A Review of Biomass-Derived Heterogeneous Catalysts for Biodiesel Production

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Abstract: The scientific community is being forced to consider alternative renewable fuels such as biodiesel as a result of the sharp increases in the price of petroleum and the increased demand for petroleum-derived products. Transesterification is a technique used to create biodiesel where a variety of edible oils, non-edible oils, and animal fats are used. For this, either a homogeneous or heterogeneous catalyst is utilized. An appropriate catalyst is chosen based on the quantity of free fatty acid content in the oil. The main distinction between homogeneous and heterogeneous catalysts is that compared to the heterogeneous catalyst, the homogeneous catalyst is not affected by the quantity of free fatty acids in the oil. Early methods of producing biodiesel relied on homogeneous catalysts, which have drawbacks such as high flammability, toxicity, corrosion, byproducts such as soap and glycerol, and high wastewater output. The majority of these issues are solved by heterogeneous catalysts. Recent innovations use novel heterogeneous catalysts that are obtained from biomass and biowaste resources. Numerous researchers have documented the use of biomass-derived heterogeneous catalysts in the production of high-quality, pure biodiesel as a potentially greener manufacturing method. The catalysts were significantly altered through conventional physical processes that were both cost- and energy-effective. The present review is intended to analyze catalysts from biowaste for making biodiesel at a minimal cost. The most recent methods for creating diverse kinds of catalysts—including acidic, basic, bifunctional, and nanocatalysts—from various chemicals and biomass are highlighted in this review. Additionally, the effects of various catalyst preparation methods on biodiesel yield are thoroughly explored.

Keywords: biomass; heterogeneous catalyst; biodiesel

1. Introduction

In recent years, nanomaterials with different architectures and supports have been playing a key role in industrial catalysis [1]. Because of worries about the destructive effects of fossil fuel usage, such as climate change, global warming, and their detrimental effects on human health, biomass is now the most popular renewable energy source, and its utilization is growing [2,3]. In reality, biomass has enormous potential for use as a source of renewable energy, with the ability to produce biofuels for heat, power, and transportation. Rising bioenergy endorsement as part of agricultural policies has resulted in a different and more fruitful utilization of land and has greatly aided in the
advancement of economic possibilities for rural areas, as well as a ramp-up in farmer income, a reduction in rural–urban migration, and environmental and cultural preservation. Recent technological advancements in biomass exploitation have led to the development of promising methods for efficiently generating heat, power, and liquid biofuels out of these widely available and affordable natural resources [4]. A blend of monoalkyl esters made from renewable bioresources known as biodiesel is of particular relevance since it is quickly becoming a significant transportation fuel. Due to its lower pollution levels, biodiesel has been promoted as a cleaner alternative to gasoline and diesel (primarily in terms of CO\textsubscript{2} emissions). A multitude of air pollutants, including particulate matter, sulfur, hydrocarbons, and carbon monoxide, can be considerably reduced by using biodiesel. The advantages of biodiesel for the environment are driving up production. However, production costs are still quite high compared to diesel fuel made from petroleum. With the addition of a solid heterogeneous catalyst, biodiesel production could lower its cost and become economically competitive with diesel. As a result, recent significant research efforts have been made to identify the appropriate catalysts.

Biomass is any organic material that originates in some way from the photosynthetic process. The definition of biomass varies because of the variability of the components, the purpose, and the place of origin. However, in a broader sense, biomass is a collection of organically derived materials, including those from plants such as crops, trees, shrubs, and algae as well as any other materials made of an organic matrix, with the exception of plastics made from petrochemical and fossil resources [5]. The most significant biomass sources include sewage [6], algae [7], aquatic crops [8], agricultural and forestry leftovers [9], animal residues [10], and waste products from the wood-processing sector [11]. They also fall under the biomass classification particularly if they cannot be reused in later processing such as municipal solid waste and waste discharges from human activities. Biomass has a remarkably diversified chemical makeup. For instance, grains and livestock waste are mostly made up of starch, whereas residues of plant origin are primarily made up of cellulose, hemicellulose, and lignin in different amounts. Obviously, various chemical characteristics come from diverse chemical structures. Figure 1 depicts the schematic diagram for the synthesis of biodiesel from biomass.

![Figure 1. Schematic diagram for the synthesis of biodiesel by transesterification. Reprinted with permission from Ref. [12]. 2022, Elsevier.](image)

Fatty acid methyl esters (FAME) are the main component of the renewable transportation fuel known as biodiesel [13,14]. These FAME are normally prepared by the transesterification of vegetable and animal fats. The demand for biodiesel is rising both domestically and internationally. Concerns over greenhouse gas (GHG) emissions and
climate change, a need for renewable/sustainable energy sources, and a desire to build domestic and more reliable fuel supplies are the main drivers behind this. Although the terms “first generation” and “second generation” biofuels are used often, they have no legal or regulatory significance [15,16]. The phrase “1st Generation” often refers to biofuels made from readily accessible, edible feedstocks utilizing proven conversion techniques. The majority of current biofuels are categorized as first generation. This comprises biodiesel created by the transesterification of triglycerides present in animal fat and vegetable oils and ethanol made through the fermentation of sugars with its source in maize, sugar cane, or sorghum, etc. The phrase “2nd Generation” can be used to describe biofuels made from cutting-edge, non-food feedstocks or via the use of modern processing technologies. The non-edible triglycerides and lignocellulose are two examples of advanced feedstocks that include algae and jatropha. Catalytic hydroprocessing of triglycerides to create sustainable fuel and thermal conversion such as pyrolysis and gasification of lignocellulose are two examples of contemporary processing technology [17,18].

Direct usage and mixing of raw oils [19], microemulsion [20], thermal cracking [21], pyrolysis [22], and transesterification [23] are some of the current processes for making biodiesel. Transesterification is by far the simplest and most economical process for producing biodiesel. Transesterification, also known as alcoholysis, is the process by which fats or oils react with an alcohol in the presence of a catalyst to produce glycerol and fatty acid methyl ester [24]. We can utilize methanol, ethanol, butanol, and amyl alcohol, among other forms of alcohol. Nevertheless, methanol is frequently employed since it is less expensive, has a short chain, reacts rapidly, and disperses readily in the reaction media [25]. Although many different FAME species can be found in biodiesel fuel made by transesterification of triglycerides, most fuels are typically dominated by a limited number of species such as lauric acid, Myristic acid, myristoleic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, gondoic acid, behenic acid, and erucic acid [26]. The most efficient technique for producing biodiesel is thought to be enzymatic transesterification. However, the highly expensive cost of the catalyst and the slower reaction rate prevent its wider use [27]. Figure 2 illustrates the mechanism for the formation of biodiesel. To produce three moles of fatty acid methyl ester and one mole of glycerol, the process needs three moles of methanol and one mole of triglyceride. Mono- and diglycerides are produced as intermediates in three sequential reversible processes that result from this. Following the reaction, the glycerol is separated by settling or centrifugation, and then it is purified for various applications. Before being employed as a diesel fuel, the methyl ester fraction is purified.

Figure 2. Formation of FAME from triglyceride [28].
1.1. Homogeneous Catalysis

At the moment, homogenous base catalysts are often used on an industrial basis to produce biodiesel [29]. The benefits of a homogeneous base catalyst, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), include high catalytic activity, faster reaction times, moderate working conditions, and readily accessible and inexpensive raw materials. Free fatty acids (FFA) and water can greatly affect the homogeneous base catalyst process [30]. Additionally, the production of soaps as a byproduct of neutralization and saponification would hinder the extraction and purification process, create a significant amount of wastewater, and increase operating costs [31]. This requirement renders this catalyst unfavorable to the environment.

For feedstock with a high FFA concentration, such as used cooking oil, unrefined vegetable oils, and animal fats, homogenous acid catalysts such as $\text{H}_2\text{SO}_4$, HCl, and $\text{H}_3\text{PO}_4$ are appropriate. The lack of sensitivity to the existence of FFA and water, the capacity to catalyze both transesterification and esterification processes, and the absence of soap byproduct production are some of its main benefits. The main obstacle to the widespread use of this catalyst, however, is its delayed response time. According to reports, base-catalyzed transesterification has a conversion rate that is around 4000 times slower than acid-catalyzed transesterification [32]. Homogeneous acid catalysts are also extremely acidic and reactive by nature. In a homogenous operation, product isolation and purification requires a number of stages, generates a lot of effluents, and increases operational costs. The recovery and recycling of homogeneous catalysts are challenging, impractical, costly, and need additional processing [33].

