



Catalysts for Transesterification of Vegetable Oils: A Review

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ABSTRACT: The transesterification of vegetable oils is a critical process in the production of biodiesel, a renewable and biodegradable alternative to fossil fuels. This process involves the substitution of alcohols for ester groups in triglycerides, facilitated by catalysts that significantly influence reaction efficiency and biodiesel quality. This review examines the roles, mechanisms, and performance of homogeneous, heterogeneous, enzymatic, and nano catalysts in biodiesel production. Homogeneous catalysts, including acidic and alkaline variants, provide high reaction rates but pose challenges in product separation and environmental sustainability. Heterogeneous catalysts offer improved reusability and separation but are limited by higher costs and lower reaction rates. Enzymatic catalysts address free fatty acid and water-related issues, producing high-purity biodiesel with reduced environmental impact, while nano-catalysts enhance reaction efficiency through high surface area and catalytic activity. Challenges such as catalyst separation, contamination, and industrial scalability are explored alongside future directions, including the development of green and biomass-derived catalysts. This study underscores the need for innovative catalytic systems to advance biodiesel production's economic viability and environmental sustainability.

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Transesterification is the method of replacing the organic functional group R' of an alcohol for the organic group R' of an ester. Often these reactions are catalysed by adding an acid or basic catalyst (Otera, 1997). The broad term for the important family of chemical reactions in which the alkoxy group of an ester is replaced to produce another is transesterification (Schuchardt *et al.*, 1998). Similar to hydrolysis except that in transesterification, an alcohol is employed instead of water, transesterification, sometimes known as alcoholysis, is the displacement of alcohol from an ester (Meher *et al.*, 2006). Vegetable oils and plant and animal fats provide the renewable resources used in biodiesels, sometimes known as biofuels. Diesel fuel is

extensively consumed in the transportation, agricultural, commercial, residential, and industrial sectors to generate mechanical energy and power (Keera *et al.*, 2011). Obtained from the transesterification of vegetable oil, biodiesel is becoming more and more important as a better fuel source than fossil fuel resources (Keera *et al.*, 2011). Known to have greater cetane number, flash point or improved lubricity efficiency (Anastopoulos *et al.*, 2009; Nabi *et al.*, 2006), these biodiesel—also known as fatty acid alkyl esters—FAAE—are a sustainable and biodegradable fuel. Three long-chain fatty acid triglyceride molecules with ester-bonded one glycerol molecule make up chemically oils and fats. These fatty acids differ from one another in length of the

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carbon chains and quantity, orientation, and placement of double bonds within these chains (Meher *et al.*, 2006). How much transesterification and side reactions occurs depends on the kind of feedstock, catalyst formulation, catalyst concentration, alcohol-to-oil ratio, reaction temperature, and reaction time (Meher *et al.*, 2006).

Triglycerides in oil or fat react with an alcohol in the presence of a catalyst to produce a transesterification reaction. Triglycerides and alcohols react in the presence of a strong acid or base during the transesterification of vegetable oils, resulting in a mixture of fatty acids, alkyl esters, and glycerol (Demirbas, 2008). When methanol is used as the alcohol, the process is then referred to as methanolysis. The overall procedure consists of three successive, reversible reactions with the formation of mono- and di-glycerides as intermediates. One mol of a triglyceride and three mol of alcohol are needed for the stoichiometric reaction. To boost the yields of the alkyl esters and enable their phase separation from the glycerol that is produced, too much alcohol is utilized (Schuchardt *et al.*, 1998). Reactant concentration, catalyst, reaction temperature, and time are critical process variables (Kumar *et al.*, 2022). According to Meher *et al.* (2006), catalysts are essential in promoting this reaction because they lower activation energy and speed up reaction rates. The transesterification reaction is generally catalyzed by acids, bases, and enzymes (Furuta *et al.*, 2004; MacLeod *et al.*, 2008; Royon *et al.*, 2007). The acidic and basic catalysts can be either homogeneous or heterogeneous. Enzymatic, heterogeneous, and homogeneous catalysts are the three main categories of catalysts utilized in the transesterification process that are examined in this review. The study also explores the associated challenges, such as separation efficiency, catalyst reusability, and industrial scalability, alongside potential innovations in catalyst development to enhance the sustainability and economic feasibility of biodiesel synthesis.

Homogeneous Catalysts: Catalyst selection is a pivotal factor in biodiesel production, as it directly influences both the efficiency of the reaction and the overall production costs. Choosing the appropriate catalyst can significantly lower operational expenses while optimizing biodiesel yield and quality (Mandari & Devarai, 2022). Among the various catalyst options, homogeneous catalysts stand out as the first conventional choice for biodiesel synthesis due to their established efficacy and simplicity in application. Homogeneous catalysts exist in the same phase—typically liquid—as the reactants, ensuring uniform mixing and interaction, which promotes

reaction efficiency. Examples of homogeneous catalysts include enzymes, non-ionic organic base compounds, and liquid-phase ionic acids and bases (Kumar *et al.*, 2022).

