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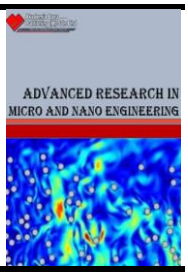

A Comprehensive Review of Biodiesel Production using Heterogeneous Catalyst

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ABSTRACT

Biodiesel, an eco-friendly alternative to petroleum diesel, is derived from vegetable oils or animal fats through transesterification. The use of heterogeneous catalysts, specifically titanium dioxide (TiO_2) and calcium oxide (CaO), in biodiesel production has garnered significant attention due to their environmental benefits and potential to replace fossil fuels. This study systematically analyses biodiesel production using TiO_2-CaO catalysts, highlighting their efficiency under various reaction conditions, catalyst preparation methods, and operational parameters. Different feedstocks, such as palm oil, cooking oils, and algal biomass, are evaluated. Methodologies reviewed include wet impregnation and photochemical techniques for catalyst synthesis, with varying reaction temperatures and times. The findings reveal that while TiO_2 and CaO have been extensively researched, the variation in methodologies hinders the development of standardized procedures like XRD, SEM, BET, and thermal analysis. Results indicate that cooking oil is a cost-effective feedstock, yielding biodiesel efficiently under optimal conditions: a methanol-to-oil ratio of 24:1, catalyst concentration of 5%, and reaction temperatures of 55-65°C. The highest biodiesel yield of 98% was achieved using palm oil. Further studies should focus on optimizing and standardizing biodiesel production processes using the TiO_2-CaO catalyst.

1. Introduction

After the 2015 Paris climate agreement, there has been a rise in renewable energy sources. The environmental impact and contribution to climate change from energy production using fossil fuels are significant. Despite the world's heavy reliance on fossil fuels for energy production, shifting to renewable sources is crucial to reduce this dependency and mitigate global warming.

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Cooking oil has emerged as a cost-effective alternative feedstock for biodiesel production, providing a more affordable option compared to palm oil, soybean oil, and sunflower oil [1]. Biodiesel is an eco-friendly alternative to petroleum diesel, produced from vegetable oils or animal fats through transesterification [2].

The renewable fuels industry depends on sustainable biodiesel production, using feedstocks like cooking oils, animal fats, and lipids from oil-producing microorganisms [3]. However, cooking oil is a cost-effective alternative feedstock for biodiesel production compared to pricier options such as palm oil, soybean oil, and sunflower oil [4]. Generally, biodiesel is produced through the transesterification reaction, where vegetable oils react with alcohol, facilitated by a catalyst [5]. This process produces fatty acid methyl esters (FAME) and glycerol, or triacetin and fatty acid ethyl ester as byproducts [6].

The standard transesterification reaction increases the oil's viscosity, negatively impacting the quality of the biodiesel produced [7]. Researchers have observed that transesterification at a low reaction temperature with a high reaction rate proceeds approximately 4000 times faster than acid catalysts [8]. Biodiesel can be used directly in engines or converted into methyl or ethyl esters through transesterification [9]. Through transesterification reactions, biodiesel can be produced from triglycerides in animal fats and plant oils using light alcohol and either alkaline or acid catalysts. Glycerine is generated as a by-product [10].

Catalysts like titanium dioxide (TiO_2) and calcium oxide (CaO) are crucial for biodiesel production. Researchers have focused on using a composite catalyst of titanium dioxide and calcium oxide (TiO_2-CaO) to produce biodiesel. However, studies on TiO_2-CaO catalysts in biodiesel production differ in raw materials, reaction conditions, catalyst preparation methods, and operational parameters. This variability hinders effective comparison and consolidation of findings, impeding the development of standardized and optimized procedures for biodiesel production with TiO_2-CaO catalysts.

This study is an investigation of biodiesel production using TiO_2-CaO catalyst by conducting a systematic review of relevant studies. We explore different raw materials, reaction conditions, catalyst preparation methods, and operational parameters. The study aims to identify gaps, present a comprehensive view of current knowledge, and pinpoint areas for further research in biodiesel production with TiO_2-CaO catalyst, building on previous research [11].

2. Biodiesel Production

Various methods are available for producing biodiesel, with transesterification being a practical and economically viable technique. Additionally, transesterification is a cost-effective method [12]. The transesterification process is widely used in industry to produce biodiesel [12,13]. During the transesterification reaction, fatty acids and alcohol interact in the presence of a catalyst. The final products are glycerin and methyl esters, known as biodiesel, as shown in Figure 1 [12].

