using the corresponding equation:

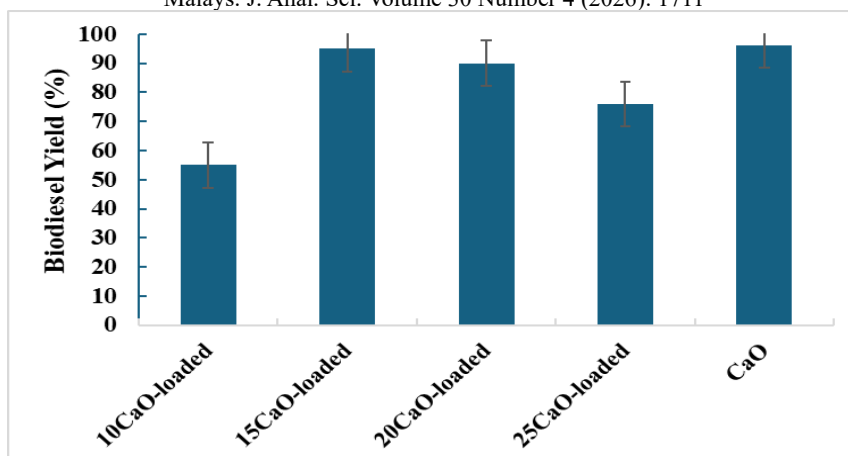


Figure 6. Impact of calcium loading on FAME yield

$$\text{Acid value} \left(\text{mg} \frac{\text{KOH}}{\text{g}} \right) = \frac{(V_f - V_i) \times N \times 56.1}{w} \times 100\% \quad (2)$$

Catalyst activity

Optimization of CaO/CS-AC catalysts in transesterification

Figure 6 shows the impact of the calcium amount on the biodiesel produced. CaO showed good catalytic efficiency in the process of transesterification, achieving a FAME yield of 97.2 wt%. However, a large portion of the catalyst was lost during the process due to the disintegration of the basic sites into the reaction medium, resulting in homogeneous catalytic behaviour [48]. Conversely, the supported catalysts showed increased FAME content from 59% to 95.0% as the CaO was loaded from 10 to 15 wt%. It was observed from the N_2 adsorption-desorption isotherm that increasing the amount of CaO significantly enhanced the catalyst's activity, which is ascribed to its overall basicity, as shown in Table 3. It can be concluded that basicity plays a crucial part in catalytic behaviour compared to surface area. As displayed in **Figure 6**, a 10 wt% Ca loading did not supply adequate active locations for the transesterification reaction. Conversely, increasing the amount beyond 15 wt% resulted in reduced performance, possibly due to crystallisation or agglomeration of Ca compounds, which causes inadequate active species distribution on the catalyst surface. Therefore, a 15 wt% Ca-loaded catalyst is considered the optimal choice for further optimization. Additionally, supported catalysts were readily restored and repurposed across numerous cycles with minimal degradation in catalytic efficiency compared to CaO alone.

Optimization of reaction parameters

To examine the ideal reaction parameters, the earlier-optimized supported catalyst loaded with 15 wt% calcium was used in the experiments. The impacts of different methanol-to-oil molar ratios, catalyst amounts, reaction times, and temperatures on the yield of biodiesel were examined, as shown in **Figure 7**.

Figure 7a illustrates how the methanol to molar oil ratios affect the FAME yield of PFAD. The formation of biodiesel requires a greater molar ratio of methanol to oil to drive the transesterification reaction in the direction of the product. It was observed that the highest biodiesel yield of 95.0% was achieved in a 10:1 methanol-to-oil molar ratio, while ratios above 10:1 lowered the biodiesel conversion. This is attributable to excess methanol, which dilutes the catalyst concentration. The results demonstrate that a 10:1 methanol to molar oil ratio is sufficient to achieve optimal catalytic performance.

