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Advancements in heterogeneous catalysts for biodiesel production: A critical review

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ABSTRACT

Biodiesel production as a renewable energy alternative has garnered global attention due to its potential to reduce greenhouse gas emissions and dependency on fossil fuels. Heterogeneous catalysts have emerged as a promising solution in the transesterification process of vegetable oils and animal fats into biodiesel, offering advantages in separation and reusability. This critical review explores recent advancements in the development of heterogeneous catalysts for biodiesel production, focusing on various types of catalytic materials, synthesis methods, and the reaction mechanisms involved. Metal-based catalysts and zeolites, as well as organic and inorganic materials, are discussed in the context of efficiency, stability, and cost. The review also highlights the challenges of industrial implementation and the potential of material and synthesis innovations to overcome them. By summarizing the latest research findings, this study aims to offer comprehensive insights to scientists and practitioners in the renewable energy field, thereby accelerating the adoption of biodiesel as a sustainable energy source.

Keywords: heterogeneous catalysts; biodiesel production; transesterification.

INTRODUCTION

In recent years, global attention to climate change issues and dependence on fossil fuels has encouraged researchers and industry to research alternative sustainable energy sources. Dependence on fossil fuels has led to the depletion of petroleum reserves from fossil sources, so the facts show that research on renewable fuels or biofuels needs to be developed. One of the alternative energy biofuels that currently needs to be developed is biodiesel (Buchori et al., 2024). Biodiesel is one of the most important fuels in the world. This fuel is produced from used cooking oil, algae, edible and non-edible vegetable oils, animal fats, fish fats, and all types of vegetable fats (Al-Aseebee et al., 2023). Biodiesel has become a major focus in efforts to reduce harmful greenhouse gas emissions. Several factors need to be considered in producing biodiesel, similar as the cost of raw material and food versus energy competition when using comestible oil as feedstock (Manab et al., 2021).

The production process of biodiesel energy can generally be carried out through the transesterification reaction stage. In biodiesel production, the transesterification reaction is the most common and widely studied reaction, utilizing alkaline earth metal oxides as solid base catalysts (Sulaiman et al., 2020). Transesterification reactions are commonly used to convert vegetable oils or animal fats into biodiesel (Baskar et al., 2018). Transesterification is a reversible response that occurs in three stages. First, the oil containing triglycerides is converted into diglycerides. Also, the diglycerides convert to monoglycerides and incipiently, become glycerol (Nurmawati et al., 2024). This reaction also involves the presence of a catalyst to form methyl esters (biodiesel) and other alcohols, where triglycerides interact with alcohols to form esters (biodiesel) and glycerol (Farouk et al., 2024). Several key elements that can influence the transesterification reaction and production rate are raw materials, the molar ratio of alcohol to raw materials, reaction time, catalyst type, catalyst concentration, mass transfer rate, reaction temperature, and reactor type (Al-Aseebee et al., 2025).

Conventional biodiesel production is carried out through the transesterification process of vegetable oil or animal fat catalyzed by homogeneous base or acid catalysts, such as NaOH, KOH, or H_2SO_4, by dissolving them in methanol. The use of homogeneous catalysts has disadvantages, namely that it is difficult to separate from the reaction mixture, this catalyst is only used once per reaction, and the resulting liquid waste can cause environmental problems (Widianingsih et al., 2024a). Then researchers developed heterogeneous catalysts that are more stable, lower corrosion of equipment, and environmentally friendly compared to homogeneous catalysts. Here are some examples of heterogeneous catalysts that have been used in the transesterification process, such as MgO, SrO, zeolite, ZnO, TiO_2, CaO, $CaCO_3$, and Al_2O_3. The use of efficient catalysts becomes very important in this process to increase the yield and speed of the reaction. Catalysts in the transesterification process can lower the activation energy, which can increase the conversion rate of biodiesel (Hazrat et al., 2024).

One promising approach in biodiesel production is the use of heterogeneous catalysts. Heterogeneous catalysts have several advantages over homogeneous catalysts, such as their ability to be separated easily after the reaction, potential for reuse, less corrosive, cost-effective, and reduced environmental pollution problems (Ismaeel et al., 2024). Heterogeneous catalysts play an important role in biodiesel production by providing cost-effectiveness and environmental benefits by reducing purification steps (Kibar et al., 2023).