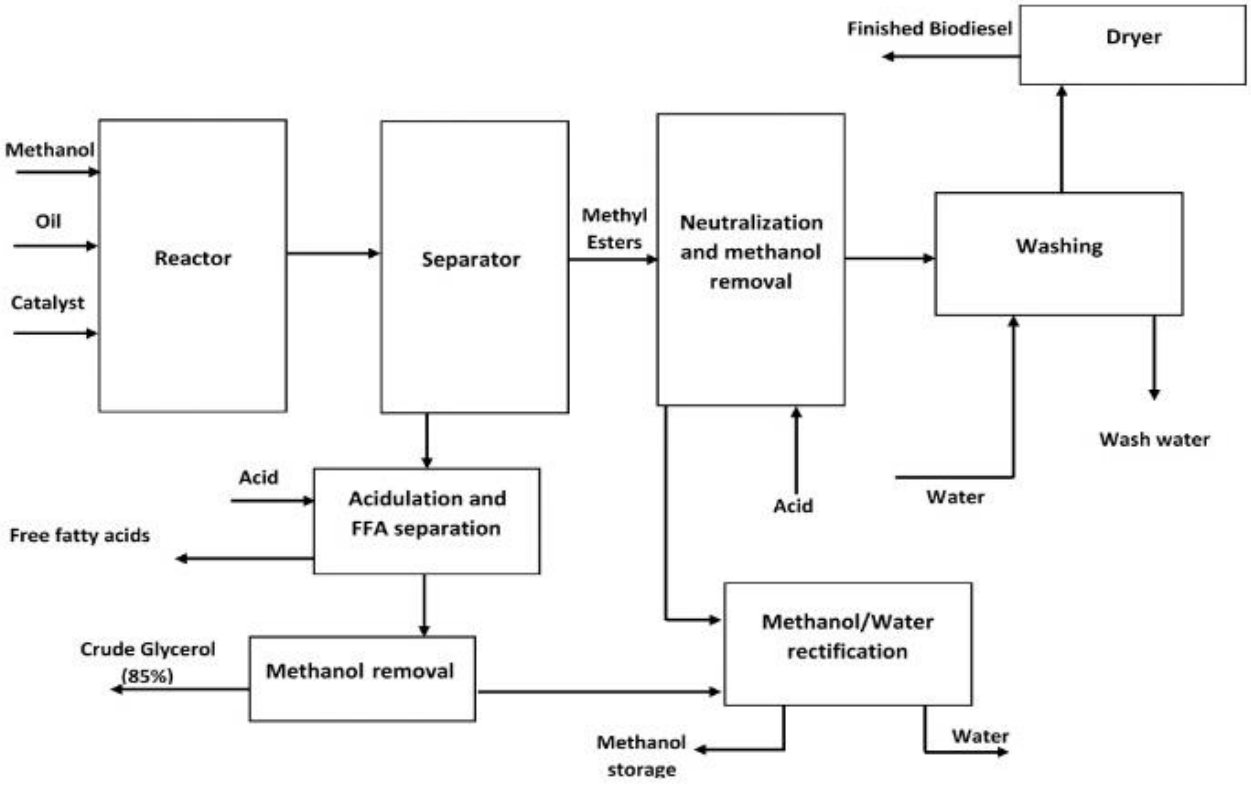

Fig. 1. Process flow scheme for biodiesel production

2.1 Transesterification Process

To understand the transesterification process for producing biodiesel from free fatty acids (FFA), heterogeneous acid catalysts and different alcohols are used, leading to the progression of transesterification reactions [14]. The conversion of vegetable oils into biodiesel often uses acids or alkaline substances as catalysts. Solid-state catalysts provide an alternative that eliminates the need for mineral acids or bases and allows for potential recyclability [15]. In biodiesel production, waste cooking oils undergo a two-phase transesterification process, as shown in Figure 2, while palm oil is processed using a base-catalyzed transesterification method [16].

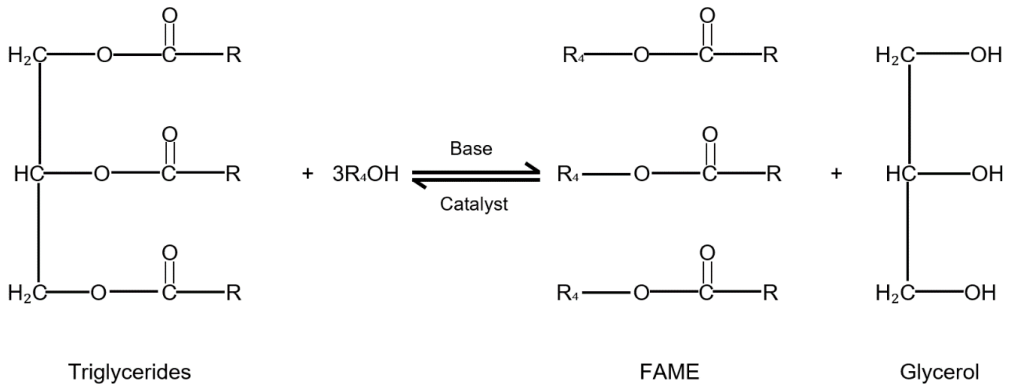

Fig. 2. Transesterification process scheme

2.2 Biodiesel Catalysts

Nano catalysts made of various substances are widely used in biodiesel production to simplify the process and reduce purification costs. Titanium dioxide (TiO_2) is a notable example of such nano catalysts [17]. A study aimed to develop a Li/TiO_2 catalyst for transesterification using wet impregnation. Different Li/TiO_2 catalysts were synthesized with varying lithium content and calcined at different temperatures. XRD analysis revealed that lithium improves catalytic performance without changing TiO_2's structure. Optimal conditions were a methanol-to-oil ratio of 24:1, a catalyst concentration of 5%, and a temperature of 55 ºC for 3 hours [14].