The most commonly employed homogeneous catalysts in esterification and transesterification processes include strong acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), as well as strong bases like sodium hydroxide (NaOH) and potassium hydroxide (KOH). These catalysts have been extensively studied and widely applied due to their high catalytic activity and ability to facilitate the conversion of triglycerides to fatty acid alkyl esters (Wang *et al.*, 2023). The choice between acidic and alkaline catalysts is primarily determined by the characteristics of the feedstock oil, particularly its free fatty acid (FFA) content and water levels.

Acidic catalysts are generally preferred for feedstocks with high FFA content and excess water. Their ability to simultaneously catalyze esterification and transesterification makes them highly effective under such conditions. Unlike alkaline catalysts, acid catalysts are less susceptible to the issues caused by FFAs, such as saponification, which can hinder biodiesel yield and complicate product separation (Kibar *et al.*, 2023). However, acid-catalyzed reactions often require longer reaction times and higher temperatures to achieve comparable conversion rates, which can limit their application in some scenarios.

In contrast, alkaline catalysts are more suitable for low-FFA feedstocks, such as refined oils. They offer faster reaction rates and require milder operating conditions, making them a popular choice for large-scale biodiesel production. Commonly used alkaline catalysts, including NaOH and KOH, are effective in achieving high biodiesel yields. However, these catalysts are highly sensitive to FFAs and water content in the feedstock. When FFAs are present, they tend to react with the alkaline catalysts to form soap, a side reaction known as saponification. This not only reduces the availability of the catalyst for transesterification but also prolongs reaction times and complicates product separation. In such cases, the neutralized FFA products are typically esterified with an alkali catalyst to mitigate the impact on biodiesel yield (Kibar *et al.*, 2023).

The critical role of catalyst selection in biodiesel production underscores the need for careful evaluation of feedstock properties and process requirements. While homogeneous catalysts offer distinct advantages in terms of reaction efficiency

and cost-effectiveness, their limitations, such as sensitivity to FFAs and water and challenges in catalyst recovery, necessitate ongoing research to improve their applicability and performance.

Homogeneous Alkali Catalyst: Homogeneous alkali catalysts are highly effective in biodiesel production, particularly when extra-pure virgin oils with low free fatty acid (FFA) content (below 0.5%) and acid values under 1 mg KOH/g are used. Under these conditions, they achieve superior biodiesel yield and purity compared to other feedstocks. This is because the low FFA content minimizes undesirable side reactions, such as saponification, which can negatively impact product quality and reaction efficiency (Mandari & Devarai, 2022). Commonly employed homogeneous alkali catalysts include alkaline metal hydroxides, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), as well as alkoxides like sodium methoxide (CH_3ONa), potassium methoxide (CH_3OK), and sodium ethoxide (NaOC_2H_5). These catalysts are favored in industrial biodiesel production due to their high catalytic activity, moderate reaction conditions, and compatibility with various alcohols like methanol and ethanol (Abelniece *et al.*, 2020).

The effectiveness of homogeneous alkali catalysts was demonstrated in a study by Dias *et al.* (2008), which compared their performance in the transesterification of virgin and waste cooking oils. The results revealed that virgin oils produced a biodiesel yield of 97%, while waste oils achieved a slightly lower yield of 92%. This difference underscores the importance of feedstock quality in determining biodiesel yield and purity. Factors such as catalyst concentration, feedstock purity, alcohol-to-oil molar ratio, and reaction temperature significantly influence the outcome of the transesterification process. For instance, while increasing catalyst concentration can accelerate reaction rates, excessive amounts may lead to soap formation. This side reaction not only reduces the effective catalyst available for transesterification but also dilutes the biodiesel with glycerol, complicating the separation process and extending reaction times (Vincente *et al.*, 2007).

Pre-treating the feedstock by heating and filtering is crucial in biodiesel production, as it eliminates impurities, suspended solids, and inorganic materials that might otherwise hinder the reaction. Such pre-treatment steps are particularly essential when using waste oils, which often contain higher levels of contaminants compared to virgin oils (Demirbas, 2008). By removing these undesirable components,

the formation of by-products during the reaction is minimized, thereby improving the overall yield and quality of the biodiesel.

Homogeneous alkali catalysts are not only efficient but also economically accessible, offering a cost-effective option for biodiesel production. They are capable of producing high-quality biodiesel within a short period, a distinct advantage over other catalyst types (Lam *et al.*, 2010). Moreover, their reaction rates are substantially higher compared to acidic catalysts. A study comparing sodium-based catalysts with KOH in methanol demonstrated that the base-catalyzed reaction was approximately 4000 times faster than its acidic counterpart (Thangaraj *et al.*, 2019).

However, homogeneous alkali catalysts come with certain drawbacks. One significant limitation is their inability to be reused or regenerated, as they are consumed during the reaction. Additionally, their partial miscibility with both biodiesel and glycerol complicates product separation from the reaction mixture. This inefficiency necessitates additional equipment for separating the catalyst, biodiesel, and by-products, thereby increasing production costs (Lopez *et al.*, 2005). Moreover, the purification process generates large volumes of wastewater, further elevating environmental concerns. The waste of oil during separation and the environmental impact of wastewater treatment are critical issues that must be addressed to improve the sustainability of homogeneous alkali catalyst-based biodiesel production (Selvakumar and Sivashanmugam, 2017).