1.2. Heterogeneous Catalysis

In recent years, research in using solid or heterogeneous catalysts in the synthesis of biodiesel has significantly grown [34]. The phases or states of heterogeneous catalysts differ from those of reactants. These are just the kinds of catalysts that usually generate active sites during a reaction with their reactants [35]. Due to the fact that it takes place in a three-phase system with a solid heterogeneous catalyst and two immiscible liquid phases such as methanol and oil, the heterogeneously catalyzed methanolysis process is exceedingly complicated. Along with methanolysis, other processes including the saponification of glycerides and methyl esters and the catalyst-assisted neutralization of FFAs also take place. The main drawbacks of this catalysis comprise higher oil/alcohol ratios and higher temperatures than in homogeneous catalysis. It is simpler to extract the catalysts from the product afterward since they are not either destroyed or decomposed in the reaction mixture. Additionally, since the recovered catalyst may be utilized again in the process, less catalyst is needed overall, reducing the expenses. The heterogeneous-based operation has a number of advantages, such as being noncorrosive, ease of separation, and having extended catalyst endurance [36,37]. Examples of heterogeneous catalysts including alkaline earth metals such as MgO and SrO are commonly employed. The most popular application of CaO is as a transesterification catalyst. As a heterogeneous base catalyst, Al is employed in the form of oxides such as $\text{Al}_2\text{O}_3$, which are supported by CaO and MgO. Numerous naturally occurring calcium sources, including eggshell, mollusk shell, and bones, are frequently employed as the starting materials for the manufacture of catalysts because they can both reduce wastes and yield catalysts with a high level of cost competitiveness. Several catalysts are on sale for basic-catalyzed reactions, including metal oxide, mixed oxide, and hydrotalcite [38]. On the contrary side, catalysts for acidic activity include various forms of carbon, zeolites, ion-exchange resin, and transition metal oxides [39]. Nevertheless, the three-phase system’s existence in a heterogeneous environment will cause a diffusion issue that will hinder the reaction [40]. The mass transfer performance is constrained by three highly immiscible phases such as solid catalyst, alcohol, and oil, which slow the pace of reaction. These solid catalysts generated from non-renewable resources and ecologically unfriendly sources suffer from a smaller number of active sites, microporosity, leaching, being poisonous, and costly [41]. Therefore, the catalyst must possess a larger pore diameter.
and greater specific surface area that support the hydrophobicity and external catalytic sites in them to make a superior solid acid catalyst.

1.3. Enzymatic Catalysis

A lipase-catalyzed approach has been devised and has been the subject of substantial research over the past 10 years to reduce the issues related to the use of acid and/or alkali for the synthesis of biodiesel [42]. The enzyme-based biodiesel process has the following benefits: (1) a more straightforward manufacturing process; (2) less energy consumption; (3) higher purity of the byproduct glycerol; (4) no soap development in the system; and (5) simple separation and recycling of immobilized enzymes [43]. The enzymatic pathway for the manufacturing of biodiesel is now viewed as an ecofriendly substitute that is increasingly feasible as new, more effective, and less expensive enzymes are now being evolved. However, the enzyme catalyst has some limitations, primarily linked to lower reaction rates, increased prices, and loss of activity or enzyme inhibition. The enzymatic catalyst may be regenerated to reduce enzyme costs, which improves the effectiveness of recovering biodiesel. Additionally, genetic engineering and the identification of high alcohol-tolerant microorganisms can be used to improve enzyme catalytic activity [44]. Introducing enzymes that can catalyze both the esterification of FFA and the transesterification of TGs will make it much easier to overcome the significant challenge posed by the existence of FFA in the precursor material that prevents transesterification using conventional techniques. Waste oils and fats include FFA that can be totally turned into biodiesel. In reality, as the FFA are immediately esterified enzymatically into FAME, the enzyme-catalyzed transesterification is more appropriate for usage on FFA-rich feedstocks including waste oils, greases, beef tallow, and lard [27].

1.4. Non-Catalyzed Process

Non-catalytic approaches have been examined for the production of biodiesel in order to overcome challenges related to traditional catalyzed (trans)esterification. Saka and Kusdiana, who explored the synthesis of biodiesel from rapeseed oil using methanol under the supercritical state in 2001, discovered non-catalytic (trans)esterification [45]. If reactions are conducted at temperatures of 239 °C and pressures 8.09 MPa above the critical point of methanol, as demonstrated in the reactions they have conducted, large yields may be reached in a short amount of time even without the use of a catalyst. Molecules have high kinetic energy and density under supercritical conditions of the alkyl donor, increasing chemical reactivity. Protic solvents have lower dielectric constants because they easily break hydrogen bonds, making them miscible with oils and fats. The authors also listed additional advantages of supercritical methanol transesterification, including easier product purification and an environmentally beneficial method. The severity of the processing conditions affecting operational safety and energy needs is the key issue with this strategy. According to the literature that is currently accessible, this technique of catalyst-free alcoholysis reactions at high temperature and pressure settings allows for strong phase solubility and less mass-transfer constraints. Since the reaction rate is drastically accelerated in the supercritical state, the reaction is guaranteed to be completed in a shorter amount of time while requiring less laborious segregation and purification processes [46].

Additionally, the presence of alcohol, which performs a double function as a reactant and a catalyst, amplifies the absence of a catalyst. Moreover, compared to the standard alkali-catalyzed process, the supercritical method (SCM) has been claimed to be more tolerant of the accompanying water and free fatty acids in the feedstock [47]. Consequently, the method is considerably more successful against different kinds of vegetable oils, which has increased interest in research considering the application of this method in an unconventional way.
2. Common Methodology for the Synthesis of Heterogeneous Catalyst

2.1. Hydrothermal

With the advantage of the economical synthesis method and ease of optimization of time and temperature, hydrothermal synthesis is an excellent method for producing bulk metal catalysts with high purity. Teo et al. studied the effectiveness of a catalyst for transesterifying crude Jatropha curcas oil (JCO), which has a high fatty acid content and was evaluated in the current study. At various synthesis times, calcium methoxide (Ca(OCH$_3$)$_2$) has been produced effectively using a cost-effective hydrothermal technique [48]. CaO was utilized as a precursor because it is widely available, reasonably priced, and ecologically safe. On the surface of CaO, Ca(OCH$_3$)$_2$ can form, and its active basic surface is exceptionally developed. Three different morphologies of Ca(OCH$_3$)$_2$ catalysts were observed, including (a) spherical particles with non-uniform sizes, (b) well-organized plate-like structures with irregular surfaces, and (c) a collection of small plate-like designs with even surfaces. The relationship between the biodiesel yield and the catalysts’ synthesis time, surface area, and shape was investigated. At ideal experimental parameters of 2 h reaction time, Ca(OCH$_3$)$_2$ was able to sustain 86% of FAME content after a 5th cycle. The optimized condition was the temperature (65 °C), 1 molar ratio (methanol: oil), and a catalyst loading (2 wt.%). For the transesterification process of non-edible Jatropha curcas oil for biodiesel synthesis, Ca(OCH$_3$)$_2$ was proved to be the better solid heterogeneous catalyst.