Another important condition is the catalyst amount, i.e., the percentage of heterogeneous catalyst used in the transesterification of PFAD, which is a key factor for the reaction to occur. The catalyst concentration determines the total active sites in a reaction that are available; thus, higher catalyst concentrations produce more biodiesel. However, when excess catalyst is used, it results in lower biodiesel yield. The transesterification of PFAD with a 15CaO/CS-AC loaded catalyst achieved the highest biodiesel conversion of 96.8 at 6 wt%, as indicated in **Figure 7b**. Nonetheless, when the catalyst amount exceeds 6 wt%, no substantial increase in biodiesel conversion is observed, which is caused by mass transfer resistance of the reactant.

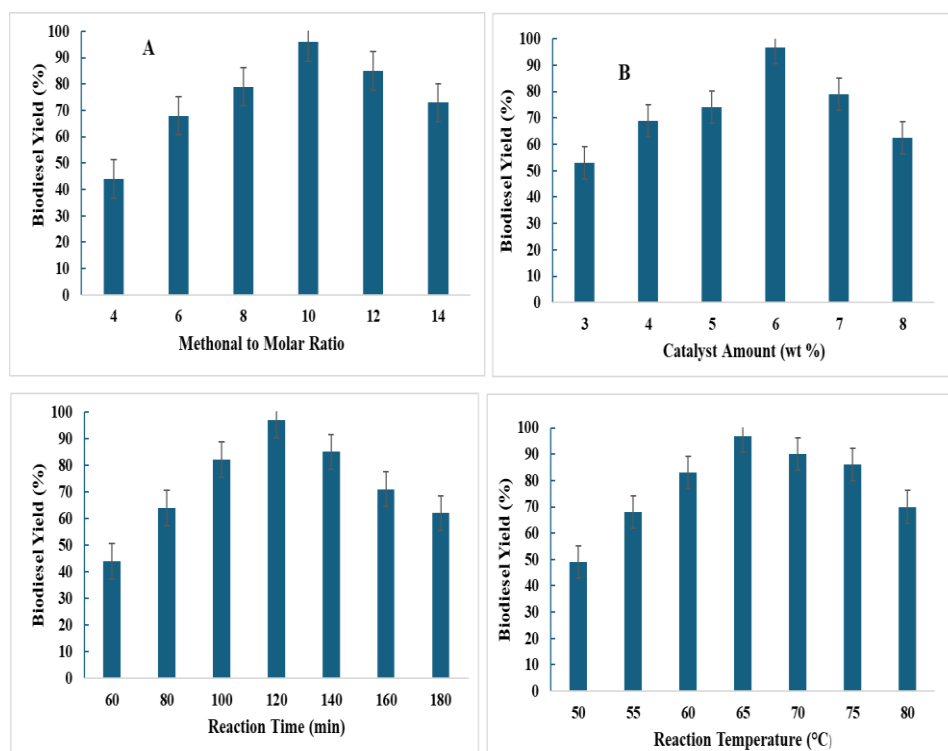


Figure 7. Impact of reaction parameters on biodiesel yield using 15CaO/CS-AC catalyst demonstrating the catalytic performance in the transesterification of PFAD. The ideal parameters for the reactions were a 10:1 methanol-to-oil molar ratio, 6 wt % catalyst, 2 hours reaction duration, and 65 °C temperature. (a) The molar ratio of methanol to oil, (b) the amount of catalyst, (c) the reaction time, and (d) the reaction temperature

The response time is shown in **Figure 7c** and varies from one to three hours. Biodiesel yield increased significantly from 45% to 80.1% within 100 minutes. The yield rose steadily, reaching 96.8% as the reaction time extended to 2 hours. However, there were no further improvements in the yield beyond this duration. Therefore, 2 hours was identified as the optimal reaction time. It is believed that after this optimal period, the production of FAME may have declined due to the onset of reverse reactions, such as the decomposition of the methyl esters.