Various materials have been explored as heterogeneous catalysts, including metal oxides, zeolites, and carbon-based materials, each with unique characteristics that affect the efficiency of the transesterification process. The challenge of heterogeneous catalysts requires designing and optimizing the physical and chemical properties of the catalyst, such as surface area, porosity, and chemical properties, to ensure optimal performance in the transesterification process (Oyekunle et al., 2023).

Although significant progress has been made in the development of heterogeneous catalysts for biodiesel production, there are still challenges that need to be overcome to improve their performance and applicability on an industrial scale. Innovations in material synthesis and reaction techniques are essential to overcome the existing barriers and accelerate the adoption of biodiesel as a viable energy source. In this critical review, we will discuss recent developments in heterogeneous catalysts for biodiesel production, evaluating different types of catalysts in terms of both challenges and future opportunities.

DEFINITION AND CHARACTERISTICS OF HETEROGENEOUS CATALYST

Heterogeneous catalysts are substances that play a role in accelerating the rate of chemical reactions, but are not directly involved in the reaction itself. These catalysts are in a different phase from the reactants in a chemical reaction, usually as solids or structures that are in a different phase from the reactants, solids that catalyze reactions between gases or liquids (Faruque et al., 2020). In the transesterification process, for example, vegetable oil and alcohol react on the surface of a solid catalyst, producing biodiesel and glycerol (Musa, 2016). The presence of heterogeneous catalysts allows the reaction to take place more quickly and efficiently, and facilitates the separation of the product from the catalyst after the reaction is complete.

One of the main characteristics of heterogeneous catalysts is their ability to be separated after the reaction process, which is an added value in industrial applications. Unlike homogeneous catalysts, which are dissolved in the reaction, the separation of heterogeneous catalysts can be done through physical techniques such as mafiltration, centrifugation or sedimentation. This not only increases the efficiency of the process, but also reduces operational costs by allowing the reuse of the catalyst in various reaction cycles (Widianingsih et al., 2024a).

Heterogeneous catalysts often have complex surface structures, which can affect their catalytic properties. For example, the particle size, surface area, and morphology of the catalyst can be obtained through various synthesis methods. Materials such as metal oxides, metal carbonates, zeolites, activated carbon, and metal nanoparticles are common examples of heterogeneous catalysts used in industry, including biodiesel production (Hamza et al., 2021).

These physical and chemical characteristics greatly influence the activation energy, selectivity, and stability of the catalyst during the reaction. Another characteristic is the thermal and chemical stability of the heterogeneous catalyst. A good catalyst must be able to withstand aggressive reaction conditions, such as high temperatures and the presence of corrosive substances. In addition, the ability to withstand the buildup of reactant or product residues during the reaction process is also important to maintain catalyst activation. Unstable catalysts can deactivate, reducing production efficiency and yield (Oboudatian and Safaei-Ghomi, 2022).

Heterogeneous catalysts also exhibit varying catalytic efficiencies, depending on several factors, including material type, structure, and the reaction conditions themselves (Zhao et al., 2017). For example, metal-based catalysts such as nickel or copper are often used in transesterification reactions due to their high reactivity towards reactants. Meanwhile, zeolites have the advantage of sorting molecules by size and shape (Yue et al., 2022), making them a good choice in applications that require high selectivity.

In addition to the advantages offered, challenges in the use of heterogeneous catalysts must also be considered. One of them is the risk of decreased catalytic activity due to the formation of a carbon layer that can hinder the access of reactants to the catalyst surface (Mao et al., 2025). The development of regeneration techniques and innovations in catalyst structural design are key to ensuring the sustainability and efficient use of catalysts in the production process.

In the context of biodiesel production, heterogeneous catalysts offer many advantages over homogenous catalysts, but the selection of the right catalyst type and effective synthesis methods remains a focus of research. With recent developments in nanotechnology and new materials, the potential for improving the efficiency and effectiveness of heterogeneous catalysts for biodiesel is increasingly promising. Further research in this area is expected to help overcome the challenges and strengthen biodiesel's position as a sustainable energy source.

TYPES OF HETEROGENEOUS CATALYST IN BIODIESEL PRODUCTION

Heterogeneous catalysts are the subject of extensive research due to their various advantages over homogeneous catalysts especially in terms of easier separation. Heterogeneous catalysts can also be reused more simply. The reuse of these catalysts can reduce production costs and also support the principle of environmental friendliness because it does not require re-refining procedures (Kibar et al., 2023). A wide variety of heterogeneous catalysts are used in biodiesel production. They are generally classified as acid catalyst, base catalyst, acid-base bifunctional catalyst, nano catalyst and biomass waste-based catalyst. Figure 1 shows the classification of catalysts in biodiesel production, namely homogeneous and heterogeneous. Each type has its own distinctive features and advantages and challenges in biodiesel production.

