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Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review

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Abstract

The excessive utilization of petroleum resources leads to global warming, crude oil price fluctuations, and the fast depletion of petroleum reserves. Biodiesel has gained importance over the last few years as a clean, sustainable, and renewable energy source. This review provides knowledge of biodiesel production via transesterification/esterification using different catalysts, their prospects, and their challenges. The intensive research on homogeneous chemical catalysts points to the challenges in using high free fatty acids containing oils, such as waste cooking oils and animal fats. The problems faced are soap formation and the difficulty in product separation. On the other hand, heterogeneous catalysts are more preferable in biodiesel synthesis due to their ease of separation and reusability. However, in-depth studies show the limited activity and selectivity issues. Using biomass waste-based catalysts can reduce the biodiesel production cost as the materials are readily available and cheap. The use of an enzymatic approach has gained precedence in recent times. Additionally, immobilization of these enzymes has also improved the statistics because of their excellent functional properties like easy separation and reusability. However, free/liquid lipases are also growing faster due to better mass transfer with reactants. Biocatalysts are exceptional in good selectivity and mild operational conditions, but attractive features are veiled with the operational costs. Nanocatalysts play a vital role in heterogeneous catalysis and lipase immobilization due to their excellent selectivity, reactivity, faster reaction rates owing to their higher surface area, and easy recovery from the products and reuse for several cycles.

Keywords Biomass waste catalyst · Nanocatalyst · Lipase · Immobilization · Feedstock oil · Supercritical fluids

Introduction

Global population growth has cultivated an expanding and continuous demand for energy. The majority of the world's total energy is utilized for industrial application, power generation, and transportation. The main contributors to the energy sector are coal, oil, and natural gas. As per the statistical review of world energy (2019 and 2020), energy consumption grew by 2.9% from 2017 to 2018, almost twice the last 10-year average growth of 1.5%. However, energy consumption in 2019 reduced to less than half in 2018, which is 1.3%. The reduction was due mainly to slower economic growth, which restricted the energy demand. The slowdown was particularly evident in the USA, Russia, and India, each of which exhibited unusually strong growth in 2018. The global energy consumption by fuel source in 2019 is shown using the pie chart in Fig. 1.

The increase in fossil fuel consumption has extremely impacted the environment and has driven climate change. The world's daily production and consumption of crude oil and an average Organization of the Petroleum Exporting Countries (OPEC) annual crude oil price per barrel are shown in Fig. 2. Overall, crude oil global production increased from 82.51 in 2006 to 95.12 million barrels per day (mb/d) in 2019. Simultaneously, oil consumption too increased from 85.3 in 2006 to 100.1 mb/d in 2019. According to the US Energy Information and Administration, reduced economic activity related to the COVID-19 pandemic changed energy demand and supply patterns in 2020, limiting the production and consumption of crude oil to 93.9 and 91.0 mb/d. However, oil supply and demand

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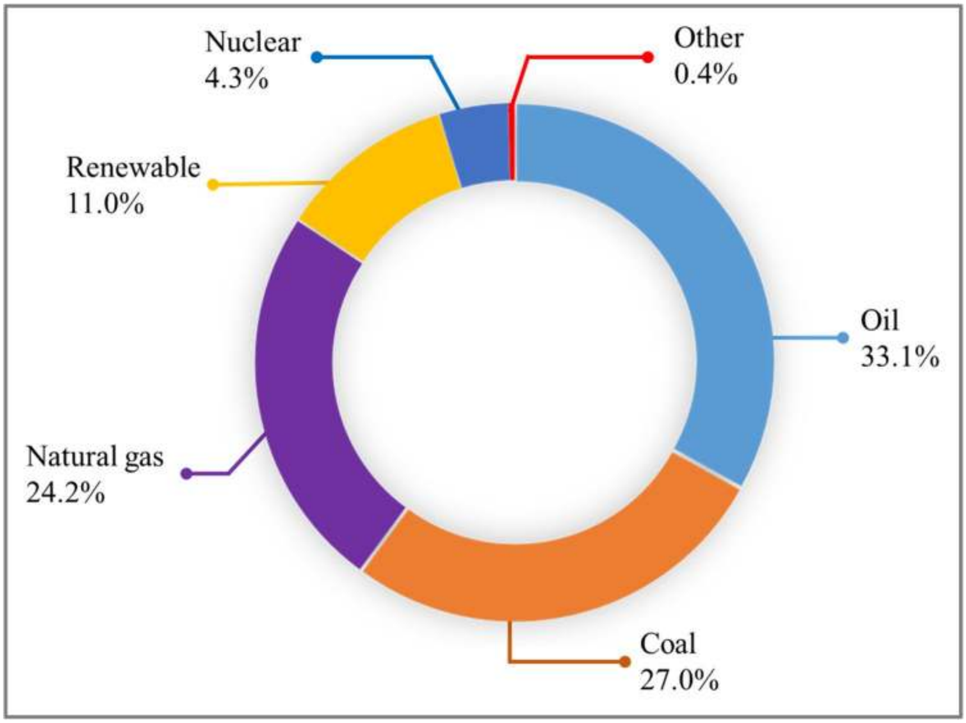