Using acid and basic catalysts, the transesterification of triglycerides from waste oilseeds fruits with methanol has been explored in heterogeneous and homogeneous systems. Macario and his co-workers performed hydrothermal synthesis to synthesize the acid catalysts MCM-41 and ITQ-6 [49]. Ionic exchange was used to load potassium onto various materials to create acid-base catalysts (obtaining K-MCM-41, K-ITQ-6), as shown in Figure 3. After 24 h of reaction at 180 °C, K-ITQ-6 catalysts produced the maximum levels of triglycerides conversion and biodiesel output. This catalyst is deactivated by potassium leaching, yet it is possible and simple to regenerate and reuse it. Soltani and his co-workers prepared a highly recyclable mesoporous SO$_3$H-GO@TiO$_2$ catalyst that has both Lewis and Brönsted acid sites for one-pot catalyzing the esterification of cheap acidic feedstocks, such as palm fatty acid distillate (PFAD), which contains a significant amount of water (3 wt.%) and FFAs > 85 wt.% [50]. The mesoporous sulfonated GO@TiO$_2$ catalyst was synthesized utilizing a two-step hydrothermal microwave-assisted technique that included post-sulfonation treatment and homogenous TiO$_2$ nanoparticle dispersion inside the GO mesopore framework [50]. After examining the effects of several GO:Ti ratios on textural characteristics, the ratio of 1:1 was chosen as the best ratio. The outcomes showed that the catalyst had high acidity with a mix of Brönsted and Lewis acid sites, as well as favorable textural qualities. Additionally, the post-sulfonation treatment had no effect on the crystalline structure of the as-prepared mesoporous GO@TiO$_2$ material. Furthermore, ten repeated esterification processes using the synthesized mesoporous SO$_3$H-GO@TiO$_2$ catalyst demonstrated good stability without further interventions.

An alternate method for creating activated carbon in the nanometer range from biomass with a large surface area is hydrothermal carbonization (HTC). In their work, RF Abdullah et al. synthesized empty fruit bunch-based activated carbon (EFBHAC) using the HTC method [51]. K$_2$CO$_3$ and Cu(NO$_3$)$_2$ were added to the activated carbon to create a bifunctional nanocatalyst for the tandem esterification and transesterification of waste cooking oil (WCO). As a consequence of hydrolysis, dehydration, decarboxylation, aromatization, and recondensation during the HTC process, the generated EFBHAC had a BET surface area (4056.17 m$^2$ g$^{-1}$), pore volume (0.827 cm$^3$ g$^{-1}$), and pore diameter (5.42 nm). The maximum biodiesel yield of 97.1% was obtained by impregnating K$_2$CO$_3$ and Cu(NO$_3$)$_2$ over EFBHAC, which resulted in high levels of basicity (9.21 mmol g$^{-1}$) and acidity (31.41 mmol g$^{-1}$). The optimized conditions were 5 wt.% catalyst loading, 12:1 methanol-to-oil molar ratio, and 70 °C for 2 h. After the fifth cycle, more than 80% of biodiesel was generated, demonstrating its high reusability. These findings demonstrate
the outstanding potential of waste materials to make bifunctional nanocatalysts that can increase biodiesel output and have commercial viability.

Figure 3. N\textsubscript{2} adsorption isotherms of catalyst (a) before and (b) after ionic exchange. Reprinted with permission from Ref. [49]. 2022, Elsevier.

In order to produce biodiesel from the transesterification of soybean oil with methanol, Mo-KIT-6 catalyst precursors produced by direct hydrothermal synthesis utilizing various Si/Mo molar ratios (10, 20, and 30) were reported by Cardoso and his group [52]. The factorial design revealed that employing the 10 Mo-KIT-6 catalysts and an alcohol/oil ratio of 20/1 at 150 °C for 3 h are the ideal conditions for optimizing biodiesel production. However, when employing the 20 Mo-KIT-6 catalysts with a 15:1 alcohol-to-oil ratio, the biodiesel output approaches its maximal potential while also benefiting from the use of less methanol, which reduces the energy required for the separation of unreacted alcohol.

2.2. Carbonization

Based on the report by Atelege, in his work, a heterogeneous catalyst made of activated carbon derived from used coffee grounds was produced utilizing KOH as an activator by the carbonization method [53]. The synthesized catalyst was characterized and assessed in terms of biodiesel and hydrogen generation efficiency, with the maximum iodine number being achieved at 600 °C carbonization temperature. Three-weight percent catalyst loading, a 9:1 methanol-to-waste cooking oil molar ratio, a reaction temperature of 90 °C, and a reaction duration of 120 min were found to be the ideal transesterification reaction conditions. The yield of biodiesel under ideal reaction conditions was 91.57%. In order to verify the catalyst’s capacity to be reused, the selected superior catalyst was successfully utilized five times. For both the transesterification and the dehydrogenation processes, the catalyst performance was nearly identical to that of the initial cycle following regeneration. Furthermore, 19.15 and 15.48 kJ/mol were estimated as the activation energies of the transesterification and methanolysis processes, respectively.

Through a transesterification process, Fernández et al. produced biodiesel using biochar and coffee husk ashes as heterogeneous catalysts [54]. The raw coffee husks were carbonized, activated, and charred to produce the catalysts. The findings demonstrated the existence of several inorganic compounds combined with the turbostratic structure, primarily K- and Ca-containing phases (in the case of the biochar samples). The synthesized biochar sample at 700 °C demonstrates a biodiesel conversion of 66%; the activated biochar catalyst prepared at the same temperature exhibited a higher biodiesel conversion (74%), which explains its outstanding specific surface area. Coffee husk ashes had the highest catalytic effectiveness (biodiesel conversion of 93%), which is consistent with their greater Ca and K salt levels when compared to biochar samples.
For the formation of biodiesel, incomplete carbonization of shrimp shell with loading KF on the resulting material and activation at a specified temperature were used by Yang and his co-workers to create a high-performance and ecologically friendly shrimp shell catalyst [55]. The transesterification of rapeseed oil with methanol was used to study the catalytic performance. The outcomes showed that the ideal preparation conditions were ideal for carbonization at 450 °C, loading KF at 25 wt.%, and activation at 250 °C. The chemical reaction using shrimp shell as the catalyst was conducted at 65 °C with a 2.5 wt.% of catalyst loading, 9:1 of a methanol/rapeseed oil molar ratio, and 3 h reaction duration to achieve the desired conversion. The catalyst shrimp shell had a porous framework morphology, and the active sites created by the interaction of the shrimp shell that had not fully carbonized with KF during the activation phase were what gave it its catalytic activity for transesterification. It was discovered that the shrimp shell has significant catalytic activity and environmentally favorable qualities, offering the possibility of using it as a heterogeneous base catalyst in the biodiesel synthesis method.

2.3. Calcination

Jayakumar et al. performed a calcination method to develop a low-cost, pollution-less, and very efficient heterogeneous catalytic synthesis for the conversion of Jatropha curcas oil (JCO) into biodiesel using waste animal (ox) bone [56]. The calcined ox bone catalyst analysis clearly demonstrated that there was a significant amount of catalytic activity for the production of biodiesel. According to the reaction time (1–4 h) and temperature, biodiesel yields at a 500 rpm agitation speed, a 5% catalyst loading rate (w/w) of oil, and a 12:1 methanol-oil ratio (molar) were monitored (313–338 °C). It was discovered that 338 °C was the ideal temperature for achieving the highest (96.82%) biodiesel output. With a frequency factor of $7.03 \times 10^6 \, \text{h}^{-1}$, the activation needed 38.55 kJ mol$^{-1}$ of energy (Ea). The experiments on reusability showed that the calcined animal bone catalyst was very stable for up to three cycles with FAME > 90%, which was considerably reduced to 61% in the fourth cycle. The findings of this analysis revealed the potential for using JCO and calcined ox bone catalyst as inexpensive and easily accessible unwanted waste materials that may be utilized as feedstock for the market-scale production of biodiesel to meet the potential needs of the community.

The potential of using discarded rohu fish (Labeo rohita) scale as a high-performance, recyclable, and inexpensive heterogeneous catalyst for the synthesis of biodiesel from soybean oil is examined in the research performed by Chakraborty et al. [57]. X-ray diffraction and thermogravimetric analysis showed that calcining hydroxyapatite over 900 °C for two hours might convert a sizeable amount of $\beta$-tri-calcium phosphate. A fibrous layer with a porous structure was seen in SEM morphological investigations of the calcined scale, and a BET surface area of 39 m$^2$/g was determined. The ideal parametric parameters were 6.27:1 (methanol/oil molar ratio), 997.42 °C (the calcination temperature), and the catalyst concentration (1.01 wt.% of oil), leading to the best FAME production of 97.73%, which was found using response surface methodology. Reusability tests depict that the developed catalyst might be used up to six more times, opening up a possible route for the production of biodiesel.