Homogeneous Acid Catalyst: Homogeneous acid catalysts play a crucial role in biodiesel production due to their ability to catalyze both transesterification and esterification processes simultaneously, regardless of the free fatty acid (FFA) content in the feedstock oil. This unique capability makes them particularly advantageous when working with oils containing high levels of FFAs, which can impede the performance of alkaline catalysts (Lam *et al.*, 2010). These catalysts facilitate better access to their active sites, enabling efficient interaction with reactants and contributing to their effectiveness in complex reactions (Mandari and Devarai, 2022).

Despite their advantages, homogeneous acid catalysts have certain limitations. They typically require a higher molar ratio of alcohol to oil and elevated reaction temperatures to achieve satisfactory conversion rates. These stringent operational requirements, coupled with the longer reaction times often needed, have limited their widespread

application in industrial biodiesel production (Wang *et al.*, 2023). Nevertheless, their tolerance to water and FFAs makes them indispensable for specific feedstocks where other catalysts may fail.

Homogeneous acid catalysts, such as sulfuric acid (H_2SO_4), sulfonic acid (H_2SO_3), hydrochloric acid (HCl), and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), belong to the Brønsted acid category. These acids are characterized by their proton-donating properties and are less sensitive to the adverse effects of FFAs. Of these, sulfuric acid (H_2SO_4) is the most commonly utilized due to its efficiency in catalyzing reactions at medium temperatures and atmospheric pressure. This makes it a practical choice for laboratory and small-scale biodiesel production settings (Mandari and Devarai, 2022).

In certain innovative approaches, homogeneous acid catalysts have demonstrated remarkable efficiency. For example, *in situ* transesterification using an acid catalyst and methanol as a solvent has been applied to biodiesel production from algal oil. This method allows for the simultaneous extraction and transesterification of algal lipids into methyl esters, streamlining the biodiesel production process. A study comparing the performance of hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) in this context found that HCl achieved a higher yield of 90% compared to 80% for H_2SO_4 under identical conditions. This indicates that HCl may be a more effective catalyst for specific applications, although its practical use is often constrained by cost and handling considerations (Kim *et al.*, 2015; Emeka-Chioke *et al.*, 2023).

However, the corrosive nature of homogeneous acid catalysts poses significant challenges. Their use requires specialized equipment made from materials resistant to corrosion, which can substantially increase production costs. Despite this drawback, these catalysts exhibit higher tolerance for water and moisture in the reaction environment, which can be critical for biodiesel production from certain feedstocks that contain water impurities (Kulkarni & Dalai, 2006). The effectiveness of homogeneous acid catalysts is further supported by research on their optimal use in biodiesel production. According to Bohlouli and Mahdavian (2019), achieving desirable performance with these catalysts involves carefully balancing key factors such as the concentration of the acid catalyst, the alcohol used (commonly methanol), and the duration of the reaction. Extended reaction times, in particular, can improve conversion rates and biodiesel yield, although they may also add to the overall production timeline and costs.

Heterogeneous catalyst: Heterogeneous catalysts, widely used in biodiesel production, are typically solid substances that operate in a separate phase from the liquid reactants. This phase distinction is a major advantage, as it allows for the straightforward recovery of the catalyst from the reaction mixture. Unlike homogeneous catalysts, which are consumed during the reaction and require complex separation processes, heterogeneous catalysts can be easily retrieved, cleaned, and reused for multiple reaction cycles. This reusability significantly reduces production costs and enhances the overall efficiency of the biodiesel production process (Mandari and Devarai, 2022). One of the key benefits of heterogeneous catalysts is their ability to mitigate soap formation, a common issue associated with homogeneous alkaline catalysts when free fatty acids (FFA) are present. Soap formation not only reduces the availability of catalysts for the transesterification reaction but also complicates product separation. Heterogeneous catalysts are more tolerant to both FFAs and water content in feedstocks, making them particularly advantageous for processing low-quality oils or waste oils that contain impurities and higher FFA levels (Mandari and Devarai, 2022).

The performance of heterogeneous catalysts in biodiesel production is influenced by various factors, including the type and quality of oil used, reaction temperature, the specific type of catalyst employed, the amount of catalyst used, and the molar ratio of alcohol to oil. These variables must be carefully optimized to maximize conversion efficiency and biodiesel yield. For example, a higher molar ratio of alcohol to oil can push the reaction equilibrium toward ester formation, while the appropriate choice of catalyst type can ensure compatibility with the feedstock characteristics (Kibar *et al.*, 2013). Heterogeneous catalysts offer additional advantages in industrial applications. Their solid form and stability make them suitable for continuous biodiesel production in fixed-bed reactors. These reactors enable the processing of larger volumes of feedstock with minimal downtime, providing the scalability required for commercial biodiesel production. The ability to reuse these catalysts over several cycles without significant loss of activity further enhances their economic feasibility. This reusability also reduces waste generation, aligning with sustainability goals in biodiesel production (Wang *et al.*, 2016; Malani *et al.*, 2018).