Acid catalyst

Heterogeneous acid catalysts are commonly used in esterification procedures to convert free fatty acids (FFA) into methyl esters (biodiesel). This heterogeneous acid catalyst has a large number of active sites and moderate acidity and hydrophobicity. In addition, this catalyst is easily recovered during the transesterification reaction and is able to overcome diffusion problems so that biodiesel yield can be significantly increased (Chozhavendhan et al., 2020). Some of the benefits of heterogeneous acid catalysts are that they are insensitive to free fatty acid (FFA) content as well as water content present in the oil.

This method is preferred when using low quality oils for esterification and transesterification. In addition, the reaction occurs simultaneously and separation of the catalyst from the product is also easy (Okechukwu et al., 2022). Some examples of heterogeneous acid catalysts include sulfated zirconia, sulfonate resins, and zeolites. Zeolite materials have been long and widely used as catalytic agents in various industries due to their environmentally friendly nature and low price. Zeolites have a large total surface area and high porosity (Pan et al., 2019).

To control its basicity, the method used is to incorporate alkali metal ions or attach basic constituents on the internal surface of zeolite pores. Disadvantages of heterogeneous acid catalysts in transesterification include the need for high reaction temperatures (60–275 °C), high alcohol to oil molar ratios (up to 40:1), and long reaction times of up to 20 hours. Transesterification of vegetable oils under supercritical methanol, the optimum condition for methyl ester production

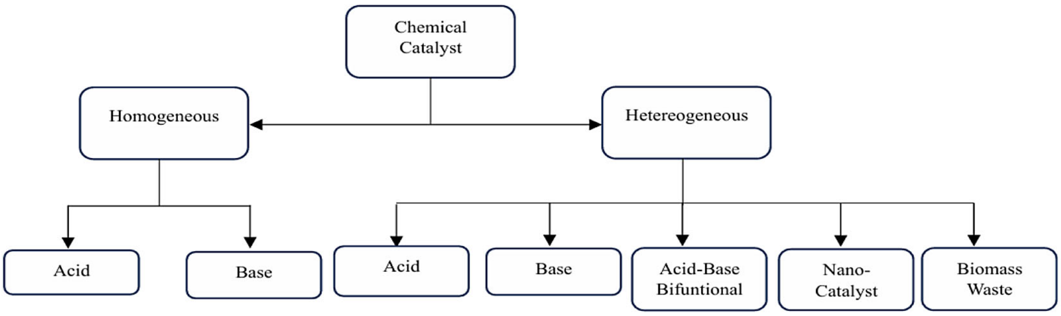

Figure 1. Classification of catalysts for biodiesel production (Ma and Mu, 2023)

were 350 °C reaction temperature, a methanol to oil molar ratio of 42, and 400 s of time 95% conversion (Kayode and Hart, 2019). In addition, the synthesis of these catalysts is expensive, and there is a possibility of catalyst leaching that can contaminate the product.

Another example of the application of heterogeneous acid catalysts is the use of p-TsOH, H_2SO_4 to Nafion-R in the synthesis process of cinnamic acid esters. Nafion catalyst, which acts as an acid catalyst in the synthesis process of cinnamic esters which will be compared with homogeneous catalysts, namely H_2SO_4 and *p*-TsOH. Fischer esterification reaction method is an esterification between an organic acid and an alcohol catalyzed. The Fischer esterification reaction is still the main method for making esters from organic acids and alcohols because it is easy to perform, flexible in substrate selection, and has an effective catalyst. This reaction process includes the activation of carbonyl groups with the help of an acid catalyst, the nucleophilic attack of the alcohol, and the elimination of water as a by-product, where the presence of water can decrease the yield because it shifts the balance towards the reactants (Mannu and Mele, 2024).

In this research, the Fischer esterification method was carried out at 100 °C for 18 hours. The process used cinnamic acid as the main substrate with two different types of alcohols as reactants, and compared the effectiveness of homogeneous and heterogeneous catalysts.