It was reported by Nair et al. that waste frying oil can be converted into biodiesel utilizing a heterogeneous catalyst made of powdered calcined clamshell (Meretrix mereterix) [58]. Clamshells calcined for 2.5 and 3.5 h at 1173 °C showed varying catalytic activity. A catalyst with increased activity and a quicker transesterification reaction time was produced after 3.5 h of calcination. According to XRF analysis, the catalyst is mostly composed of calcium (97%) as well as some minor elements such as Na, Si, Fe, Sr, Al, Mn, and S. Figure 4 represents the XRD spectrum of the catalyst before and after the reaction. The calcined clamshell’s surface area was determined to be 2.6 m$^2$/g$^{-1}$, and 3.0 g of catalyst and 6.03:1 (methanol to oil molar ratio) at 333 °C in 3 h were determined to be the best values for key variables. On the basis of variable optimization, high yields (>89%) and conversions (>97%) were attained.
According to the experiment performed by Li and his co-researchers, the catalyst used was rice husk that had been pyrolyzed and sulfonated using strong sulfuric acid [59]. The catalyst was then applied to catalyze the transesterification and esterification of WCO to produce biodiesel. The conversion of FFAs to FAME in the presence of the catalyst achieved 98.17% after 3 h and 87.57% after 15 h. In comparison, the standard solid acid catalyst Amberlyst-15 only produced FFA conversion and FAME yields of 95.25 and 45.17%, respectively. As a result, the produced catalyst displayed a high catalytic activity for both transesterification and esterification to occur simultaneously.

The transformation of potato peel as a possible source of bio-oil and green heterogeneous catalysts has been reported by Daimary and his co-workers using pyrolysis [60]. The thermochemical conversion’s biochar waste was recycled as a clean, sustainable, and recyclable source for heterogeneous catalysts. The alkali and alkaline-rich biochar was reclaimed through calcination and converted into bio-based mixed metal oxide and carbonates. Reasonably high bio-char (29.50%) was observed to be generated at 500 °C, which was also the optimal operating temperature for pyrolysis. The high potassium concentration (36.54%) in both the oxide and carbonate forms of the produced catalyst contributed to its high catalytic activity. The optimal parameters of temperature, methanol-to-oil ratio, duration, and catalyst loading were used to achieve the highest oil conversion (97.50%) possible. Utilizing an integrated process for catalyst synthesis, food waste was converted into high-value products including biochar and bio-oil.

In another work by Bhatia and the team, WCO was subjected to transesterification using a heterogeneous catalyst made by a pyrolyzing waste cork (Quercus suber), as shown in Figure 5 [61]. The findings of the experiment reveal that the optimum FAME conversion (98%) was achieved at alcohol:oil ratios of 25:1, catalyst loadings of 1.5% \textit{w/v}, and temperatures of 65 °C for heterogeneous catalysts produced at 600 °C. WCO is used to generate biodiesel, which is mainly made up of FAME in the ascending order C18:1, C18:2, C16:0, C18:0, C20:0. The cetane number (CN) 50.56, higher heating value (HHV) 39.5, kinematic viscosity 3.9, and density 0.87 were determined as the properties of the generated biodiesel.

Hazm et al. described the anaerobic pyrolysis of waste polyethylene terephthalate food containers to produce plastic waste char (PWC), which was then transformed into an acidic solid catalyst for the biodiesel production process [62]. Such a strategy may enable the development of biofuels while also offering a potential answer to the PW environmental problem. Here, plastic waste was carbonized at 600 °C to produce a carbon precursor, which was then subjected to three sulfonation ratios of sulfuric acid (1:10, 1:15, and 1:20), resulting in a series of solid acid sulfonated carbon catalysts, PWC-SO\textsubscript{3}H (a), (b), and (c). The PWC-SO\textsubscript{3}H catalysts that were created were thermally stable up to 375 °C. A mesoporous textural morphology with non-uniform dispersion of the sulfonate group was

![Figure 4. XRD of clamshell (a) calcined at 1173 K for 3.5 h and (b) after use. Reprinted with permission from Ref. [58]. 2022, Elsevier.](image-url)
discovered via surface morphology screening. The esterification of PFAD with methanol then assessed the effectiveness of the catalysts in producing biodiesel. The best conversion of PFAD-derived biodiesel (96.9%) was produced by the PWC-SO3H (b) catalyst with an impregnation ratio (1:15) under the ideal experimental parameters of 5 wt.% catalysts at 110 °C for 2 h and an 18:1 PFAD molar ratio with methanol. According to research on recyclability, the PWC-SO3H (b) catalyst may be reused for four subsequent reactions while still having a high level of catalytic activity.

![Diagram of transesterification process](image)

**Figure 5.** Pictorial representation of transesterification of waste cooking oil by using a heterogeneous catalyst prepared by pyrolysis of waste cork (Quercus suber). Reprinted with permission from Ref. [61]. 2022, Elsevier.

### 2.5. Impregnation

The investigation performed by Mahesh et al. proposed wet impregnation to synthesize a heterogeneous catalyst (KBr/CaO) using conventional calcium oxide and potassium bromide [63]. Tests on this solid catalyst for transesterification of used cooking oil were conducted. Techniques such as FTIR, XRD, and SEM were used to analyze the produced catalyst. Regression models revealed that the ideal conditions were ideal for a 12:1 methanol:oil ratio, a 3 wt.% catalyst loading, and a 1.8 h reaction time.

The work performed by Alsharif et al. concentrated on developing a heterogeneous catalyst for the transesterification process by wet impregnating lithium onto TiO2 [64]. With varying quantities of Li (20, 30, 40 wt.%) and at varying calcination temperatures, a series of Li/TiO2 was produced (450, 600, 750). The most effective catalysts, with a transesterification yield of 98%, were determined to be the Li/TiO2 catalysts with 30% w/w Li and calcined at 600 °C. The highest catalyst performance was obtained using a methanol-to-oil ratio of 24:1, a 5 wt.% catalyst loading, and reaction temperatures of 55 °C for three hours. According to the kinetic studies, the transesterification process was acceptable with the zero-order hypothesis. However, with each subsequent usage, the reusability lowers.

Wang et al. reported the synthesis of biodiesel from soybean oil, very stable heterogeneous catalysts synthesized by the method of impregnation where the carbonates’ suspension solutions were over the electric furnace dust (EFD) [65]. The single impregnation with K2CO3 suspension solution can only enhance its catalytic performance in the
initial phase, whereas in the process of impregnating with various suspension solutions of CdCO$_3$, BaCO$_3$, CaCO$_3$, and SrCO$_3$ and being calcined at high temperature did not enhance the catalytic performance of the EFD powder. A kinetic study using Na$_2$CO$_3$@EFD was conducted, and it was noticed that the values 32.81 kJ/mol (activation energy) and 3760.85 /min (frequency factor) were both lesser than those for the solid base catalysts that have been previously reported. This suggested that the as-prepared Na$_2$CO$_3$@EFD catalyst was a potential candidate for industrial use in biomass transformation to energy.

2.6. Sol-Gel

Using the sol-gel process, Shimada and his group created four catalysts that altered the molar ratios [66]. They produced two zinc aluminates (Al:Zn = 1:0.1 and Al:Zn = 1:1) and two potassium aluminates (Al:K = 1:0.1 and Al:K = 1:1). The heterogeneous catalyst underwent one transesterification and five recycling processes while displaying an amorphous structure. Comparable to homogeneous catalysts, the reaction time was less than that of heterogeneous catalysts. Because the catalyst may be recycled, this may lower the expenses associated with producing biodiesel. With strong catalytic activity (97.58% ester concentration and 92.94% yield) and effective biodiesel production, the novel catalyst also generated wastewater and glycerin with less residue.

Salinas and his co-workers synthesized La$_2$O$_3$-ZrO$_2$-mixed oxides with different La$_2$O$_3$ contents (0, 1, 2, 3, and 5 wt.%) and calcined them at 600 °C using the sol-gel technique [67]. The synthesis of biodiesel from canola oil through a transesterification process served as the benchmark for catalytic activity. According to the characterization results, the development of La$_2$O$_3$ monolayers and the degree of m-ZrO$_2$ basicity significantly impact the generation of biodiesel. The 3% La$_2$O$_3$-ZrO$_2$ catalyst produced a higher conversion of biodiesel (56% at 4 h) in the presence of basic sites and the creation of a monolayer of La$_2$O$_3$.