Moreover, the use of heterogeneous catalysts in fixed-bed reactor systems provides operational flexibility and efficiency. Fixed-bed reactors allow for continuous flow processing, where the reactants

pass through a packed bed of catalysts, ensuring consistent contact and reaction rates. This setup minimizes interruptions for catalyst replacement and simplifies the overall process management, making it a preferred choice for large-scale biodiesel production facilities. Additionally, the robust nature of heterogeneous catalysts ensures their performance is less affected by reaction conditions, further enhancing their reliability in industrial applications.

Heterogeneous alkaline catalyst: Solid alkali catalysts are highly regarded for their superior catalytic potential when compared to solid acid catalysts, making them a valuable option in biodiesel production. This greater catalytic efficiency is attributed to their strong base properties, which effectively promote the transesterification reaction, resulting in faster reaction rates and higher yields. Solid alkali catalysts encompass a broad range of materials, including alkaline oxides, alkaline earth metal oxides, hydrotalcite, metallic salts, anion exchange resins, and zeolites. These catalysts are engineered with extensive surface areas, allowing for greater contact between the catalyst and reactants, which enhances catalytic activity and efficiency (Li *et al.*, 2020; Talha and Sulaiman, 2016).

One of the most exciting developments in this field is the use of waste materials as sources for heterogeneous alkaline catalysts. Materials such as shells, ash, and bone have been successfully converted into effective catalysts for biodiesel production. These waste-derived catalysts not only reduce production costs but also align with principles of sustainability and waste valorization, making them an eco-friendly solution for the biodiesel industry. For example, calcined eggshells and animal bones, which are rich in calcium carbonate and calcium phosphate, have shown great promise as low-cost and efficient catalysts. The utilization of these waste materials minimizes environmental impact by repurposing by-products that would otherwise contribute to waste streams (Bohlouli and Mahdavian, 2019).

A significant advantage of heterogeneous alkali catalysts lies in the operating conditions they require. The transesterification process using these catalysts is typically carried out under relatively low pressure and temperature, which contributes to their practicality and cost-effectiveness. Unlike processes that rely on high-temperature or high-pressure conditions, the reaction facilitated by solid alkali catalysts is more energy-efficient, reducing overall operational costs. This efficiency makes them particularly attractive for mass production of

biodiesel, where large-scale processing demands cost-effective and scalable solutions. Furthermore, the reaction proceeds rapidly and yields high conversion rates without the need for intermediate steps, simplifying the process and enhancing its commercial viability (Wang *et al.*, 2023).

Heterogeneous alkali catalysts also offer other operational benefits, such as ease of recovery and reusability. Their solid-state nature allows for straightforward separation from the reaction mixture, enabling multiple cycles of use without significant loss of catalytic activity. This reduces waste generation and contributes to the economic and environmental sustainability of biodiesel production processes. Additionally, their compatibility with a wide range of alcohols and oils enhances their versatility, making them suitable for various feedstocks, including low-grade oils with higher impurity levels.

Heterogeneous acid catalyst: Heterogeneous acid catalysts play a pivotal role in the production of biodiesel, serving as a viable alternative to homogeneous acid catalysts for both esterification and transesterification reactions. Unlike their homogeneous counterparts, these solid catalysts offer significant industrial advantages due to their structural and functional properties. The presence of Brønsted and Lewis acid active sites in heterogeneous acid catalysts makes them highly effective. Brønsted acid sites act as proton donors and are particularly well-suited for esterification reactions, while Lewis acid sites, which accept electron pairs, contribute to their versatility and applicability across various reaction conditions (Guldhe *et al.*, 2017; Wang *et al.*, 2023).

One of the primary benefits of heterogeneous acid catalysts is their ability to address some of the critical limitations of homogeneous acid catalysts, particularly vessel corrosion and the toxic effects associated with corrosive substances. Homogeneous acid catalysts, such as sulfuric acid, are notorious for causing equipment degradation, necessitating the use of specialized and expensive materials for reactors. In contrast, heterogeneous acid catalysts are less corrosive, reducing both maintenance costs and environmental risks. Their moderate acidity and hydrophobicity further enhance their functionality, making them a more sustainable choice for industrial biodiesel production (Mandari and Devarai, 2022).

Heterogeneous acid catalysts are characterized by their high density of active sites, which significantly boosts reaction efficiency. These active sites facilitate

improved contact between the reactants and the catalyst surface, reducing diffusion limitations and enhancing the overall rate of reaction. Additionally, their solid-state nature allows for easy recovery and reuse, which not only minimizes catalyst wastage but also contributes to cost efficiency. The reusability of these catalysts aligns with the growing demand for sustainable industrial practices, making them a preferred choice for large-scale biodiesel production (Wang *et al.*, 2023).