Researchers discovered that titanium dioxide-based catalysts with excellent CO_2 adsorption and desorption abilities were highly effective in transesterifying canola oil, even without pre-treatment [15]. A study used unaltered and copper-enriched TiO_2 catalyst to synthesize biodiesel from palm oil, as depicted in Figure 3. The highest yield was obtained at 45°C with a 20:1 methanol-to-oil ratio. The quality of the biodiesel was evaluated through tests and GC-MS analysis, while its composition was determined using various parameters [17]. However, TiO_2 nanoparticles are used in ternary fuel mixtures to decrease reliance on fossil fuels and emissions. Among the blends tested, Blend 6, consisting of 20% biodiesel, 10% bioethanol, 70% diesel, and 65 ppm TiO_2, showed superior performance. It improved brake thermal efficiency by 1.23% and brake-specific energy consumption (BSEC) by 2.1% compared to pure diesel fuel [18].

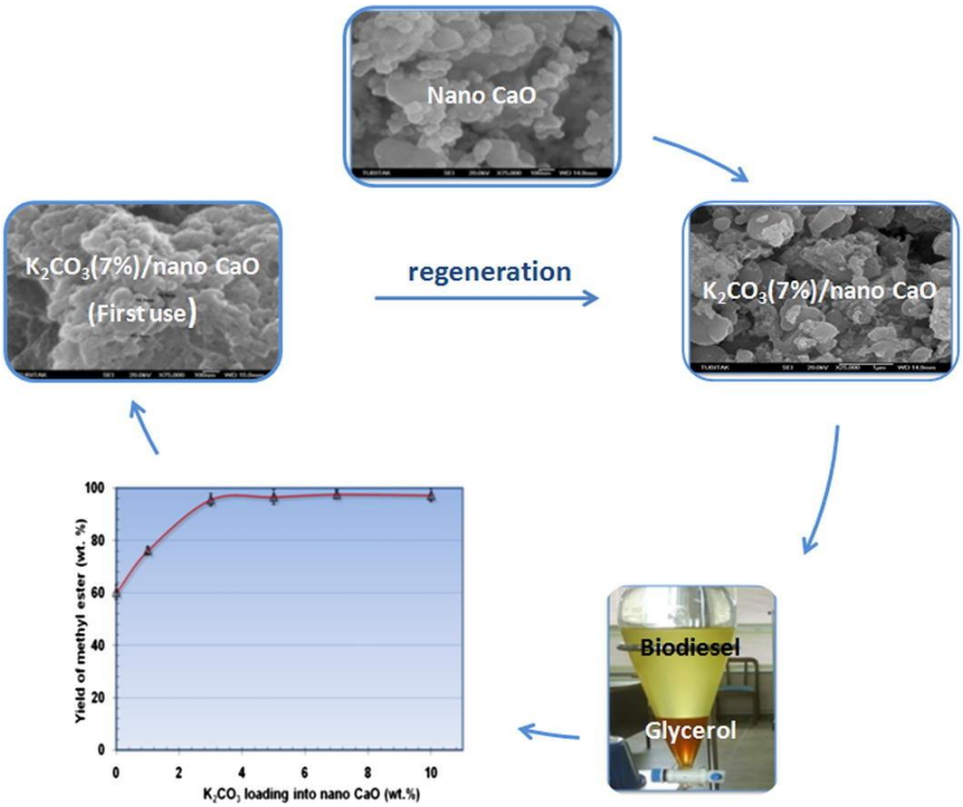

Fig. 3. Biodiesel production from canola oil

Calcium oxide (CaO), an alkaline substance, is well-known as a highly researched solid catalyst with strong basic properties and low solubility in methanol. Its affordability allows for the creation of a methoxide ion when methanol interacts with a hydroxide ion [19,20]. Compounds of Calcium oxide (CaO) can be derived from sources like eggshells and fly ash. Eggshells contain about 10% CaO by

weight. Additionally, natural catalysts such as MgO, CaO, SiO_2, Fe_2O_3, and heterogeneous CaO catalysts can be synthesized from Chicoreus Brunneus shells [21,22].