The results of the reaction between compounds are shown in Table 1. The use of Nafion (heterogeneous catalyst), as a catalyst agent only resulted in a conversion of 31% when the same operating conditions were used as the application when using homogeneous catalysts. When the reaction was carried out for a longer period of about 48 hours, the reaction yield increased to 78%. Another interesting point is when phenethyl ester is used as a reacting agent that replaces the cyclohexanol reactant. This reactant replacement will result in a percent conversion of 90% in 18 hours at 100 °C. This event shows that nafion catalyst is a promising heterogeneous catalyst to be used as esterification reagent of cinnamic acid and its derivatives.

Basically, Nafion-R catalyst acts as a heterogeneous catalyst in the mechanism of esterification reactions between carboxylic acid compounds and alcohol derivatives. This can be observed through the esterification reaction mechanism of cinnamic acid with cyclohexanol which yields a conversion of 78%, as well as the reaction with phenethyl alcohol which gives a higher conversion, which is around 93%. Overall, catalyst selection and reaction conditions largely determine the efficiency and final yield of the Fischer esterification process.

Base catalyst

Heterogeneous base catalysts are commonly used in transesterification reactions because they have high reactivity under relatively mild conditions. However, side reactions such as glyceride saponification, methyl ester formation, and FFA neutralization can occur during the methanolysis process with base catalysts (Shahedi et al., 2021). In addition, the presence of heterogeneous base catalysts can also inhibit the separation of glycerol from the formed methyl esters. One example of a type of heterogeneous base catalyst is the CaO compound derived from eggshell waste (Roschat et al., 2020). The utilization of animal waste for biodiesel production has many benefits. Previous research has shown the effectiveness of CaO compounds derived from animal shells or bones.

Table 1. Data result from the reaction between cinnamic acid compound and phenethyl alcohol compound (Mannu and Mele, 2024)

No	Time (hour)	Temperature (°C)	Catalyst, mmol	Substrat	Yield (%)
1	18	100	H_2SO_4, 0.98 mmol	Cinnamic Acid + Cyclohexanol	85
2	18	100	p-TsOH, 0.98 mmol	Cinnamic Acid + Cyclohexanol	85
3	18	100	Nafion, 0.98 mmol	Cinnamic Acid + Cyclohexanol	31
4	48	100	Nafion, 0.98 mmol	Cinnamic Acid + Cyclohexanol	78
5	18	100	Nafion, 0.98 mmol	Cinnamic Acid + Phenethyl Alcohol	78

The research process of making biodiesel begins with the preparation of raw materials, namely used cooking oil, as well as CaO catalysts obtained from eggshell waste. Various variables were applied to determine the optimal calcination operating conditions in preparing the CaO catalyst. The eggshell waste was then calcined at various temperatures, namely 600, 700, 800, 900, until 1100 °C, with time variations of 1, 2, and 3 hours (Alsaiari et al., 2023). The transesterification reaction was carried out at 50–100 °C, with a stirring speed of 600 rpm and a mole ratio of oil to methanol of 1:9 or 1:12.

Biodiesel produced from the transesterification reaction using eggshell-based CaO catalysts with variations in temperature and calcination time was then analyzed to determine its physical properties, such as density and viscosity. This analysis aims to evaluate the physical characteristics of biodiesel products. The results of the biodiesel density and viscosity measurements can be seen in (Table 2) below.

Based on the data in Table 2, The results revealed that as the activation temperature for eggshell in 3 hours. In comparison to other catalysts, the 950 °C calcined catalyst had the highest catalytic and showed strong catalytic activity which may be due to the catalyst's surface containing an optimal number of active sites. Under ideal conditions, catalyst loading 4 wt.%, 9:1 ethanol to oil molar ratio, reaction temperature 75 °C, and reaction time 3 hours. The 950 °C catalyst functioned commendably, yielding a maximum biodiesel yield of 88%. The high BET surface area, and optimal pore volume of this catalyst, created increased transesterification activity in the surplus cooking oil. The density value has met the SNI 7182-2012 standard, while the viscosity value is close to the standard limit set.

Some of the advantages of heterogeneous base catalysts are relatively faster reaction rates, mild reaction conditions, less energy-intensive, easy to separate from the reaction mixture, high possibility of reusing and regenerating the catalyst and less corrosive (Faria et al., 2020).