The materials commonly used as heterogeneous acid catalysts include sulfonated solids, zeolites, resins, heteropoly acids (HPA), mixed metal oxides, and sulfated metal oxides. Each of these materials brings specific advantages to biodiesel production. For example, zeolites are valued for their highly structured porous framework, which enhances reactant accessibility and catalytic efficiency. HPAs, which are composed of oxygen and metal atoms in a cluster arrangement, are particularly effective due to their high acidity, stability, and environmental compatibility (Badruzzaman *et al.*, 2020; Farabi *et al.*, 2019).

Despite these advantages, heterogeneous acid catalysts are not without limitations. They typically require longer reaction times and higher temperatures to achieve optimal conversion rates, which can increase energy consumption and operational costs. However, these drawbacks are often outweighed by their benefits, such as reduced toxicity, ease of separation, and compatibility with biodiesel filtration processes. Moreover, the environmental impact of heterogeneous acid catalysts is considerably lower than that of homogeneous catalysts, as they generate fewer harmful by-products and are easier to handle and dispose of safely (Downlawson *et al.*, 2020; Wang *et al.*, 2023). Among the various types of heterogeneous acid catalysts, HPAs stand out as particularly promising. Their unique molecular structure, comprising metal-oxygen clusters, allows them to perform exceptionally well under a wide range of reaction conditions. HPAs also exhibit high thermal and chemical stability, making them a durable and reliable choice for continuous biodiesel production processes (Wang *et al.*, 2023).

Nano-catalysts: Nanoparticles, defined as spherical or pseudo-spherical particles with diameters smaller than 100 nanometers, have emerged as transformative tools in catalytic processes, representing one of the earliest practical applications of nanotechnology (Bankovic-Illic *et al.*, 2017). Their unique physicochemical properties make them indispensable for various industries, including biodiesel production,

where their advantages are evident from environmental, social, technological, and scientific perspectives. These advantages include exceptional selectivity, high durability, and remarkable recyclability, which collectively address some of the key challenges faced in industrial catalytic applications (Bohlouli and Mahdavian, 2019).

The exceptional efficiency of nanocatalysts in biodiesel production is largely attributed to their high surface area-to-volume ratio, which results in a large number of active sites for substrate interactions. These nanoscale pores allow for enhanced reactant access and facilitate faster reaction rates, improving overall catalytic efficiency. Consequently, optimizing nanomaterials to achieve greater yields, simpler separation processes, enhanced reusability, and accelerated reaction kinetics has become a central goal in the advancement of biodiesel technologies (Mandari and Devarai, 2022).

In addition to their catalytic efficiency, nanocatalysts boast high levels of crystallinity, thermal stability, chemical durability, and adsorption capacity. These properties enable them to perform reliably under a wide range of reaction conditions, making them well-suited for industrial biodiesel production. Moreover, their ability to effectively store energy and maintain consistent activity across multiple cycles underscores their potential to lower production costs and reduce waste, further enhancing their appeal as sustainable catalytic solutions (Vijayalakshmi *et al.*, 2020; Christian *et al.*, 2023).

Various methods are employed to synthesize nanocatalysts, each tailored to achieve specific structural and functional properties. These methods include sol-gel processes, microwave combustion, co-precipitation, self-propagating combustion, incipient wet impregnation, hydrothermal synthesis, gas condensation, and chemical vapor deposition. Each technique offers distinct advantages in terms of particle size control, surface morphology, and catalytic performance, allowing for the development of nanocatalysts that meet the specific demands of biodiesel production (Fattah *et al.*, 2020).

The practical potential of nanocatalysts in biodiesel synthesis has been demonstrated in numerous studies. For instance, Singh *et al.* (2020) synthesized biodiesel using a CoO-NiO-promoted sulphated ZrO₂ superacid oleophilic catalyst. This nanocatalyst exhibited outstanding performance, achieving a biodiesel yield of 96.8% under mild reaction conditions. Notably, the catalyst retained its activity across five reuse cycles, with minimal performance

degradation after reactivation. Such reusability highlights the economic and environmental benefits of nanocatalysts, as they reduce the need for frequent catalyst replacement and minimize waste generation.

In addition to their impressive yield rates and recyclability, nanocatalysts are known for their ability to operate effectively under relatively mild conditions. This reduces the energy input required for biodiesel production, contributing to more sustainable and cost-effective processes (Otache *et al.*, 2022). Depending on the specific catalyst design, their activity can be sustained over multiple cycles, often exceeding five or more, which underscores their long-term operational viability.

Enzymatic catalysts: The use of enzymatic biocatalysts for biodiesel production represents a cutting-edge alternative to traditional chemical methods that rely on alkali or acid catalysts. Enzymatic catalysts, often referred to as biocatalysts, have emerged as a transformative solution to many of the challenges associated with conventional catalytic processes. These challenges include sensitivity to free fatty acids (FFAs) and water content in raw materials, as well as the formation of unwanted by-products such as soap. By addressing these issues, biocatalysts have demonstrated their potential to enhance the efficiency, sustainability, and environmental compatibility of biodiesel production processes (Mandari and Devarai, 2022; Bohlouli and Mahdavian, 2019).