Zinc oxide (ZnO) and nickel oxide (NiO) catalysts can be used to produce biodiesel through transesterification, replacing fossil fuels. Palm seed oils, when used with ZnO and NiO nanoparticles, yielded biodiesel at 96.23% and 94.27%, respectively. Analysis using AFM and FTIR confirmed nanoparticle sizes and biodiesel composition [23]. Researchers discovered that the most effective method for converting palm oil to biodiesel involves microwave heating at 150 watts, a 9:1 alcohol-to-oil ratio, 5% catalyst concentration, 450 RPM stirring speed, and a 60-minute reaction time, which significantly boosts the reaction rate [24].

Researchers synthesized a highly efficient CaO-based catalyst from abalone shells modified with ethanol. The catalyst's properties were evaluated using XRD, SEM (Figure 4), BET analysis, and the Hammett indicator. The modified catalyst, particularly at 100°C, exhibited enhanced surface area, basicity, and smaller crystalline size, resulting in a 96.2% biodiesel yield, surpassing the unmodified catalyst's 87.5%. Moreover, it remained reusable after five cycles [25]. A calcium oxide catalyst derived from ostrich eggshells was used in palm oil transesterification with ultrasonic energy. The catalyst performed similarly to standard calcium carbonate, producing 92.7% biodiesel. It showed great reusability, suggesting possible cost savings in biodiesel production [26].

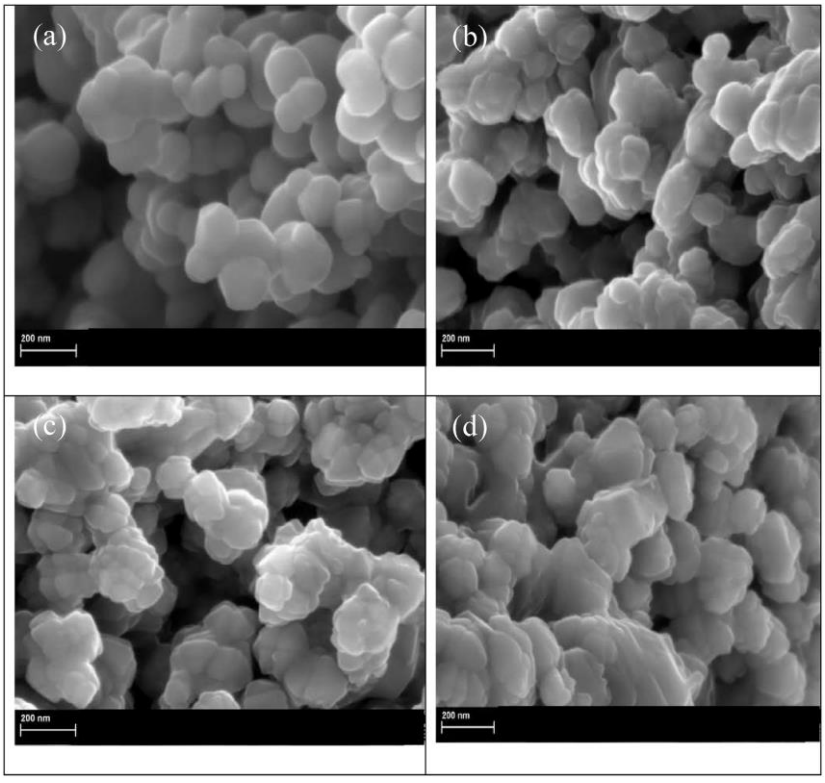

Fig. 4. SEM analysis for CaO catalyst

Researchers optimized biodiesel production using CaO as a catalyst and n-hexane to enhance methanol solubility through a Box-Behnken design. Under optimal conditions (59.7°C, 4 hours 22 minutes, 14.76:1 methanol to oil ratio, 0.905:1 n-hexane to oil ratio), they achieved a 97.7% conversion rate [27]. Researchers used waste chicken eggshells as a catalyst for biodiesel production from waste cooking oil, conducting the first life cycle assessment of a heterogeneous catalyst in this context. The results indicated a lower environmental impact compared to traditional methods, showcasing the potential of eggshells as a cost-effective catalyst [28]. Furthermore, researchers

studied the use of potassium acetate (PA) modified calcium oxide (CaO) as a solid base catalyst for biodiesel production through methanol transesterification. Optimal yields were obtained using 2.0% PA/CaO for bitter almond oil (91.22%) and 1.0% PA/CaO for waste fish oil (93.30%) at a 9:1 methanol-to-oil ratio, 60°C, and 120 minutes. The catalyst maintained a yield of up to 75% after four cycles, enhancing fuel properties to meet ASTM D 6751 standards, confirmed by 1H NMR analysis [29].

Researchers synthesized and evaluated Zn-doped CaO nano catalysts for converting waste cooking oil into biodiesel. They used XRD, FTIR, SEM, EDX, and TEM for characterization and optimized Zn doping levels, catalyst loading, methanol-to-oil ratio, and reaction duration using Response Surface Methodology. The study achieved an optimal conversion rate of 96.74% with a 20:1 methanol-to-oil ratio, 5 wt.% catalyst loading, 65°C temperature, and a 4-hour reaction time [30].