Acid-base bifunctional catalyst

Biodiesel is a mixture of fatty acid alkyl esters (FAAEs) produced through the transesterification process of triglycerides (TGs) or esterifying of free fatty acids (FFAs) using methanol and the addition of a catalyst, resulting in FAMEs and glycerol (Buasri et al., 2023). Acid-base bifunctional catalysts are solid heterogeneous catalysts that have both acidic and basic active sites. These catalysts have been the focus of research in various organic reactions over the past decade (Ramli et al., 2017). This catalyst is designed to convert FFA into biodiesel through esterification reaction and triglycerides into biodiesel through transesterification reaction simultaneously (Kadier et al., 2018).

The presence of acidic and basic active sites on the catalyst surface allows simultaneous esterification-transesterification reactions without being affected by water content (Ramli et al., 2017). In addition, the physico-chemical properties of the catalyst can be modified as needed so as not to be affected by the presence of water or FFA during the transesterification process (Mansir et al., 2018).

Acid-base bifunctional catalysts can be synthesized through several methods, including impregnation, coprecipitation, sol-gel, and physical mixing. The wet impregnation method is the most widely used due to its ease of preparation, which involves mixing precursors (usually in the form of salts and mixed oxides) with distilled water for 5–6 hours, followed by drying at 110 °C for 24 hours and calcination. This method is suitable for synthesizing support catalysts because it can create many active sites on the catalyst surface that are beneficial for esterification and transesterification processes (Mansir et al., 2018).

Table 2. Effects of calcination temperature on the eggshell catalyst activity (Alsaiari et al., 2023)

T (°C)	Biodiesel yield (%)
600	50
700	63
800	72
950	88
1000	74
1100	59

Several studies have been conducted on acid-base bifunctional catalysts for biodiesel production (Nizah et al., 2014). Examined Fe/DSHM-SNH2 acid-base bifunctional catalysts prepared using a two-step condensation method. This catalyst has a hollow core and two spatial shells with different active centers, allowing esterification and transesterification reactions to be carried out in one synthesis reactor. The maximum yield was 85.36% by weight, with a reaction temperature of 60 °C, a reaction time of 4.5 hours, a methanol/oil molar ratio of 6:1, and 6% by weight of catalyst. This catalyst showed excellent recyclability with a yield above 80% for 3 reaction cycles.

Lee et al. (2015) also studied castor oil-based biodiesel production using $CaO-La_2O_3$ acid-base catalysts, focusing on catalyst stability and process sustainability. The bonding of Ca and La metal oxides resulted in a good dispersion of CaO on the composite surface, enhancing the acid and base active sites. The Ca/La atomic ratio also affected the biodiesel conversion, with the highest yield (98.7%) at a Ca/La ratio of 8, reaction time of 3 hours, reaction temperature of 160 °C, methanol/oil ratio of 25:1, and catalyst weight of 3% by weight. However, when the Ca/La ratio reached 10, the stability of the catalyst decreased because the catalyst surface was saturated with CaO species.

Nano-catalyst

Nano-Catalyst consist of catalyst particles with nanometer size and have a very large surface area, having unique characteristics that have nano-sized pores that provide high surface area and active sites for interaction with the substrate. The use of nano-catalyst can significantly increase the specific surface area of catalysts, thereby increasing production efficiency (Husin et al., 2018) (Abdullah et al., 2020). Nano-catalyst also show advantages in reaction selectivity, which means they can help improve the quality of the final product, i.e. methyl ester (FAME).

Using nanocatalysts with very high surface area, the catalyst can increase catalytic activity, which can accelerate the reaction rate in biodiesel production. Fabrication and modification of nanocatalysts of high surface to volumeratio, catalytic stability, and high catalytic activity is significant in optimizing the parameters of biodiesel production. This also helps to protect the environment by reducing pollution from chemicals used when making nanocatalysts (Bano et al., 2020). Heterogeneous nano-catalyst such as CaO, MgO, and KF/CaO have been shown to be effective in improving biodiesel production efficiency. Some of the advantages of heterogeneous nanocatalysts include high reactivity, high selectivity and their environmentally friendly use. The following is a summary of biodiesel conversion results from various oil sources using heterogeneous nano-catalyst.

In Table 3, it can be seen that the use of heterogeneous nano-catalyst in biodiesel production has shown promising results, with biodiesel conversion (BCY) reaching above 95% for several types of vegetable and used cooking oils. Nanocatalyst such as CaO, MgO, and KF/CaO have been shown to be effective in increasing the efficiency of transesterification reactions. In addition, nanocatalysts can also be reused, reducing production costs and environmental impact.