Pure αFe$_2$O$_3$ and αFe$_2$O$_3$$_1$$_x$/ZnO$_x$ nanoparticles were synthesized by Maleki et al. using the sol-gel method [68]. The sonochemical technique was used to examine the ability of pure αFe$_2$O$_3$ and αFe$_2$O$_3$$_1$$_x$/ZnO$_x$ nanoparticles to produce biodiesel from canola oil. x = 0, 40, and 80 weight percent. The dispersion of ZnO is well integrated into the structure of Fe$_2$O$_3$, improving the basicity of the nanocatalyst by producing oxygen vacancy, according to the CO$_2$-TPD and Raman data. The catalytic performance of ZnO was optimally included when x = 47.24 wt.%. In addition, the optimized nanocatalyst had dimensions of 40 nm and a form of a needle or hexagon. The reaction was optimized, and the highest biodiesel output was 94.21%. However, after seven successive cycles of reusing the best catalysts, findings indicate that Fe$_2$O$_3$/ZnO nanoparticles performed better catalytically and were more stable than pure Fe$_2$O$_3$. The findings of the engine test show that canola biodiesel’s high oxygen content significantly improves fuel combustion conditions, especially in B30 (30% biodiesel/70% diesel).

2.7. Co-Solvent Preparation

In this research, Pham et al. examined the optimal conditions for biodiesel synthesis with 10 wt.% isopropanol (IPA) as a co-solvent and the transesterification kinetics at various IPA concentrations [69]. The transesterification process was assigned in a heterogeneous state, which includes both FAME and glycerol [GL] phases in the IPA quantity of 5 to 25 wt.% as the GL phase developed and isolated from the FAME phase. The correlation coefficient (r) between the rate constant and IPA amount was 0.97 (p < 0.05), indicating that the transesterification rate increased as IPA quantity increased. The following were the ideal transesterification parameters for producing biodiesel from canola oil with 10 wt.% IPA: 1.0 wt.% KOH, a 6:1 molar ratio of MeOH to oil, and a 30 °C reaction temperature. Phase separation following the reaction was able to be facilitated, and waste was decreased by transesterification using 10% IPA. Since IPA recovered at a rate of >96% during the FAME step, IPA was able to be recycled. These findings showed that IPA was a more effective co-solvent for producing biodiesel from feedstocks derived from plant oils.
A homogeneous reaction procedure employing acetone as a co-solvent for the transesterification of vegetable oils with methanol and the inclusion of a potassium hydroxide catalyst have been proposed by Okitsu and his team [70]. The impacts of the primary factors, such as the quantities of acetone and KOH, the molar ratio of methanol to oil, and the reaction temperature, on FAME production were examined. The ideal parameters were 25 wt.% acetone and 1 wt.% KOH catalyst in oil, 4.5 wt.% methanol in oil, and a reaction temperature of 25 °C. After 30 min, the transformation of vegetable oil to FAME under these circumstances approached 98%.

The research by Akkarawatkoosith et al. focuses on a quick and efficient method for concurrently raising gasoline quality and biodiesel synthesis. To achieve this, co-solvent technology was used [71]. The transesterification of ethanol and palm oil in a microtube reactor at supercritical conditions served as the basis for experiments. The isopropanol was added to the process and served as a co-solvent to improve the homogeneity of the mixture as well as a source of reactant to synthesize isopropyl esters. Considering reaction temperature, pressure, residence time, and the ethanol-to-oil molar ratio, large biodiesel yields were produced after the addition of isopropanol at milder parameters than those described in the literature. Biodiesel quality was improved, especially the cloud and pour points, which were superior to those produced using more traditional methods.

3. Biodiesel Production Using Heterogeneous Catalysts

A number of feedstocks were used to produce biodiesel. The choice of feedstock is crucial to the production of biodiesel since it affects a variety of variables, including chemical composition, yield, and biodiesel quality. The availability, pricing, amount of oil, and physical and chemical characteristics of the feedstocks can all be taken into consideration. Both edible and non-edible vegetable oils are used extensively in the production of biodiesel. Vegetable oils’ primary component, triglyceride, controls the chemical and physical properties of these feedstocks, as well as the quality of biodiesel. Figure 6 represents the flowchart for the production of biodiesel using the heterogeneous catalyst.

![Flowchart of biodiesel synthesis using heterogeneous catalyst](image)

**Figure 6.** Flowchart of biodiesel synthesis using heterogeneous catalyst. Reprinted with permission from Ref. [12]. 2022, Elsevier.
3.1. Edible Plant Oils

Because edible oils are used in the manufacturing of biodiesel and the food business, two significant industries, there is a growing need and demand for them. Numerous edible plant oils, including coconut, rapeseed, palm, canola, peanut, olive, mustard, soybean, and sunflower, have been used in the production of biodiesel. As a result of these types of feedstocks’ low FFA and water content, as well as their simple conversion method, first-generation biodiesel are produced using them. However, rising production costs and questions about food versus fuel are the primary drawbacks of edible feedstocks that have prompted many researchers to look for more dependable alternatives. Crops containing edible oil require growing agricultural areas and are weather-dependent. Additionally, moving these commodities from their growing site to the plant location may raise the overall cost of making biodiesel. Therefore, producing biodiesel from food oils is not worthwhile and indicates the need for greater study into using less expensive and more friendly feedstocks.

The study by Bambase et al. looked at the usage of OH-impregnated CaO as a heterogeneous catalyst in the conversion of refined coconut oil into crude biodiesel [72]. The effects of NaOH content (10–20% (w/v) solution), calcination temperature (550–700 °C), and calcination duration were investigated using the wet impregnation technique (2–5.5 h). Using OH-impregnated CaO as a catalyst, refined coconut oil was transesterified with methanol at 60 °C to produce biodiesel. The results indicate that when 20% (w/v) NaOH solution was employed during impregnation with calcination at 600 °C for 2 h, a 66.36% conversion to biodiesel could be accomplished in 10 min. Tetrahydrofuran was added as a co-solvent, which further boosted conversion to 81.70%. This is equivalent to the 85.98% conversion rate attained when employing NaOH as a catalyst under identical reaction conditions.

The comparative physicochemical and catalytic analyses of metal oxide MgO catalysts in a transesterification process using rapeseed are presented by Szkudlarek and his group [73]. It was thoroughly assessed how the Si/Al ratio in the catalytic material affected their catalytic characteristics in the process under study. Additionally, the impact of the zeolite’s ZSM-5 form on the catalytic reactivity of catalysts made of magnesium oxide was looked at. The impregnation approach was used to create a number of MgO/ZSM-5 catalysts in order to accomplish the major objectives of this study. The MgO catalyst based on ZSM-5 with the greatest silica-to-alumina ratio had the best activity in the investigated process, and 10% MgO/ZSM-5 (Si/Al = 280), which demonstrated the greatest value of higher fatty acid methyl esters (94.6%) and a high yield of triglyceride conversion (92.9%), was the best active catalyst combination in the transesterification process. The alkalinity, methanol-specific sorption characteristics, and large specific surface area of this system relative to the other MgO-based catalysts under investigation all contribute to its high activity.

Wild olive (Olea oleaster) plant oil was selected as a potential feedstock for effective biodiesel synthesis by Islam and his co-workers [74]. Various concentrations of 12-tungstophosphonic acid (TPA) were added to mixed oxides of aluminium and chromium to produce biodiesel from inexpensive local wild olive oil. Transesterification utilizing a Cr-Al mixed oxide catalyst coated with TPA allowed the biodiesel process to be completed in a single step. The optimal parameters of the oil/methanol molar ratio of 1:21, reaction temperature of 80 °C, catalyst dose of 4 wt.%, reaction periods of 5 h, and stirring speed of 600 rpm led to the highest 93% biodiesel production. The reusability tests, which were interesting, revealed that the synthesized catalyst maintained outstanding stability and reusability for up to five runs in the biodiesel synthesis from wild olive oil. Additionally, the synthetic biodiesel complies with all applicable international criteria.