One of the primary advantages of enzymatic biocatalysts is their ability to handle feedstocks with high FFA and moisture content without compromising biodiesel yield or quality. Unlike traditional alkaline catalysts, which react with FFAs to form soap and lead to lower biodiesel yields, enzymatic catalysts produce high-purity biodiesel regardless of feedstock quality. This capability is particularly advantageous when using low-cost, readily available feedstocks, such as waste cooking oil, which often contain high levels of impurities. The ability of enzymatic catalysts to directly convert such feedstocks into high-quality biodiesel reduces raw material costs and expands the range of viable inputs for biodiesel production (MacEiras *et al.*, 2010).

Enzymatic biocatalysts are typically composed of enzymes known as lipases (triacylglycerol acylhydrolases, EC 3.1.1.3), which are naturally occurring in bacteria, fungi, plants, and animals. Lipases are highly versatile and efficient, catalyzing the hydrolysis of triglycerides into FFAs and glycerol at the water-lipid interface. Beyond hydrolysis,

lipases can also facilitate other reactions critical to biodiesel production, including alcoholysis (transesterification), acidolysis, aminolysis, esterification, and interesterification. This broad functionality makes lipases a key component in modern biodiesel production technologies (Lima *et al.*, 2019).

The advantages of lipase-based enzymatic catalysts extend beyond their functionality. Lipases are non-toxic and exhibit excellent resistance to organic solvents, allowing them to operate effectively under a wide range of reaction conditions. Furthermore, their insensitivity to the presence of FFAs in feedstocks eliminates the need for pre-treatment steps, which are often required in conventional processes. This reduces both processing time and operational costs, making enzymatic biodiesel production more economically viable. Lipases are also reusable, retaining their activity across multiple cycles, which contributes to sustainability and cost-efficiency in industrial applications (Selvakumar and Sivashanmugam, 2017).

From an environmental perspective, enzymatic catalysts offer significant benefits. Traditional chemical catalysts generate large volumes of wastewater and other pollutants due to their reliance on harsh chemicals and the formation of by-products such as soap (Otache *et al.*, 2021). In contrast, enzymatic processes are cleaner and more environmentally friendly, as they produce minimal waste and operate under milder conditions. The use of biocatalysts aligns with the principles of green chemistry, promoting sustainable practices in biodiesel production while reducing its environmental footprint.

Challenges and future directions: Despite extensive research, there are still restrictions on the use of both homogeneous and heterogeneous catalysts. Some of the problems with catalysts include the following:

- Separation is a problem for homogeneous catalysts. The residual catalyst significantly affects the quality of biodiesel, and although heterogeneous solid catalysts are easy to separate, they still don't meet the requirements for industrial use.

- The issues of contamination and catalyst poisoning arise when homogeneous catalysts are used. Significant contamination generation can also result from issues with saponification and active site leaching.

- The primary issues with heterogeneous catalysts are their short catalyst lifetime, low reaction rate, and high fabrication cost.

For future directions, the following aspects are to be addressed:

- To enhance the current catalyst types and accomplish industrial-scale biodiesel applications, the transition of heterogeneous catalysts from laboratory research to industrial applications must be further accelerated. To increase the stability and reusability of homogeneous catalysts, the development of ionic liquid catalysts derived from homogeneous catalysts is being encouraged.
- To lower the related expenses, create effective biodiesel production catalysts derived from biomass. The catalysts' service life and reaction efficiency have both increased since the introduction of HPA heterogeneous catalysts and nanocatalysts with superior catalytic qualities.
- Investigate eco-friendly green catalysts like DES and create effective green catalysts made from biomass for the production of biodiesel.

Conclusion: Biodiesel production requires a focus on economic factors, including feedstock costs, reagent costs, and catalyst use and recovery. Homogeneous and heterogeneous catalysts are widely studied for biodiesel production, but their main drawbacks include inability to be easily separated from the reaction mixture, waste formation, and unwanted side reactions. Heterogeneous catalysts, like solid alkali and acid catalysts, offer the advantage of being easily separable from the reaction mixture, reducing costs and waste. Enzymatic catalysts, like lipases, are gaining attention due to their non-toxicity, high selectivity, and ability to operate under milder conditions. However, they face challenges such as higher reaction temperatures, longer times, and long-term stability issues. As demand for sustainable biodiesel production increases, research and development are needed to improve efficiency, stability, and cost-effectiveness. Innovations in catalyst regeneration and recycling technologies will also make these processes more economically competitive with traditional methods.