Fig. 1 Global energy consumption by fuel source in 2019

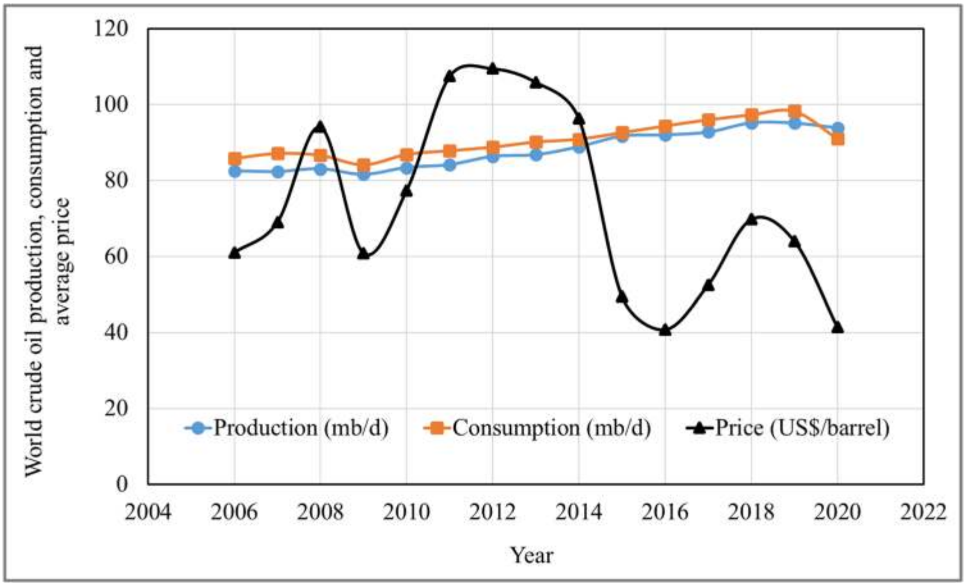

Fig. 2 Global production, consumption, and average prices (US$) of crude oil from 2006 to 2020

are presumed to increase to 99.5 and 104.1 mb/d by 2026, respectively.

If the consumption of natural resources like coal, gas, and oil continues in similar lines, they can last only for the next 200, 70, and 40 years, respectively [1]. According to the WHO, carbon emission increased by 0.5% in 2019. This change is less than half of the last 10-year average, which is 1.1% per year. As a result of exposure to ambient air pollution, about 4.2 million human deaths occur every year due to heart disease, stroke, lung cancer, and chronic diseases. Predominantly, 91% of the world's population lives in places exceeding the WHO air quality guidelines. Due to the excess usage of fossil fuels, increased environmental concerns have received global attention in the past 25 years. Thus, there is an imperative need to research and implement alternative renewable energy sources to replace fossil fuels with ecological and economic considerations [2].

Biodiesel is referred to as fatty acid monoesters derived from the transesterification of triglycerides and esterification of free fatty acids with alcohol [3, 4]. Various acyl acceptors are used in biodiesel production, such as methanol, ethanol, propanol, and butanol. The feedstock used for biodiesel production primarily includes first-generation oils (edible oils), second-generation (non-edible oils, waste cooking oils (WCO), and animal fats), third-generation algal biomass, and fourth-generation oils (metabolically engineered algal biomass with low lignin and cellulose content) [5]. In the current scenario, biodiesel is an alternative clean-burning fuel for existing diesel engines without any modifications due to its similar structure and physiochemical properties to the existing diesel fuel. It is biodegradable, less toxic, non-polluting, non-flammable, sustainable, and eco-friendly [6].