Nano catalysts for biodiesel production provide an overview of the strengths and weaknesses in this research area. The methodologies used are important, but inconsistencies and scalability issues must be resolved. Exploring new nano catalysts and hybrid systems could improve catalytic performance and reduce costs. Research indicates that TiO_2, CaO, and other metal oxides have the potential to increase biodiesel yields and catalyst reusability.

3. Methodology

The methodology for biodiesel production using heterogeneous catalysts is a critical area of study that significantly impacts process efficiency and sustainability. This study aims to offer a comprehensive comparison of biodiesel production studies, focusing on methodologies. By examining materials, catalyst preparation methods, catalyst characteristics, and the transesterification reaction, this review emphasizes advancements and challenges in the field.

3.1 Materials

Materials used to produce biodiesel used TiO_2-CaO catalyst went through several generations. The first generation used CaO and TiO_2 catalysts from Sigma-Aldrich, and 99.8% pure methanol from Fluka [31] (palm 4). As feedstocks, palm oil [31,32] (4,5) and vegetable palm oil (VPO) are used as feedstock to produce biodiesel [33]. The second generation used waste cooking oils as feedstock and eggshell and TiO_2 nanoparticles were ground and mixed using a mechano-chemical method [34] (who 2). The third generation used biomass (algal) as feedstock. Chemicals, biomass, and reagents were purchased from Thomas Baker [35]. Methanol is also used as the reaction medium, and chlorella vulgaris considered biomass [36]. However, the difference in raw materials, all generations used TiO2-CaO as a catalyst to produce biodiesel.

All generations provide knowledge of the performance metrics of the TiO_2-CaO catalyst, including reaction rates, yield percentages, and process efficiencies. The use of waste cooking oil as a feedstock in the second generation has significant cost savings and waste reduction. The third generation's use of algal biomass showed promising results in terms of sustainability and potential scalability.

3.2 Catalyst Preparation

The preparation of TiO_2-CaO catalyst depends on the generation of biodiesel production. The wet impregnation method is used in the first generation [31,33]. The catalyst (TiO_2-CaO) was mixed in a 1:1 weight ratio, heated at 100°C for 120 minutes to remove water, activated at 600°C for 300 minutes, and then stored in a desiccator after cooling [31,33]. The wet impregnation method was

used in the first generation, but subsequent investigations did not consider the mixing ratio and catalyst calcination conditions [32]. Moreover, there are differences in studies, like the solid-solid phase mixing method [31] and the consistency in cooling and storage practices [32,33].

In the second generation, a TiO_2-CaO catalyst was developed by immobilizing CaO nanoparticles from eggshells onto a TiO_2 support. This involved a process of collecting, cleaning, calcination, and mixing under specific conditions. A mixture of 20 mg CaO immobilized TiO_2 and silver nitrate was stirred for 12 hours at room temperature, washed, and dried [34].

In the third generation, the wet impregnation method [35] and the photochemical method using TTIP involve multiple steps such as drying, calcination, irradiation, and UV treatment [36]. The optimal conditions for algal biomass production were a catalyst molar ratio of 0.25 and a calcination temperature of 700°C [35]. The photochemical method guarantees the creation of a precise TiO_2-CaO nano catalyst through specific processing steps, including UV irradiation and a multi-step purification process [36].

The development of TiO_2-CaO catalysts for biodiesel production has shown significant improvement and methodical variations across different generations. Combining wet impregnation with photochemical methods represents a sophisticated approach to catalyst preparation. However, the process complexity increases production costs and technical barriers. The precise control needed for UV treatment and multi-step processing may limit practical application in large-scale operations.

3.3 Transesterification Reaction

The most common method to produce biodiesel is transesterification. Various studies have utilized this process with a TiO_2-CaO catalyst, as shown in Figure 5. The procedure typically involves heating cooking oil and adding methanol and a catalyst to a reaction vessel. Most studies conduct reactions at approximately 65°C, with one exception at 50°C [35]. The transesterification reaction time can vary, typically lasting 1 hour [31] the duration ranges from 30 to 150 minutes [33] 2 hours [32,34] and 8 hours [35]. The filtration process begins with the catalyst, and the mixture is left to separate overnight [31]. Moreover, the filtration step may include procedures like washing biodiesel and drying [33,33].