The impact of temperature on biodiesel yield of PFAD was examined between 50 °C to 80 °C in an interval of 5 °C, with other parameters set at 2 hours response time, a mole ratio of 10:1, and a catalyst dosage of 6 wt.%, as illustrated in **Figure 7d**. An observable enhancement in the biodiesel output occurred upon raising the reaction temperature from 50 °C to 65 °C, with a maximum biodiesel output of 95.5% achieved at 65 °C. Once the temperature reached 70 °C, the reaction rate did not further accelerate because of the vaporisation of liquid methanol into the gaseous phase.

Reusability study

To determine the stability of the catalysts during the transesterification process, the pre-optimised 15CaO/CS-AC catalyst was recovered and reused. Repeated reuse of the catalyst was performed under ideal parameters: reaction temperature, 65 °C; reaction duration, 2 hours; molar ratio of methanol to oil, 10:1; and 6 wt% catalyst dosage. This was achieved by thoroughly washing the catalyst surface with methanol and tetrahydrofuran, then drying in an oven under vacuum at 105 degrees Celsius following its extraction from the reaction medium. The catalyst (15CaO/CS-AC) effectiveness exhibited a decline from 96.8% to 74.1% throughout the initial five rounds of the reaction, as shown in **Figure 8**. This reusability study suggests that a calcium-based carbon is more stable and sustainable than CaO alone.

Physicochemical properties of the biodiesel synthesized

Table 4 shows the difference between the EN 14214 standard and the biodiesel produced. It must meet this standard before biodiesel can be used in an engine. It is clear from the fact that all properties listed in the table are within the EN 14214 standard.

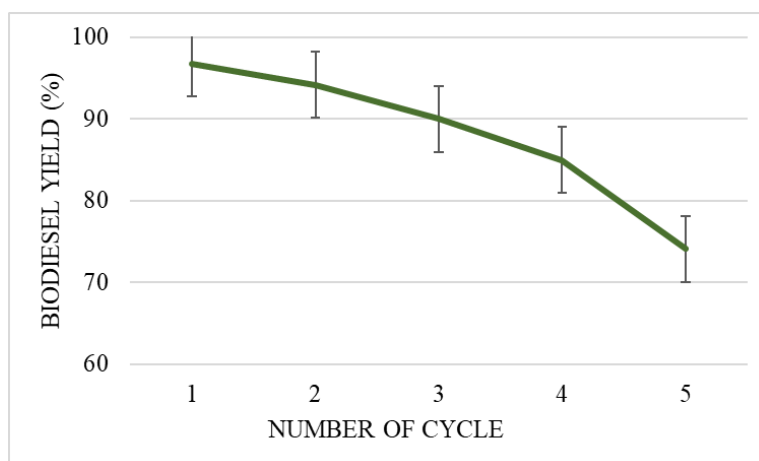


Figure 8. Reusability study of the synthesized 15CaO/CS-AC sample

Table 4. Physicochemical properties of biodiesel synthesized using 15CaO/CS-AC catalyst

Properties	Unit	EN 14214	Biodiesel
Iodine value	g Iodine/100 g	<120	63.4
Ester content	wt%	>96.5	96.8
kinematic viscosity	mm ² /s	3.5 to 5.0	3.9
Acid value	mg KOH/g	<0.5	0.9
Pour point	°C	-	3.2
Flash point	°C	>101	159
Density	kg/m ³	860–900	871

The synthesised biodiesel exhibited an ester content of 96.8 wt%, surpassing the EN 14214 minimum requirement of 96.5 wt%. This high methyl ester concentration confirms the efficiency of the esterification and transesterification process and the superior catalytic activity of the 15 wt% CaO/CS-AC catalyst. The kinematic viscosity of 3.9 mm²/s lies comfortably within the EN 14214 range (3.5–5.0 mm²/s), ensuring proper fuel atomization and injection characteristics during combustion. The density value of 871 kg/m³ also falls within the acceptable limit (860–900 kg/m³), indicating a balanced hydrocarbon composition that promotes efficient combustion and energy output [47]. The acid value of 0.9 mg KOH/g, although slightly higher than the EN 14214 maximum (0.5 mg KOH/g), remains acceptable for PFAD-based biodiesel, which often contains trace free fatty acids and residual monoesters. The modest acid content implies good storage stability and minimal risk of corrosion or injector fouling in engines [1]. Meanwhile, the iodine value of 63.4 g I₂/100 g indicates moderate unsaturation, conferring an excellent balance between oxidative stability and cold-flow properties, a critical feature for biodiesel