Conventional methods employed for biodiesel production are direct use and blending, thermal cracking (pyrolysis), micro-emulsion, and transesterification. Among these methods, transesterification is the most used technique due to its advantages over the other production methods, such as the employment of a variety of feedstocks, improvement in the fuel characteristics by reducing the fuel viscosity, miscibility of the biodiesel with any proportion of fossil fuel, cost-effectiveness, and high conversion efficiency. Glycerol is produced as a by-product in this method, which is also a high-value chemical [7]. Catalysts used in transesterification reactions are classified as chemical (acid or alkali) and biological catalysts. The chemical catalytic transesterification is industrially adopted due to its higher yields and ability to catalyze second-generation feedstocks. However, significant challenges associated with the chemical process include difficulty in product recovery and catalyst reusability. Heterogeneous and enzyme catalytic transesterification overcomes these problems and reduces the overall process cost [8].

The current review focuses on biodiesel production using different catalysts such as homogeneous catalysts involving single-step acid and alkali catalyst and two-step biodiesel production where the acid and base are used to produce biodiesel using esterification followed by a transesterification reaction. Heterogeneous catalytic biodiesel production with acid, base, acid–base bifunctional, nanocatalyst, and catalysts derived from biomass waste is discussed. Enzyme catalysts such as free/liquid lipase formulations, immobilized lipase on different carrier matrices (conventional and nanomaterials), and various lipase immobilization techniques in practice are reviewed. Biodiesel production using supercritical fluids with and without catalyst was discussed. And the effect of co-solvent in the reaction was also discussed.

Transesterification/Esterification

Transesterification/esterification is a chemical conversion of lipids such as vegetable oils and animal fats reacting with alcohol to form fatty acid alkyl esters (FAAE). In the esterification process, the free fatty acid (FFA) reacts with alcohol to produce FAAE and water [4]. In transesterification, triglycerides react with alcohol and produce FAAE and glycerol. Transesterification is also known as alcoholysis, in which an alcohol exchange occurs from an ester by another alcohol. This reaction is similar to the hydrolysis reaction, except alcohol is used in place of water. Transesterification consists of sequential reversible steps of converting triglycerides to products. In the first step, triglycerides react with alcohol to convert to diglycerides and then convert diglycerides to monoglycerides and glycerol, producing one alkyl ester at each stage [9].

Various factors affecting biodiesel yield in transesterification reactions include reaction time, temperature, pressure, type of catalyst and concentration, type of feedstock oil, alcohol to oil molar ratio, and mixing. Different feedstock oils have been extensively used for biodiesel production with primary or secondary alcohols consisting of 1–8 carbon atoms. Around 60–80% of the biodiesel production cost is associated with raw materials. Therefore, the overall biodiesel cost can be significantly reduced using low-cost waste cooking oils, animal fats, and non-edible oils [10, 11].

The transesterification process is a reversible reaction. Therefore, an excess of alcohol is required to drive reaction equilibrium towards the formation of the product. The types of alcohol used in this process include short-chain, long-chain, and cyclic alcohols. However, methanol and ethanol are commonly used because of their availability, polarity, superior reactivity, and low cost [1]. The varied composition of feedstock oils necessitates the investigation of the best catalysts for efficient biodiesel production. The transesterification reaction is classified into non-catalytic and catalytic processes using various generation feedstock oils and different solvents. Different catalysts, feedstock oils, and solvents used for biodiesel production via transesterification/esterification reactions are shown in Fig. 3.

Non-catalytic Supercritical Fluid Transesterification

A supercritical fluid (SCF) is a compound or a mixture above its critical pressure and temperature but below the pressure required to condense it into a solid. Under these conditions, both gas and liquid phase densities become identical, and their difference vanishes. Biodiesel can be produced by transesterifying SCFs such as methanol, ethanol, ethyl acetate, dimethyl carbonate, and methyl acetate