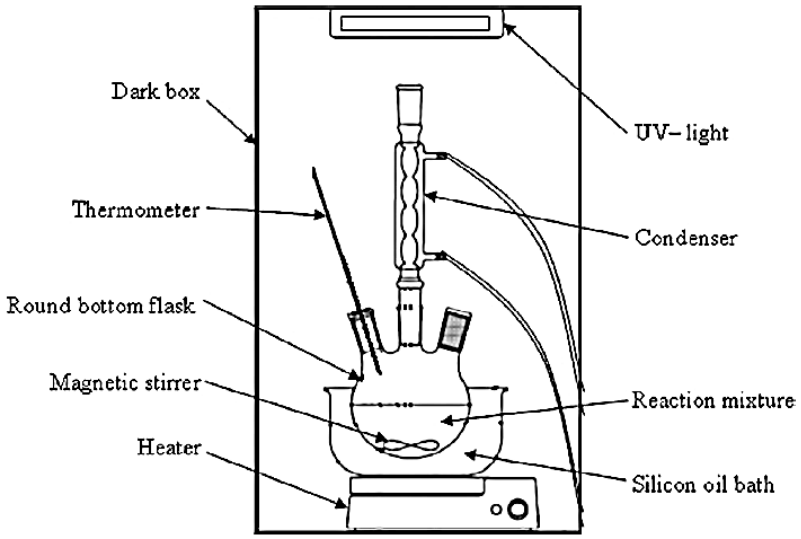

Fig. 5. Schematic diagram of reflux transesterification of palm oil under UV light

The uniformity of the transesterification process in preheating and the addition of methanol and catalyst indicates a well-established procedure. The optimal reaction temperature of 65°C aligns with the boiling point of methanol, ensuring efficient reaction rates. A study using 50°C may explore energy-saving methods or different catalytic efficiencies. The wide range of reaction times, from 30 minutes to 8 hours, underscores the potential influence of factors like catalyst type, oil quality, and methanol-to-oil ratios on reaction kinetics.

4. Result and Discussion

4.1 Catalyst Characterization

The most common characterization tools for biodiesel include BET analysis, XRD analysis, SEM analysis, and thermal analysis. BET analysis evaluates catalyst characteristics, like the surface area of the TiO_2-CaO catalyst, which varies based on calcination temperature as shown in Table 1 [31]. The surface area initially decreases from 200°C to 400°C, peaks at 600°C, and then decreases again at 800°C[33]. An optimal calcination temperature of around 600°C is suggested to maximize surface area, potentially impacting catalytic activity. The BET analysis quantifies the surface area, pore volume, and mean pore diameter of synthesized nanoparticles, essential for understanding catalysts' textural properties that impact their catalytic performance and efficiency [36]. The BET analysis determined the specific surface areas of synthesized nanoparticles, allowing for a quantitative comparison of catalyst samples or calcination temperatures. A high surface area is usually linked to enhanced catalytic activity because of the increased availability of active sites.

Table 1
Surface area of calcination temperature for TiO_2-CaO catalyst

Calcination temperature (°C)	BET surface area (m^2/g)
200	14.3675
400	10.5597
600	22.9605
800	15.4284

The calcination temperature significantly affects the catalytic characteristics of the TiO_2-CaO catalyst. Some techniques recommend a fixed calcination temperature of 900°C for 2 hours [34], the temperature ranges for these techniques vary from 200°C to 800°C [31] with possible variations in reaction times [33]. SEM analysis is used to study the surface morphology and structural characteristics of synthesized nanoparticles. Adding TiO_2 to CaO led to a more uniform particle distribution and reduced agglomeration compared to using CaO alone, improving catalytic performance [33]. The scanning electron microscope (SEM) image of ground eggshell powder after calcination showed increased microporosity and smaller particle size, suggesting a successful structural transformation that enhances catalytic activity [34]. The scanning electron microscopy (SEM) images shown in Figure 6 displayed nanoparticles of various shapes and sizes, offering valuable information about the quality and uniformity of the synthesized particles [36].