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Data Availability Statement: Data are available upon request from the corresponding author

REFERENCES

Abelniece, Z; Laipniece, L; Kampars, V. (2020) Biodiesel production by interesterification of rapeseed oil with methyl formate in presence of potassium alkoxides. *Biomass Conv. Bioref.* **12**, 2881–2889. 10:1–9. <https://doi.org/10.1007/s13399-020-00874-z>

Anastopoulos, G; Zannikou, Y; Stournas, S; Kalligeros, S. (2009). Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies*, **2**(2), 362–376. <https://doi.org/10.3390/en20200362>

Badruzzaman, A; Yuda, A; Ashok, A; Kumar, A. (2020) Recent advances in cobalt based heterogeneous catalysts for oxygen evolution reaction. *Inorg. Chim. Acta* **511**, 119854. <https://doi.org/10.1016/j.ica.2020.119854>

Bankovic-Ilic, IB; Miladinović, MR; Stamenković, OS. (2017). Application of nano CaO based catalysts in biodiesel synthesis. *Renew. Sustain. Energy Rev.* **72**: 746–760. <https://doi.org/10.1016/j.rser.2017.01.076>

Barnwal, BK; Sharma, MP (2005). 'Prospects of biodiesel production from vegetable oils in India', *Renewable and Sustainable Energy Reviews*, **9**(4), 363–378. Available at: <https://doi.org/10.1016/j.rser.2004.05.007>.

Bohlouli, A; Mahdavian, L (2019). Catalysts used in biodiesel production: a review. *Biofuels*. **12**. 1–14. 10.1080/17597269.2018.1558836.

Christian, IO; Christopher, OU; Chris, AC; Marytheresa, ON; Izuchukwu, UD; Chinyere, NR; Chukwuemeka, UM (2023). Synthesis, Antimicrobial and Antioxidant Properties of Gly-Gly Based Dipeptide. *Am. J. Appl. Sci. Res.*, **9**(3), 109–114. doi: 10.11648/j.ajasr.20230903.14

Demirbas, A. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Convers. Manag.* **49**(1), 125–130. <https://doi.org/10.1016/j.enconman.2007.05.002>

Donlawson, C; Nweneka, DO; Orié, KJ; Okah, R (2020). Synthesis and bioactivity of 1-((2-carbamoylguanidino)(furan-2-ylmethyl) urea. *Am. J. Anal. Chem.* **11**(7), 280–288. DOI: [10.4236/ajac.2020.117022](https://doi.org/10.4236/ajac.2020.117022)

Emeka-Chioke, EA; Udeozo, PI., Nsude, OP; Uchechukwu, TO; Orié, KJ; Ogbobe, O. (2023). Synthesis of Bio-based Polyol Via Epoxidation and Hydroxylation of Shea Butter Fats. *Int. J. Appl. Chem.* **14**(2), 28–36.

Farabi, MSA; Ibrahim, ML; Rashid, U; Taufiq-Yap, YH (2019). Esterification of palm fatty acid

- distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo. *Energy Convers. Manag.* 181, 562–57. <https://doi.org/10.1016/j.enconman.2018.12.033>
- Fattah, IM; Ong, HC; Mahlia, TMI (2020). State of the art of catalysts for biodiesel production. *Front Energy Res.* 8:1–17. doi: 10.1016/j.enconman.2019.112263
- Furuta, S; Matsushashi, H; Arata, K (2004). Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catal. Commun.* 5, 721–723. <https://doi.org/10.1016/j.catcom.2004.09.001>
- Guldhe, A; Singh, P; Ansari, FA (2017). Biodiesel synthesis from microalgal lipids using tungstated zirconia as a heterogeneous acid catalyst and its comparison with homogeneous acid and enzyme catalysts. *Fuel* 187:180–188. <https://doi.org/10.1016/j.fuel.2016.09.053>
- Keera, ST; El Sabagh, SM; Taman AR (2011). Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst. *Fuel.* 90(1), 42–47.
- Kibar, ME; Hilal, L; Çapa, BT; Bahçivanlar, B; Abdeljelil, BB (2023). Assessment of homogeneous and heterogeneous catalysts in transesterification reaction: a mini review. *ChemBioEng Reviews*, 10(4), 412–422. Available at: <https://doi.org/10.1002/cben.202200021>.
- Kim, B; Im, H; Lee, JW (2015). In situ transesterification of highly wet microalgae using hydrochloric acid. *Bioresour. Technol.* 185:421–425. <https://doi.org/10.1016/j.fuel.2010.07.046>
- Kulkarni, MG; Dalai AK (2006). Waste cooking oil an economical source for biodiesel: a review. *Ind Eng Chem Res.* 45: 2901–2913. <https://doi.org/10.1021/ie0510526>
- Kumar, A; Osembo, S; Namango, S; Kiriamiti, K (2022). Heterogenous Basic Catalyst for Transesterification of vegetable oils: A review. *Sustainable Research and Innovation Conference* (pp. 59–68)
- Li, H; Wang, Y; Ma, X (2020). A novel magnetic CaO-based catalyst synthesis and characterization: enhancing the catalytic activity and stability of CaO for biodiesel production. *Chem Eng J* 391:123549. <https://doi.org/10.1016/j.cej.2019.123549>
- Lima, LGR; Gonçalves, MMM; Couri, S (2019). Lipase production by *Aspergillus niger* C by submerged fermentation. *Brazilian Arch Biol Technol* 62:1–14
- López, DE; Goodwin, JG; Bruce, DA; Lotero, E. (2005). Transesterification of triacetin with methanol on solid acid and base catalysts. *Appl. Catal. A Gen.* 295, 97–105. <https://doi.org/10.1016/j.apcata.2005.07.055>
- MacEiras, R; Cancela, A; Vega, M (2010). Enzymatic alcoholysis for biodiesel production from waste cooking oil. *Chem. Eng. Trans.* 19:103–10
- MacLeod, C.S; Harvey, A.P; Lee, A.F; Wilson, K. (2008) Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chem. Eng. J.* 135, 63–67. <https://doi.org/10.1016/j.cej.2007.04.014>
- Malani, R.S; Sardar, H; Malviya, Y (2018). Ultrasound-intensified biodiesel production from mixed nonedible oil feedstock using heterogeneous acid catalyst supported on rubber de-oiled cake. *Ind Eng Chem Res.* 57:14926–14938. <https://doi.org/10.1021/acs.iecr.8b02793>
- Mandari, V; Devarai, SK (2022). Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review. *Bioenerg. Res.* 15, 935–961. <https://doi.org/10.1007/s12155-021-10333-w>
- Meher, L; Vidyasagar, D; Naik, S (2006). Technical aspects of biodiesel production by transesterification—a review. *Renew.Sust Energy Reviews*, 10(3), 248–268. Available at: <https://doi.org/10.1016/j.rser.2004.09.002>.
- Nabi, M. N., Akhter, M. S., & Shahadat, M. M. Z. (2006). Improvement of engine emissions with conventional diesel fuel and diesel–biodiesel blends. *Bioresour. Technol.* 97(3), 372–378. <https://doi.org/10.1016/j.biortech.2005.03.013>
- Otera, J. (1993). Transesterification. *Chemical Reviews.* 93 (4): 1449–1470. <https://doi.org/10.1021/cr00020a004>