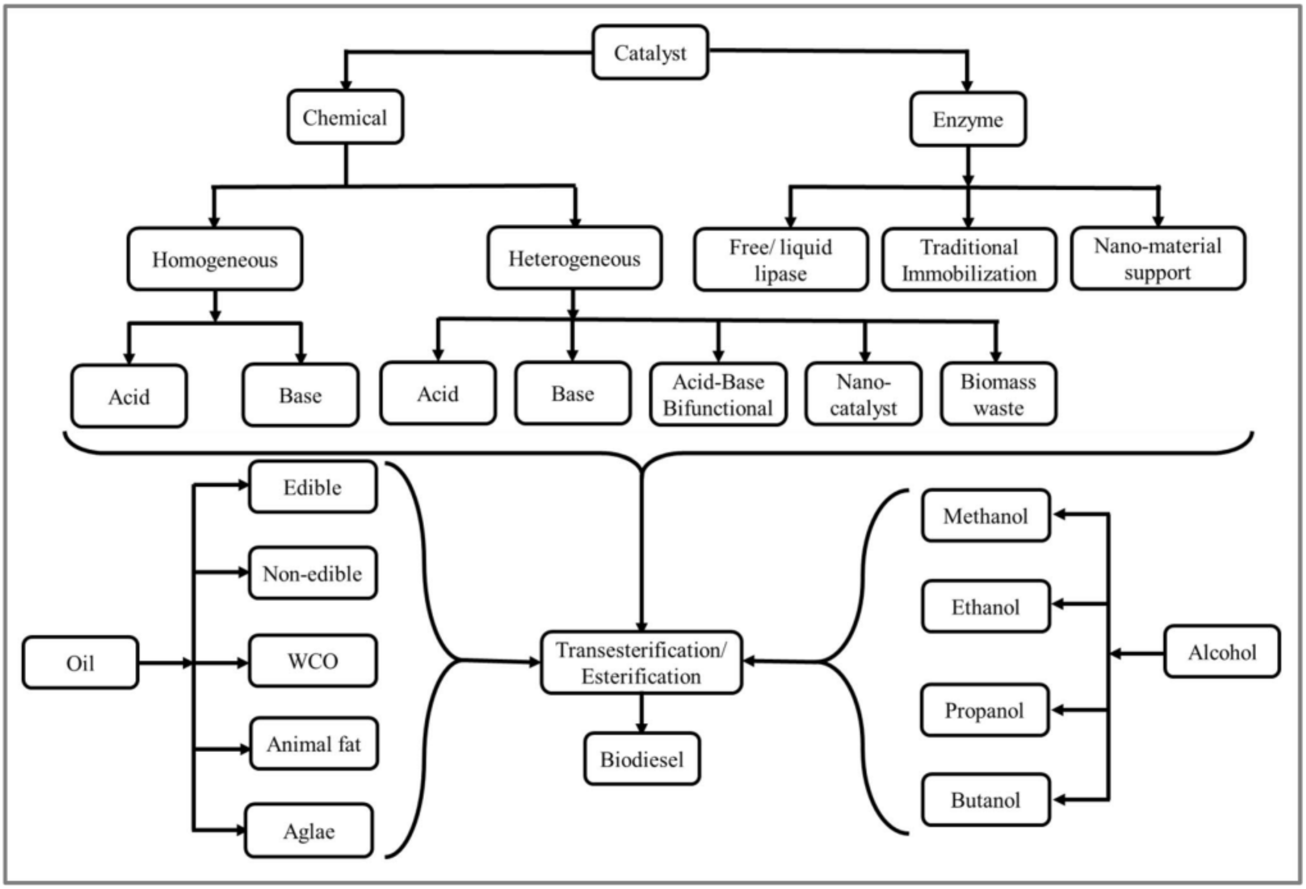

Fig. 3 Classification of catalysts, feedstock oils, and solvents used for biodiesel production via transesterification/esterification reactions

Table 1 Non-catalytic and catalytic biodiesel production using various supercritical fluids with the optimum reaction conditions for maximum biodiesel yield