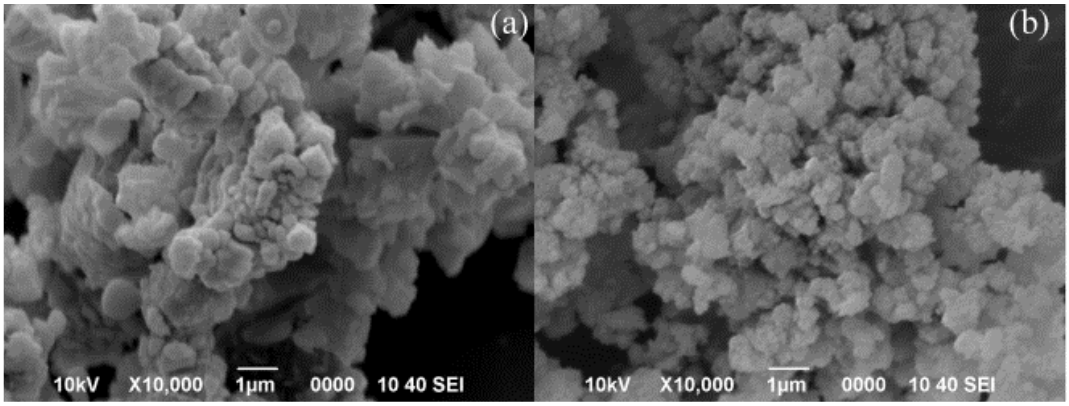

Fig. 6. SEM images of (a) CaO and b) CaO-TiO_2 catalysts

The X-ray Diffraction (XRD) analysis provided important insights into the crystalline phases and structural properties of the catalysts. The analysis confirmed the presence of characteristic peaks for CaO and TiO_2, as shown in Figure 7(a), indicating the formation of mixed oxide phases and their influence on catalytic performance [33]. Moreover, X-ray Diffraction (XRD) analysis reveals distinct peaks for CaO and TiO_2 phases in Figure 7(b), demonstrating the successful conversion of calcite to crystalline mineral phases and the creation of lime, anatase, and rutile crystallites [34]. Furthermore, X-ray Diffraction analysis is utilized in biomass biodiesel to identify different crystalline phases, such as CaO and TiO_2 polymorphs (shown in Figure 8). The analysis includes examining crystallite size and phase purity to highlight the connection between crystalline structure and catalytic properties [36]. The X-ray Diffraction (XRD) analysis offers essential data on phase composition, structural integrity, and thermal transformations, crucial for improving catalyst synthesis and enhancing catalytic efficiency.

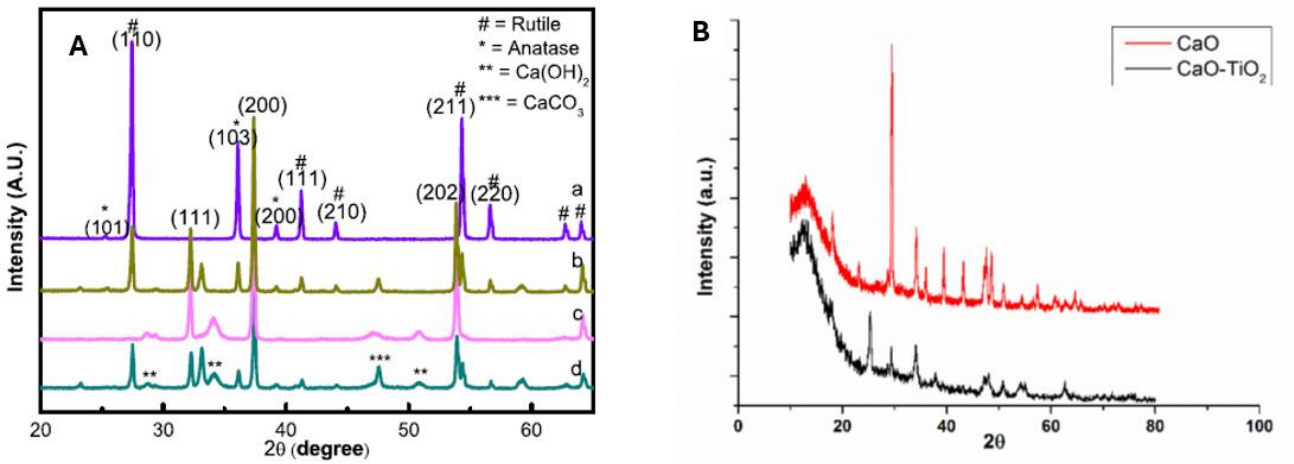

Fig. 7. XRD pattern of (a) Picks of TiO_2-CaO catalyst (b) CaO and CaO-TiO_2 calcination at 600 °C