3.2. Non-Edible Plant Oils

Because they include some harmful elements, non-edible resource oils are not fit for human consumption. Therefore, it is anticipated that the use of non-edible vegetable oils
will assist biodiesel to be more cost-competitive than the use of food-grade vegetable oils. Non-edible vegetable oils provide a number of benefits over edible ones when used as diesel fuel, including mobility, quick availability, renewability, a greater rate of combustion, lower sulfur, and aromatic content, as well as a better rate of biodegradability. However, a significant disadvantage is that the majority of non-edible oils have high levels of free fatty acids (FFAs), which raises the price of producing biodiesel. Vegetable oil contains a variety of fatty acids, depending on the plant’s species and environmental factors that affect its growth. Non-edible oilseed crops come in a variety of forms, including the Jatropha tree (Jatropha curcas), Karanja (Pongamia pinnata), mahua (Madhuca indica), castor bean seed (Ricinus communis), neem (Azadirachta indica), rubber seed tree (Hevea brasiliensis), tobacco seed (Nicotiana tabacum), and rice bran, etc. Over the past few years, a great deal of research has been done on the manufacture of biodiesel from various non-edible oilseed crops.

By hydrothermally treating Jatropha oil in an autoclave reactor with TiO$_2$/CaO base and SO$_4$/TiO$_2$ acid catalysts, biodiesel from Jatropha oil has been produced by Pratika and their team [75]. Utilizing H$_2$SO$_4$, the acid catalyst was synthesized by sulfating TiO$_2$. By loading TiO$_2$ on CaO, the basic catalyst was prepared. This study produced the greatest basicity and acidity catalysts from TiO$_2$/CaO and SO$_4$/TiO$_2$ catalysts, respectively. They were used for the esterification of Jatropha oil to lower its free fatty acid content and the transesterification of esterified Jatropha oil to produce biodiesel. The ST-2-400 catalyst among the SO$_4$/TiO$_2$ catalysts had an ideal total acidity of 6.93 mmol NH$_3$/g. With a catalyst weight of 3%, an oil-to-methanol ratio of 1:15, and a reaction period of 90 min, this catalyst was capable of lowering the FFA level of Jatropha oil from 1.22% to 0.59%. The TiO$_2$/CaO catalyst with the highest total basicity, TC-20-800, had a total basicity of 28.67 mmol HCl/g. Using 3% of TC-20-800 catalyst and 65°C for 90 min, Jatropha oil was converted into biodiesel by esterification. Approximately 79.68% of biodiesel could be produced with the TC-20-800 catalyst.

The goal of the investigation carried out by Pandiangan et al. was to learn more about the best alcohol for converting rubber seed oil into biodiesel [76]. In this investigation, three distinct kinds of short-chain alcohols, including methanol, ethanol, and 2-propanol, were used for the transesterification of rubber seed oil. Each alcohol was utilized in a 3:1 ratio with the oil, and transesterification was performed at 70°C for 6 h with a 10% MgO/SiO$_2$ catalyst present. Gas chromatography–mass spectrometry (GC-MS) examination of the transesterification products was used to verify the conversion of fatty acids in the oil into esters. The findings indicated that methanol, ethanol, and 2-propanol are the alcohols that are most reactive, with percentages of oil conversion to products of 90.1, 73.3, and 63.2%, respectively. These findings suggest that methanol is the best alcohol for transesterifying rubber seed oil.

The study by Khan and his team describes the synthesis and use of praseodymium-doped mussel shell-based CaO catalysts for the transesterification process that produces biodiesel using castor oil [77]. Wet chemistry was successfully employed to create Pr-CaO catalysts, which were then used as a stable, effective, and reasonably priced heterogeneous catalyst for the transesterification of castor oil and methanol to produce ecologically friendly and green biodiesel. In contrast to the yield of FAME produced by undoped, calcined CaO, which was roughly 80%, a FAME yield of 87.42% was obtained using a 7% Pr-CaO mixed oxide catalyst under ideal reaction conditions of 2.5 wt.% catalysts, an oil/methanol ratio of 8:1, and a temperature of 65°C.

3.3. Waste Cooking Oil

Rezania et al. looked at the possibility of using LaPO$_4$ foam as a heterogeneous catalyst to convert highly acidic WCO into biodiesel [78]. Under the study’s circumstances, a 5:1 methanol-to-oil molar ratio and a reaction temperature of 90°C resulted in a 91% FAME yield in 120 min using 2.5 wt.% LaPO$_4$. The outcomes showed that LaPO$_4$ foam might function well as a heterogeneous catalyst with outstanding catalytic efficiency (>90%), facile
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isolation, and great stability. The research was performed by Mohadesi et al. to find out if WCO could be converted to biodiesel using a clay/CaO heterogeneous catalyst [79]. Clay was used for creating the catalyst, which was then calcined using calcium oxide. Natural soil components such as clay include a lot of amorphous silica. High surface area silica with an amorphous structure was created by processing calcium oxide and heating at 800 °C. The response surface approach assessed the impact of five parameters—reaction temperature, catalyst concentration, oil-to-methanol volume ratio, toluene concentration, and reaction time—on the biodiesel’s purity (RSM). The conversion rate was 97.16% under ideal circumstances, which included a temperature of 54.97 °C, a catalyst concentration of 9.6 wt.%, an oil-to-methanol volume ratio of 1.94 vol:vol, a toluene concentration of 16.13 wt.%, and a reaction duration of 74.32 min. The catalyst preparation may be utilized as a reliable and affordable catalyst for the manufacture of biodiesel because the catalyst recovery test results revealed that it could be utilized up to five times.

The technique for converting WCO to biodiesel by transesterification was examined by Kataria and their team [80]. For the best biodiesel generation, the base-catalyzed transesterification under various reactant ratios—such as the molar ratio of alcohol to oil and the mass ratio of catalyst to oil—was examined. The ideal ratio and amount of zinc-doped calcium oxide were found to be 12:1 and 5 wt.%, respectively, for base-catalyzed transesterification of WCO. The calorific value, flash point, and density of the generated biodiesel were evaluated and contrasted with those of regular diesel.

3.4. Animal Fats

Animal fat wastes (AFWs), a non-edible feedstock, have recently gained wide acceptance as an alternative to vegetable oils in biodiesel production. They are inexpensive, preserve the environment, and improve the grade of the resulting biodiesel fuel (low NOx emissions, high cetane number, and oxidative stability). AFWs are an excellent feedstock for making biodiesel as a consequence.

Mutreja et al. reported MgO impregnated with KOH as a heterogeneous catalyst for the transesterification of mutton fat with methanol [81]. With 4 wt.% of MgO-KOH-201 (MgO impregnated with 20 wt.% of KOH), the mutton fat (fat) with methanol (1:22 M ratios) at 65 °C demonstrated > 98% conversion to biodiesel in 20 min and the 1H NMR spectrum of mutton fat and biodiesel. The quantity of KOH impregnation (5–20 wt.%), the amount of catalyst (1.5–4 wt.%, catalyst/fat), the reaction temperature (45–65 °C), the ratio of fat to methanol (1:11 to 1:22), and the impact of adding oleic acid, water, or palmitic acid (1 wt.%) were the reaction conditions that were optimized.

In order to perform the transesterification of pig fat into biodiesel, an alumina-doped calcium oxide nanocomposite was reported as a heterogeneous catalyst by Cherian’s group [82]. Waste egg shells that had been doped with alumina were used to create calcium oxide. The methanol:oil molar ratio, catalyst concentration, reaction duration, and temperature were changed to optimize the generation of biodiesel. The 8% (w/w) (catalyst loading), 9:1 (methanol-to-oil ratio), 65 °C (reaction temperature) at 90 min of reaction period was found to be optimal. They resulted in the highest biodiesel synthesis of 92.5%.

It was reported by Seffati et al. that by employing chicken fat and a CaO/CuFe2O4 nanocatalyst (shown in Figure 7) during the transesterification process, biodiesel was formed [83]. The impact of several factors, including the methanol-to-oil ratio (4:1–24:1), reaction duration (0.5–6 h), reaction temperature (50–80 °C), and catalyst concentration (0.5–7%), was carefully examined in order to find the biodiesel manufacturing process with the maximum output. The outcome showed that a 15:1 methanol-to-oil ratio, 4 h reaction duration, reaction temperature of 70 °C, and a catalyst concentration of 3%, which was 94.52%, produced the maximum biodiesel yield. The optimally generated biodiesel was then blended with different percentages of gasoline.
Due to its oleaginous character and quick growth rate, microalgal biomass is a viable feedstock for the production of biofuels. Additionally, since its production does not compete with the area used for growing crops, the conflict between food and fuel is eliminated.