- Otache, MA; Duru, RU; Achugasim, O; Abayeh, OJ (2021). Advances in the modification of starch via esterification for enhanced properties. *J. Polym. Environ.*, 29(5), 1365-1379. <https://doi.org/10.1007/s10924-020-02006-0>
- Otache, M. A., Duru, R. U., Ozioma, A., & Abayeh, J. O. (2022). Catalytic methods for the synthesis of sugar esters. *Catal. Ind.*, 14(1), 115-130. <https://doi.org/10.1134/S2070050422010068>
- Romero, R; Luz, S; Nativi, R (2011). Biodiesel Production by Using Heterogeneous Catalysts. *Alternative Fuel* [Preprint]. Available at: <https://doi.org/10.5772/23908>.
- Royon, D; Daz, M; Ellenrieder, G; Locatelli, S (2007). Enzymatic production of biodiesel from cotton seed oil using t-butanol as a solvent. *Bioresour. technol.*, 98(3), 648-653. Available at: <https://doi.org/10.1016/j.biortech.2006.02.021>
- Schuchardt, U., Sercheli, R., & Vargas, R. M. (1998). Transesterification of vegetable oils: a review. *J. Braz. Chem. Soc.*, 9, 199-210. <https://doi.org/10.1590/s0103-50531998000300002>.
- Selvakumar, P; Sivashanmugam, P (2017). Optimization of lipase production from organic solid waste by anaerobic digestion and its application in biodiesel production. *Fuel Process Technol* 165:1–8. <https://doi.org/10.1016/j.fuproc.2017.04.020>
- Singh, S; Mukherjee, D; Dinda, S. (2020) Synthesis of CoO–NiO promoted sulfated ZrO₂ super-acid oleophilic catalyst via co-precipitation impregnation route for biodiesel production. *Renew Energy* 158:656–667. <https://doi.org/10.1016/j.renene.2020.05.146>
- Talha, N.S; Sulaiman, S (2016). Overview of catalysts in biodiesel production. *ARPN J Eng. Appl. Sci.* 11:439–442
- Tan, YH; Abdullah, MO; Kansedo, J; Mubarak, NM; Chan, YS; Nolasco-Hipolito, C (2019). Biodiesel production from used cooking oil using green solid catalyst derived from calcined fusion waste chicken and fish bones. *Renew. Energy.* 139, 696–706. <https://doi.org/10.1016/j.renene.2019.02.110>
- Thangaraj, B; Solomon, P.R; Muniyandi, B (2019). Catalysis in biodiesel production - a review. *Clean Energy* 3:2–23. <https://doi.org/10.1093/ce/zky020>
- Vijayalakshmi, S; Anand, M; Ranjitha, J (2020). Microalgae-based biofuel production using low-cost nanobiocatalysts. In: Yousuf A (ed) *Microalgae cultivation for biofuels production. Elsevier Inc., London*, 251–263. <https://doi.org/10.1016/B978-0-12-817536-1.00016-3>
- Wang, B; Wang, B; Shukla, S. K; Wang, R (2023). Enabling Catalysts for Biodiesel Production via Transesterification. *Catalysts*, 13(4), 740. <https://doi.org/10.3390/catal13040740>
- Wang, HG; Shi, G.L; Yu, F; Li, RF (2016) Mild synthesis of biofuel over a microcrystalline S₂O₈²⁻/ZrO₂ catalyst. *Fuel Process Technol.* 145:9–13. <https://doi.org/10.1016/j.fuproc.2016.01.021>