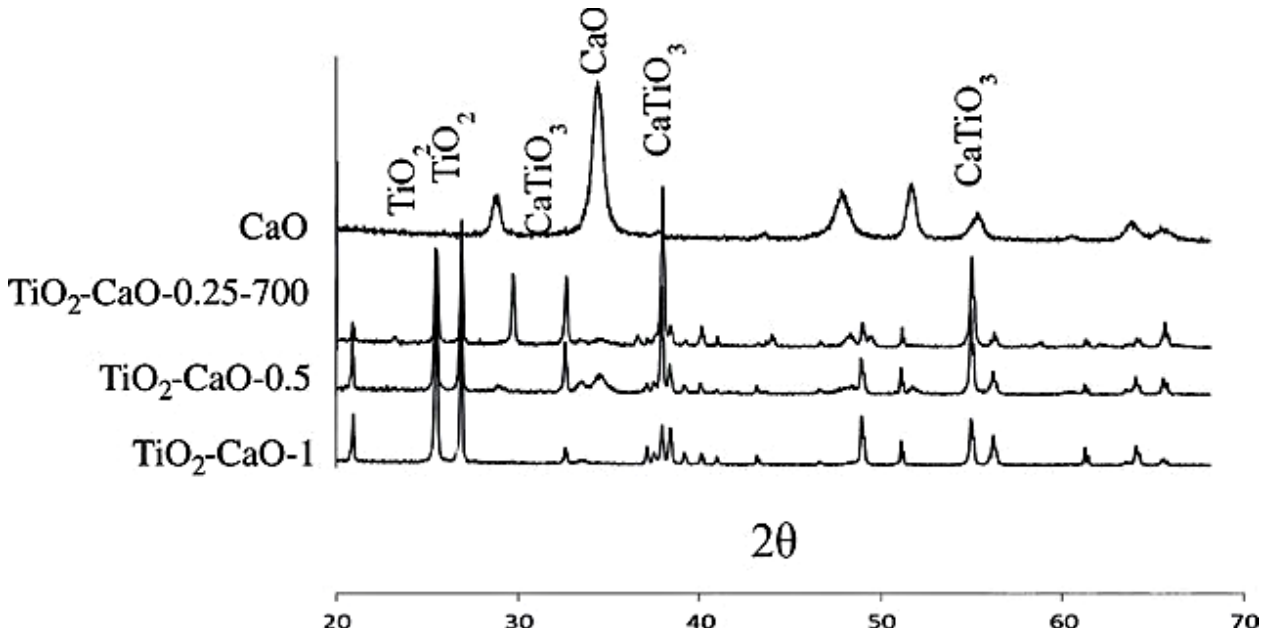

Fig. 8. XRD patterns for various TiO_2-CaO catalyst samples

Biodiesel catalysts are characterized using BET, XRD, SEM, and thermal analysis to understand performance and optimize catalysts. These methods highlight the significance of calcination temperature, with BET analysis identifying 600°C as optimal for maximizing surface area, SEM showing enhanced particle distribution with TiO_2 addition, and XRD providing insights into crystalline phases to confirm successful catalyst synthesis. The characterization techniques for the TiO_2-CaO catalyst are shown in Table 2.

Table 2
Catalyst characteristics analysis techniques for TiO_2-CaO

Feedstock	Catalyst	Catalyst characterization techniques
Palm oil	TiO_2-CaO	BET
Vegetable palm oil	TiO_2-CaO	BET
Palm oil	TiO_2-CaO	BET - XRD - SEM
Waste cooking oils	TiO_2-CaO	XRD - SEM - EDS - XPS
Biomass (Algal)	TiO_2-CaO	TGA - DTG - XRD - SEM
Biomass (Algal)	TiO_2-CaO	BET - XRD - SEM - EDS

4.2 Biodiesel Characterization

Biodiesel characterization evaluates biodiesel properties and production efficiency using catalysts, optimization conditions, and advanced techniques. Biodiesel yield reflects the efficiency of converting oils to biodiesel, enhanced by catalyst preparation methods and reaction conditions. Biodiesel yield from palm oil feedstock range from 87.78% [31] to 98% [33], from waste cooking oils (WCO) 97% [34], and from biomass (algal) maximum yield from 51.6% [36] to 86.4% [35]. Various techniques are used for biodiesel characterization, including the gravimetric method using palm oil as feedstock [31,33] or biomass (algal) [36]. This technique can be represented by the following equation

$$\text{Biodiesel Yield}\,\% = \frac{\text{Weight of biodiesel produced (mL)}}{\text{Weight of oil used (mL)}} * 100$$

Gas Chromatography-Mass Spectrometry (GC-MS) is used for biodiesel characterization [32], quantifying the concentration of fatty acid methyl esters (FAMEs) to determine yield. Additionally, 1H Nuclear Magnetic Resonance (1H NMR) Spectroscopy is employed for biodiesel characterization [34], analyzing peak integration to calculate conversion rates and yield. These techniques offer precise measurements of biodiesel yield shown in Table 3, crucial for optimizing production processes and ensuring efficiency in biodiesel synthesis.

Table 3
Biodiesel optimum yield from different feedstock using TiO_2-CaO catalyst

Feedstock	Catalyst	Characterization technique	Optimum yield
Palm oil	TiO_2-CaO	Gravimetric method	87.78 %
Vegetable palm oil	TiO_2-CaO	Gravimetric method	98 %
Palm Oil	TiO_2-CaO	GC-MS	96.67%
Waste cooking oils	TiO_2-CaO	1H NMR	97 %
Biomass (Algal)	TiO_2-CaO	Gravimetric method	86.4 %
Biomass (Algal)	TiO_2-CaO	The gravimetric method and GC-MS	51.6 %

5. Conclusion

This study provides a comprehensive review of biodiesel production using the TiO_2-CaO catalyst, emphasizing its potential as a sustainable alternative to fossil fuels. Despite advancements, inconsistencies in methodologies pose challenges in standardizing and optimizing production processes. The review underscores the economic and environmental benefits of using cooking oil as a feedstock and the superior catalytic performance of TiO_2-CaO. Comparing TiO_2, CaO, and TiO_2-CaO composites, the TiO_2-CaO catalyst consistently shows the highest efficiency and yield, especially with cooking oil as feedstock. Methodological inconsistencies hinder the development of standardized processes, particularly in catalyst preparation methods like wet impregnation and photochemical techniques. Further research is needed to simplify these processes and reduce costs. Future studies should address these inconsistencies, explore new catalyst preparation parameters, and scale up production methods to enhance the feasibility of biodiesel as a renewable energy source.

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