With CaO and 80 wt.% CaO-Al₂O₃ as catalysts, Narula et al. investigated the methods to improve the process parameters for the transesterification of algal oil [84]. The process of low-temperature transesterification was chosen. Response surface methodology was used to obtain an 88.89% biodiesel production with a methanol/oil volumetric ratio of (3.2:10) in 125 min at a temperature of 50 °C. It was shown that the volumetric ratio of methanol to oil, catalyst concentration, and reaction duration all significantly impacted yield. Additionally, this concept including a heterogeneous catalyst may be employed in the industry to produce biodiesel from algae oil quickly and cheaply by adjusting the process variables.

In work conducted by Abdala et al., calcium-doped zinc oxide nanocatalysts were produced in a UV shaker and used to examine heterogeneous transesterification of algal oil to biodiesel [85]. The prepared catalyst was exposed to various UV and non-UV light sources, calcium concentrations of 0.01, 0.03, and 0.05 M, and calcination temperatures of 600, 700, and 800 °C. The impacts of the various catalyst preparation parameters were investigated for the transesterification of algal oil, as shown in Figure 8. The catalyst that obtained a 99.18% yield of biodiesel and had a calcium loading of 0.05 M and a calcination temperature of 700 °C was thought to be the most appropriate nanocatalyst. With a 76% yield, the catalyst was utilized three times.

The production of bio-oil from algal biomass and the synthesis and characterization of a noble CaO-based heterogeneous catalyst for the conversion of bio-oil to biodiesel was conducted by Malpani and co-workers [86]. In a Soxhlet system, the bio-oil was extracted from the algal biomass using hexane as the solvent, and then it was transesterified using noble heterogeneous catalysts based on CaO to produce biodiesel. Among all the catalysts prepared, one with a TiO₂:CaO molar ratio of 0.25 and a calcination temperature of 700 °C was shown to be the best suited.

3.6. Biodiesel Production for Biomass-Derived Heterogeneous Catalysts

In a report by Roy and Mohanty, de-oiled microalgae was used as biomass that was subjected to carbonization, followed by sulfonation, to create a new carbon-based solid acid catalyst, as illustrated in Figure 9 [87]. It was found how several catalyst synthesis
parameters, such as carbonization reaction temperature, sulfonation time, and concentration of $\text{H}_2\text{SO}_4$, affected the catalyst’s surface acidity and the conversion of free fatty acids. The FTIR examination and XPS analysis both showed that the de-oiled microalgal biomass-based solid acid catalyst was mostly made up of carboxylic, sulfonic, and phenolic groups. Under ideal transesterification parameters, FAME production of microalgal oil and WCO was 94.23% and 96.25%, respectively. Up to the fourth cycle, the catalyst had a high catalytic activity with FAME conversion > 90%. FT. Yani et al.’s research describes the use of a source of water hyacinth biomass to produce a heterogeneous catalyst to lessen the adverse effects of water hyacinth’s extensive use on the environment [88]. Hyacinth biomass that had been crushed up was calcined at 600 degrees to create the catalyst. $\text{K}_2\text{CO}_3$ was then added as a co-catalyst using the impregnation technique. The surface topography, particle size, and atom composition of a water hyacinth catalyst with $\text{K}_2\text{CO}_3$ impregnation were examined in order to better understand the consequences of the impregnation. It was investigated how well the synthesized catalyst handled the transesterification of palm oil into biodiesel. Methanol and oil had a molar ratio of 12:1, and 15% of the catalyst was loaded. The procedure used 15% of the hyacinth-based catalyst impregnated with 10% $\text{K}_2\text{CO}_3$ and produced the best yield (97.57%).

![Figure 8. Transesterification of algal oil to biodiesel. Reprinted with permission from Ref. [85]. 2020, American Chemical Society.](image)

To lower the cost of producing biodiesel, a highly effective, low-cost catalyst that can transesterify oil at ambient settings is needed. Tarigan et al. reported that a passion fruit peel could be used to create a new heterogeneous catalyst [89]. Using a factorial design, the catalytic activity of calcined waste passion fruit peel (WPFP), which mainly contains potassium in the forms of chloride and carbonate, has been assessed. This included examining the interactions between the molar ratio of oil to methanol, the weight of the catalyst, and the reaction time with respect to three different reaction conditions: 65, 45, and room temperature. Given that the leaching investigation revealed a drop of 22% in catalyst weight, specific amounts of catalyst must be added in order to reuse the catalyst. The prospect of cost is made possible by calcined WPFP’s capacity to catalyze transesterification at room temperature.

Boz et al. used $\text{Al}_2\text{O}_3$ nanoparticles coated with KF that were calcined and utilized as heterogeneous catalysts to undergo transesterification of vegetable oil with methanol to produce biodiesel [90]. The study’s variables included the ratio of KF to $\gamma\text{-Al}_2\text{O}_3$, calcination temperature, the molar ratio of methanol to oil, temperature and duration of the transesterification process, and catalyst concentration. Under the catalyst preparation and transesterification conditions of 15 wt.% KF loading, 773 °C calcination temperature, eight hours of reaction time at 338 °C, use of 3 wt.% catalysts, and a 15:1 molar ratio of methanol to oil, a methyl ester yield of 97.7 ± 2.14% was produced. The acquired high basicity of
the catalyst surface (1.68 mmol/g) and the high surface-to-volume ratio of the $\gamma$-Al$_2$O$_3$ nanoparticles were thought to be responsible for the unusually high transformation of vegetable oil to biodiesel. Table 1 shows the various other biomass-derived heterogeneous catalysts used for diesel production.

**Figure 9.** Pictorial representation of biodiesel synthesis using de-oiled microalgal biomass by carbonization, followed by sulfonation, to synthesize a new carbon-based solid acid catalyst. Reprinted with permission from Ref. [87]. 2021, Elsevier.

**Table 1.** Biomass-derived heterogeneous catalysts for biodiesel production.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Feedstock</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-glucose</td>
<td>Oleic acid and stearic acid</td>
<td>44 $\mu$mol/min</td>
<td>[91]</td>
</tr>
<tr>
<td>Starch</td>
<td>Waste cooking oil</td>
<td>95%</td>
<td>[92]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Waste cooking oil</td>
<td>88%</td>
<td>[92]</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Waste cooking oil</td>
<td>80%</td>
<td>[92]</td>
</tr>
<tr>
<td>Lime stone</td>
<td>Soybean oil</td>
<td>93%</td>
<td>[93]</td>
</tr>
<tr>
<td>Lime mud</td>
<td>Peanut oil</td>
<td>94%</td>
<td>[94]</td>
</tr>
<tr>
<td>Red mud</td>
<td>Soybean oil</td>
<td>94%</td>
<td>[95]</td>
</tr>
<tr>
<td>Dolomite rock</td>
<td>Palm kernel oil</td>
<td>99%</td>
<td>[96]</td>
</tr>
<tr>
<td>Chicken eggshell</td>
<td>Palm olein oil</td>
<td>94%</td>
<td>[97]</td>
</tr>
<tr>
<td>Snail shell</td>
<td>Palm olein oil</td>
<td>93.20%</td>
<td>[97]</td>
</tr>
<tr>
<td>Mussel shell</td>
<td>Chinese tallow oil</td>
<td>90%</td>
<td>[98]</td>
</tr>
<tr>
<td>Quail eggshell</td>
<td>Palm oil</td>
<td>98.00%</td>
<td>[99]</td>
</tr>
<tr>
<td>Pig bones</td>
<td>Palm oil</td>
<td>&gt;90.00%</td>
<td>[100]</td>
</tr>
<tr>
<td>Sheep bones</td>
<td>Canola oil</td>
<td>95.15%</td>
<td>[101]</td>
</tr>
<tr>
<td>Turkey bones</td>
<td>mustard oil</td>
<td>91.22%</td>
<td>[102]</td>
</tr>
</tbody>
</table>
4. Optimization of Reaction Parameters for Biodiesel Production Using Heterogeneous Catalysts

One normally needs a large number of results to completely cover the input area in order to optimize the reaction condition. For instance, the methanol-to-oil ratio, temperature, catalyst loading, reaction time, and stirring rate with a fixed type of catalyst and oil feedstock are factors that determine the outcome of biodiesel output. Further discussion of these parameters’ effects follows.