Biomass waste-based catalyst

Biomass waste-based catalysts are made from biomass waste which includes various sources such as eggshells, clam shells, animal bones, rice husks, and bagasse (Hamza et al., 2021). Table 4 shows the results of biodiesel conversion calculations using these biomass sources. Since they are non-toxic, non-corrosive, and eliminate wastewater production, solid catalysts made from biomass are an eco-friendly solution. Moreover, most of them are made from biomass, which is a cheap and easily accessible material. Furthermore, the catalyst itself is biodegradable, so no disposal issues will arise immediately. Although the use of biomass as a catalyst source can reduce waste, the production process and use of the catalyst itself can generate additional waste that needs to be properly managed (Ao et al., 2024).

Table 3. Conversion results of biodiesel from vegetable oil using nanocatalysts (Noiroj et al., 2009)

Nano-catalyst	*Feedstock*	MOR	Temp (°C)	Catalyst content (wt.%)	Time (h)	BCY (%)
KOH/Al_2O_3	*Palm oil*	15:1	70	3	3–6	91.07
Lipozyme TLIM	*Rapeseed oil*	4:1	35	3	12	95
KF/CaO	*Tallow seed oil*	12:1	65	4	2	96.8
$CaO/Al/Fe_3O_4$	*Rapeseed oil*	15:1	-	6	3	98.71
CaO-CeO2	*Refined palm oil*	20:1	85	5	3	95

Comparison of homogeneous and heterogeneous catalyst in biodiesel production

When making biodiesel, basic homogeneous catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) are often used. These catalysts are easily available and have a high level of reactivity with relatively affordable production costs. However, the homogeneous base catalytic process has some disadvantages. In transesterification reactions, the use of homogeneous base catalysts faces challenges such as difficulty in separation, complexity of product purification, and selectivity that depends on the free fatty acid (ALB) content in the feedstock (Prasad, 2017). In addition, homogeneous catalysts cannot be reused thus increasing the overall operational cost (Changmai et al., 2020).

Heterogeneous catalysts, on the other hand, offer a number of advantages over homogeneous catalysts. Among them, only a few unit operations and product separation and purification processes are required to produce biodiesel. It allows the catalyst to be reused, as well as producing higher quality glycerol. The production of biodiesel via catalytic transesterification produces crude glycerol as a co-product along with biodiesel (Arun et al., 2021), heterogeneous is also more environmentally friendly as it minimizes waste production and reduces corrosion of equipment (Widianingsih et al., 2024b). Examples of frequently used heterogeneous catalysts include calcium oxide (CaO) and other transition metal oxides. Heterogeneous catalysts are considered more efficient in terms of sustainability as the catalysts can be reused in multiple reaction cycles. This is crucial in lowering production costs and making the process more environmentally friendly. In contrast, although homogeneous catalysts have faster reaction times, they tend to be more difficult to treat after the reaction and generate a lot of waste that must be disposed of.

During the transesterification process of crude oil, free fatty acids (FFAs) can react with alcohols, resulting in soap formation, which can reduce biodiesel production and cause other problems (Jayaprabakar et al., 2024). Basic homogeneous catalysts can act to react with FFAs to form certain types of soaps that can hinder the process of separating biodiesel from glycerol, significantly affecting the final biodiesel yield. However, bifunctional catalysts in solid form have the ability to perform both esterification and transesterification processes simultaneously, making them more suitable for use in feedstocks with high FFA content without the need for pretreatment.

In recent years, there have been developments in the use of biomass-based heterogeneous catalysts and nanoparticles as more favorable options due to their environmentally friendly and stable nature and large surface area. These catalysts allow for increased conversion of free fatty acids into biodiesel, as well as lower overall energy requirements. Examples of these innovations are the use of catalysts from palm kernel shell ash and zeolite-based catalysts.

Homogeneous catalysts, such as NaOH or $NaOCH_3$, are more selective to specific feedstocks. They are often used to make biodiesel

Table 4. Biodiesel conversion results using biomass waste-based catalysts (Hamza et al., 2021)

Catalyst	Biomass source	Temperature (°C)	Reaction time (hour)	Biodiesel conversion (%)
CaO from eggshells	Eggshells	65	3	99
CaO from animal bone	Cow bone	70	4	96
KOH from rice husk	Rice husk	60	2	92
MgO from sugarcane bagasse	Sugarcane bagasse	75	5	90

with the same feedstock to produce a product that is more consistent in quality (De Lima et al., 2016). However, this process requires more stringent operating conditions, such as temperature and pressure, to be successful. In contrast, heterogeneous catalysts, which are more physically stable, allow operation under a wider range of conditions and are more flexible for larger industrial scales. Heterogeneous catalysts such as CaO-supported mesoporous SBA-15 are also more tolerant to temperature and pressure variations, which makes them useful in significant industrial applications (Thangaraj et al., 2019).