derived from waste-based feedstocks [55]. The flash point of 159 °C is substantially above the EN 14214 minimum of 101 °C, signifying low volatility and excellent handling safety. A high flash point is crucial in reducing fire hazards during storage, transportation, and use. Additionally, the pour point of 3.2 °C reflects good low-temperature fluidity, ensuring the fuel remains pumpable under tropical and subtropical environmental conditions [56]. Collectively, the produced biodiesel satisfies most of the EN 14214 standard, demonstrating its suitability as a renewable diesel substitute.

Analysis of the catalytic efficiency of carbon-derived catalysts

Table 5 compares the synthesized 15CaO/CS-AC catalyst with previously reported carbon-derived catalysts used in biodiesel generation. The compiled information confirms that the recently synthesized catalyst exhibits catalytic behaviour comparable with other carbon-derived catalysts from the literature. Notably, it provides significant reusability; this improvement is largely owing to the limitations of using CaO alone, which often leaches and dissolves

Table 5. Analysis of the catalytic efficiency of carbon-derived catalysts reported

Catalysts	Support	Reaction Parameters					Reference
		Molar Ratio	Catalyst Amount (wt%)	Temp. (°C)	Time (min)	Biodiesel Yield (%)	
AC/KOH	Malt bagasse	12:1	10	65	120	91.8	[59]
MAC@CaO	Almond shells	15:1	6	60	60	93.2	[15]
Ca/AC	Peach shells	8:1	5	65	160	96.0	[60]
CaO/K ₂ CO ₃ /BC	Algal biochar	18:1	4	65	3.20	98.83	[58]
RSS/CaO	Rubber seed shell	12:1	10	70	180	68.6	[57]
CaO/PMF	Palm fly ash	10:1	1	70	120	86.20	[37]
AC/CaO	Mollusk shells	40:1	11	120	180	96.0	[61]
CaO/CS-AC	Coconut shells	10:1	6	65	120	96.8	Present study

calcium into the reaction medium. To overcome these issues, CaO is commonly supported on other materials to enhance its catalytic activity and stability. As reported by [57], synthesized CaO supported on rubber seed shell produces biodiesel from waste cooking oil, and achieved a yield of 68.6%, which is lower than the current study. This low yield may be due to excessive temperature and time of 70 °C, 3 hours. Similarly, [15] obtained a biodiesel conversion of 93.2% from sunflower oil using the MAC@CaO catalyst; this report is closer to this work, which may be attributed to similar reaction conditions. In another study [58] attained a biodiesel yield of 98.83% from CaO/K₂CO₃ catalyst on biochar using edible waste oil, which was above the value of the present work. This is likely due to the source of the catalyst support, the molar ratio of 18:1, and the duration of the reaction. This study indicates that the 15CaO/CS-AC catalyst is highly effective for transesterification and holds considerable promise for industrial applications.

Conclusion

This study successfully synthesised a calcium-based carbon catalyst (CaO/CS-AC) from coconut shell biomass through carbonization, chemical activation, and calcium impregnation. Several characterization studies were conducted using BET, SEM-EDX, XRD, FTIR, and basicity analysis, confirming its high surface area, well-dispersed active sites, and strong basic properties suitable for biodiesel generation. In the esterification and transesterification of PFAD, the 15CaO/CS-AC catalyst exhibited the highest activity, reaching the peak possible biodiesel yield of 96.8% under ideal parameters: PFAD to methanol ratios of 10:1, catalyst dosage of 6, reaction temperature of 65 °C, and reaction duration of 2 hours. The minimal

loss of activity after five runs shows the applicability of this catalyst for sustainable and cost-efficient biodiesel generation from low-grade feedstocks. Thereafter, contributing to both waste valorization and renewable energy development.

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