The goal of Mohamed et al.’s research was to create a new catalyst that is as effective as the one that was used to make biodiesel from WCO [103]. Fast pyrolysis of rice straw was used to create a heterogeneous solid acid catalyst, which was then subjected to a sulfonation procedure. Concentrated sulfuric acid was used to produce it. The reaction temperature, time, catalyst concentration, temperature, and methanol:oil molar ratio were all investigated as they affected the transesterification process. Biodiesel had a maximum bulk yield of 90.37%, FAME content was approximately 97.71 wt.% , the raw material conversion efficiency was 90.38 wt.%, and FFA% conversion was 91.1% under the ideal conditions of 10 wt.% catalysts and methanol:oil molar ratio of 20 for 6 h at 70 °C.

Mares’ group examined the catalytic activity of acai seed ash for the methyl transesterification of soybean oil to produce biodiesel [104]. To find the ideal conditions for catalyst formation, açaí seeds were calcined at various temperatures (500–900 °C) and times (2–5 h). The ideal conditions were 100 °C, an 18:1 alcohol:oil molar ratio, 12.0% (w/w) catalyst concentration, and a 1 h reaction time, which produced biodiesel with 98.5 ± 0.21% ester content. The catalyst characterization revealed that the high metal oxide content and carbonates with basic surface sites, which make them extremely effective for biodiesel production, gave them their catalytic activity. Following the regeneration procedure, the yield was calculated to be more than 80.0%. The catalyst has several benefits, including being derived from commonly accessible biomass waste, perhaps inexpensive, and being simple to synthesize, making it a green and effective catalyst for the generation of biodiesel.

As a heterogeneous catalyst, waste chicken eggshell-derived CaO particles were synthesized by Attar’s group [105]. In order to produce biodiesel from CWO, ultrasonic technology was used along with CaO as a catalyst. Response surface methodology (RSM) based on central composite design (CCD) was used to examine and optimize the effects of reaction parameters on biodiesel yield and specific energy consumption (SEC), such as catalyst loading (6–12 w/w%), methanol-to-oil ratio (6:1–12:1), ultrasonic power (150–300 W), and reaction time (20–40 min). Except for the impacts of the molar ratio on SEC, the results indicated substantial effects of the factors on biodiesel yield and SEC. Additionally, the ideal parameters for the reaction were a catalyst loading of 6.04 wt.%, an oil-to-methanol molar ratio of 8.33, an ultrasonic power of 299.66, and a reaction duration of 39.84 min, which produced a biodiesel yield of 98.62% and an SEC of 5.01 kJ g−1.

In the use of industrial catalytic processes, catalyst deactivation—the gradual loss of catalytic activity and/or selectivity—is a topic of major and continuing concern. The annual cost to the industry of replacing catalysts and shutting down processes is in the billions. The design and operation of a large-scale catalytic process face significant problems in preventing catalyst degradation. Catalyst deterioration can happen in a variety of ways. One of the dozen impurities present in the feed, for instance, could poison a catalyst. Carbon or coke formed by the cracking/condensation reactions of hydrocarbon reactants, intermediates, and/or products could also block the catalyst’s surface, pores, and voids. According to published research, there are three main reasons for the deactivation of CaO-based catalysts for transesterification: leaching of active sites, surface poisoning, and/or pore-clogging [106]. In order to prevent ambient CO₂ interaction with the catalyst right after removal from the reaction mixture, Endalew et al. coated the CaO-based catalyst with glycerol [107]. The collapse of the layered structure is the final factor in the deactivation of CaO-based catalysts. Due to its huge accessible surface area for the catalyst to react on, mesoporous catalysts have attracted a lot of attention for the manufacture
of biodiesel [17]. However, the mesopores of CaO-based catalysts can disintegrate at moderate-to-high temperatures.

5. Summary and Future Perspective

One of the key requirements for the development of biodiesel is the need for a more affordable fuel. Traditional catalysis, which uses a homogenous basic catalyst, produces a significant amount of effluent and is susceptible to purifying issues. Therefore, the final result of this method cannot be guaranteed to be pure biodiesel. In this review, we have explained various types of catalysts, with a special focus on the heterogeneous catalyst. Various synthesis procedures in heterogeneous catalysts were also described in detail. The types of heterogeneous catalysts used in biodiesel were also given more attention. The parameters affecting biodiesel production were carefully analyzed for better understanding. We have found that the catalyst’s performance is influenced by the temperature and duration of the calcination. Due to its fundamental character, the heterogeneous catalyst made from biomass materials promotes sustained development and yields excellent results in the conversion of triglycerides. More organic compounds need to be examined despite the investigation of a variety of inexpensive biomass-derived catalysts that have been provided.

Researchers concentrated on the manufacture of FAME from various renewable sources as an efficient method in this setting. The manufacturing of biodiesel has been proposed using a number of techniques. Transesterification is seen to be the best option out of all the procedures now in use. Heterogeneous catalysts have many benefits over homogeneous catalysts, including the ease with which continuous reactors may be realized, the generation of cleaner glycerol, and the lack of both the need to neutralize the alkaline catalyst and the requirement to replenish the spent catalyst. These benefits have made it possible for heterogeneous catalysts to provide another potent route for the generation of FAME. The kind of oil, the molar ratio of alcohol to oil, the temperature, and the type of reactor are the primary factors that affect the solid catalyst’s reactivity. Therefore, choosing these factors at their best is an important first step. Since only the external-surface active species of the porous solid support are engaged in the reaction, and considering that these catalysts may sometimes be recovered, heterogeneous catalysts are viewed as somewhat promising.

Processing non-edible and waste oil or fat with a high FFA concentration can be conducted using non-catalytic and heterogeneous acid-based-catalyzed biodiesel synthesis processes. Temperature optimization is essential in attaining an acceptable biodiesel yield among the investigated reaction parameters. The mass transfer restriction among the alcohol and oil phases is significantly lessened when co-solvent is used in heterogeneously catalyzed three-phase systems, which increases biodiesel yield while lowering the values of other optimized parameters such as reaction time, reaction temperature, catalyst concentration, and methanol. Algal lipids have far less comprehensive compositional data available than vegetable oils. Few of the more than 40,000 known algae species have FA compositional characteristics. The tremendous compositional heterogeneity between several algae species is evident, nevertheless. Compared to ordinary vegetable oils, certain species exhibit substantially greater degrees of unsaturation.

The current investigation results showed that the basicity and acidity of the catalyst’s characteristics are crucial for the generation of biodiesel. Numerous literature studies contend that transesterification directly correlates with the basicity of the catalyst. Similarly to this, the catalyst’s acidity determines its esterification activity. With an increase in catalyst acidity, the esterification activity rises. Aside from the fact that these biomass-derived materials are relatively scarce in nature for commercialization prospects, the high energy requisite for catalyst modification to increase its activity, the rapid decline of catalyst efficiency due to the interaction of basic sites with ambient CO₂ and water, as well as the possibility of an active site drop caused by reaction with FFA and leaching of CaO into the polar solvent, invite further research into these resources.
The study’s primary goal is to enhance already employed biodiesel production techniques as well as create new methods for producing biodiesel that may satisfy industrial demands. It is challenging to improve upon presently used processes and introduce new ones in order to enhance biodiesel production, particularly in the sector. In addition to the reusability of the catalyst, efficient reactor design, and exploitation of alternative resources, several strategies are investigated to reduce the cost implications. The use of the biomass-derived heterogeneous catalyst for biodiesel synthesis appears to be a viable option since it eliminates the laborious issues associated with homogeneous processes. Exploring trash or biomass as a source of catalysts might lower the price of commercially available solid catalysts and open up new uses for the waste. While the quantitative (yield) influence of catalysts has been extensively covered in the literature review, the relevance of the qualitative function of catalysts is unclear. Because of this, researchers currently have a limited grasp of catalyst behavior while working under dynamic reaction settings. Government assistance in the form of tax exemptions or reductions, as well as the establishment of regulations that promote the use of recycled materials from waste, is required to develop waste into catalysts. In other words, if encouraged, waste-derived catalysts might boost the economy and create jobs. More research and development of catalysts produced from biomass are required to enhance the catalytic performance for the manufacture of biodiesel and other chemical processes.

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