THE STABILITY OF HETEROGENEOUS CATALYST

The stability of heterogeneous catalysts is influenced by several factors, including pore structure, surface area, acid-base strength, and resistance to leaching of active metals. A stable catalyst should be able to maintain its activity over several reaction cycles without experiencing significant performance degradation. Several studies have shown that metal oxide-based catalysts such as CaO, MgO, and ZnO have good stability, but are susceptible to leaching under harsh reaction conditions (Lee et al., 2014).

One approach to improve the stability of heterogeneous catalysts is to modify their surface through metal impregnation or the addition of support materials such as zeolite, silica, or alumina. For example, CaO catalysts supported on alumina (CaO/Al_2O_3) show better stability because alumina prevents calcium leaching into the reaction mixture (Wang et al., 2007). Comparison of stability of several heterogeneous catalyst in biodiesel production: biodiesel conversion CaO between 80–85% (low stability), AI_2O_3 between 90–95% (high stability), MgO between 85–90% (medium stability), etc. In addition, the use of carbon-based catalysts has also attracted attention due to their corrosion resistance and ability to be regenerated.

Besides material modification, operating conditions such as temperature, pressure, and alcohol-oil molar ratio also affect catalyst stability. High temperature can increase the reaction rate but also potentially damage the catalyst structure. Therefore, optimization of the reaction conditions is crucial to ensure the long-term stability of the catalyst (Delbecq and Len, 2018).

Catalyst regeneration is an important aspect in maintaining its stability. The regeneration process involves cleaning the catalyst from carbon deposits or organic compounds attached to its surface. Some commonly used regeneration methods include calcination, washing with organic solvents, or treatment with inert gases. Catalysts that can be regenerated easily have a higher economic value as they reduce the cost of biodiesel production.

EASE OF SEPARATION OF CATALYST FROM END PRODUCT

Catalysts play an important role in various chemical reactions, both in industry and research. One of the main challenges in the use of catalysts is their separation from the final product once the reaction is complete. The ease of separation of the catalyst from the final product is a crucial factor in process efficiency, production cost, and environmental sustainability (Sheldon et al., 2007).

One commonly used approach is the use of heterogeneous catalysts. Heterogeneous catalysts, such as zeolites or metals supported on solids, can be easily separated from the reaction mixture through filtration or centrifugation. This is in contrast to homogeneous catalysts, which dissolve in the reaction mixture and require more complex separation techniques, such as extraction or distillation.

In addition, the development of magnetic catalyst technology has provided an innovative solution for catalyst separation. Magnetic catalysts, which contain magnetic particles such as Fe_3O_4, can be separated from the reaction mixture by using an external magnetic field. This method is not only efficient but also environmentally friendly as it reduces the use of organic solvents (Polshettiwar et al., 2011). In addition to physical methods, chemical approaches can also be used to facilitate catalyst separation. For example, the use of catalysts coated with certain polymers or organic materials allows separation through changes in pH or temperature (Ockwig et al., 2005). This method is known as "stimulus-responsive catalyst" and is gaining popularity in industrial applications.

Sustainability is also an important consideration in catalyst separation. The use of catalysts that can be recycled or reused not only reduces production costs but also minimizes chemical waste. Some recent studies have shown that nanoparticle-based catalysts can be used for up to several reaction cycles without significant loss of activity.

However, challenges remain, especially on an industrial scale. Separation of the catalyst from the final product on a large scale often requires specialized equipment and significant energy. Therefore, research is ongoing to develop more efficient and energy-efficient catalysts and separation methods.

EFFICIENCY OF HETEROGENEOUS CATALYST IN BIODIESEL PRODUCTION

Heterogeneous catalysts have been shown to significantly improve the efficiency of biodiesel production through the transesterification process. Compared to homogeneous catalysts, heterogeneous catalysts offer advantages such as ease of separation from the product, high thermal stability, and the ability to be reused, thereby reducing production costs and environmental impact (Zhang et al., 2003).

Heterogeneous catalysts such as CaO, MgO, and zeolites have shown oil-to-biodiesel conversion above 90% under optimal reaction conditions of 60–70 °C and methanol-oil molar ratios of 6:1 to 12:1 (Lee et al., 2014). In addition, transition metal-based heterogeneous catalysts, such as Ni and Co, supported on porous materials such as silica or alumina, have been developed to improve catalytic activity and reaction selectivity (Lachter et al., 2024). The efficiency of heterogeneous catalysts is also influenced by the surface area and pore structure of the catalyst, which facilitate reactant adsorption and product release (Alves et al., 2023). Thus, the use of heterogeneous catalysts not only improves biodiesel production efficiency but also supports environmental sustainability through waste reduction and catalyst recycling (Garcia et al., 2008).

HETEROGENEOUS CATALYST RECYCLING

Heterogeneous catalysts play an important role in biodiesel production through the transesterification process. However, after several

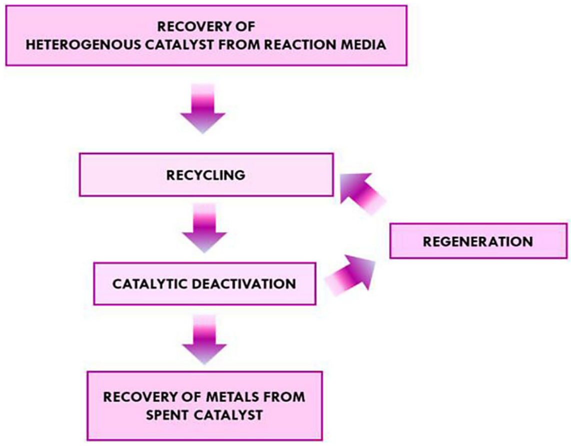

Figure 2. Catalyst recycling mechanism (Miceli et al., 2021)

cycles of use, the catalyst may deactivate due to the buildup of organic compounds, carbonate formation, or loss of surface activity. Therefore, catalyst recycling is an important step to maintain efficiency and reduce production costs.

The provisions for catalysts that should be recycled include catalysts that still have a stable chemical and physical structure, and have not suffered permanent damage. Aspects that need to be considered in catalyst recycling include catalyst separation from the product, washing, drying, and reactivation.

In Figure 2 the recycling mechanism starts with the separation of the catalyst from the reaction mixture using filtration or centrifugation. The catalyst is then washed with organic solvents such as methanol or ethanol to remove residual oil, glycerol, and other by-products. After washing, the catalyst is dried at 100–150 °C to remove moisture. If the catalyst is deactivated due to the formation of carbonate compounds (as in the case of CaO catalysts), reactivation is done through calcination at 400–600 °C.

Results after recycling show Table 5 that the catalyst can retain its activity up to 80–95% of the initial activity, depending on the type of catalyst and reaction conditions. For example, CaO catalysts can be reused for up to 5–10 cycles

Table 5. Comparison of catalyst recycling methods (Mukhtar et al., 2022)

Catalyst	Number of cycles	Initial conversion (%)	Conversion after recycling (%)	Reactivation method
CaO	5	95	90	Calcination (600 °C)
MgO	7	92	85	Washing + drying
Zeolit	10	88	80	Washing + calcination
Ni/SiO_2	8	90	82	Washing + calcination

with biodiesel conversion remaining above 90% (Mukhtar et al., 2022).

CONCLUSIONS

Heterogeneous catalysts have become an important solution in biodiesel production via transesterification process, offering advantages such as ease of separation, reusability, and environmental friendliness. Various types of heterogeneous catalysts, including acidic, basic, acid-base bifunctional catalysts, nanocatalysts, and biomass waste-based catalysts, have been developed to improve reaction efficiency and stability. Catalysts such as CaO, MgO, and zeolites showed biodiesel conversion above 90% under optimal conditions, with temperatures of 60–70 °C and methanol-oil molar ratios of 6:1 to 12:1. Acid-base bifunctional catalysts enable simultaneous esterification and transesterification reactions, suitable for feedstocks with high FFA content.

The advantages of heterogeneous catalysts over homogeneous catalysts include ease of separation, reuse, and waste reduction. However, challenges such as catalyst deactivation due to buildup of organic compounds or carbonate formation still need to be addressed. Innovations in material synthesis, such as the use of nanocatalysts and biomass waste-based catalysts, have shown great potential in improving catalyst stability and efficiency. Catalyst recycling through processes such as calcination and leaching is also an important aspect to maintain sustainability and reduce production costs.

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