SCF and oil	Alcohol to oil molar ratio	Catalyst and loading (wt%)	Temperature (°C)	Pressure (MPa)	Reaction time (min)	Biodiesel Yield (%)	Reference
Non-catalytic SCF							
Dimethyl carbonate: *Jatropha curcas* oil	40:1	-	300	9	40	97	[14]
Ethyl acetate: palm oil	50:1	-	350	200	20	78.3	[15]
Ethanol: *Schizochytrium limacinum* algae oil	10:1	-	250	20	50	> 95	[12]
Methanol: *Chlorella protothecoides* algae oil	19:1	-	320	152	31	90.8	[16]
Ethanol: *Chlorella protothecoides* algae oil	33:1	-	340	170	35	87.7	[16]
Methyl acetate: *Nannochloropsis salina* algae oil	40:1	-	310	100	60	72	[17]
Catalytic SCF							
Dimethyl carbonate: soybean oil	6:1	CH_3KO, 2	80	-	15	99	[18]
Methanol: *Spirulina* oil	18:1	Ba-Ca-Zn, 2.5	65	-	120	98.94	[19]
Ethyl acetate: palm oil	30:1	Al_2O_3, -	380	20	45	96.8	[20]
Methanol: soybean oil	45:1	Pd/Al_2O_3, 5	300	20	15	90	[21]

using vegetable oils in the absence of a catalyst [12, 13]. Various SCFs used for biodiesel production are summarized in Table 1.

The addition of the co-solvent lowers the critical points of the reaction mixture. Supercritical co-solvent carbon dioxide ($scCO_2$) is the most popular SCF because of its non-flammability, low toxicity, and low critical parameters. Although $scCO_2$ is a greenhouse gas, it is considered a green solvent as it is chemically inert under most conditions. High production of CO_2 as a by-product in industries makes it cheap [22]. Increasing the amount of CO_2 as a co-solvent to the methanol and *spirulina* oil reaction mixture from 0.0005 to 0.003 g CO_2/g methanol increased the biodiesel yield from 46 to 72% at 300 °C [23]. Tsai et al. [24] produced biodiesel in a continuous tubular reactor with and without $scCO_2$ as a co-solvent. The experiments were conducted for the reaction temperature ranging from 280 to 320 °C and the pressure ranging from 10 to 25 MPa. A 70% FAME yield was achieved at 320 °C and 10 MPa in 23 min with a 25:1 methanol to sunflower oil molar ratio without using the $scCO_2$ as a co-solvent. Then $scCO_2$ was used as a co-solvent with the same experimental conditions and found that the presence of CO_2 did not increase the reaction rate or yield of biodiesel.

The SCF reaction's pressures and temperatures vary in the range of 10–55 MPa and 200–400 °C, respectively, and sometimes more than mentioned. The dielectric constant of supercritical alcohol is less than the alcohol in its normal conditions. Therefore, it approaches the dielectric constant of non-polar feedstock oil such as oils and fats, creating a tendency to form a single-phase system with alcohol and oil. The increase in the pressure increases the alcohol's ionic product; hence, alcohol acts as a solvent and the acidic catalyst in its supercritical state [17]. These features enable FFA's presence, and water content in the feedstock oil does not affect the supercritical biodiesel production. Hence, feedstock oil pretreatment is not required [25]. In a continuous supercritical methanol process, the ester synthesis was favored by adding water externally to the reaction medium in the soybean oil transesterification. The fatty acid ethyl ester (FAEE) yield was increased from 22.7 to 68.8% when the water content increased from 0 to 10 wt% [26]. The same phenomenon was observed in the transesterification of *Chlorella protothecoides* microalgae oil with supercritical methanol and ethanol. The yields of FAME and FAEE were increased from 58.6 to 88% and 60 to 84.1%, respectively, when the water content increased from 0 to 10 wt% in the reaction mixture. The increase of yield is because of the catalytic role of the water in the reaction medium and the reduction of fatty acid degradation [16].

There are several notable advantages associated with the non-catalytic SCF process compared to conventional chemical methods. Since there is no catalyst used in the non-catalytic SCF process, no separation or recycling of the catalyst is required, making the product purification simple and more comfortable. In this process, the presence of water and FFA content in the feedstock oil does not affect the transesterification, which means low-quality substrates can also be used. In addition, this process requires less time to reach equilibrium, which helps to scale up continuous biodiesel production [27]. Dona et al. [28] investigated biodiesel production using supercritical methyl acetate in a continuous tubular packed bed reactor with soybean oil and *macauba* oil with different FFA compositions at 20 MPa. Macauba oil yielded 83% at 325 °C, whereas soybean oil yielded 44% at 350 °C at the same optimum conditions of 45 min and solvent to oil molar ratio of 5:1. *Macauba* oil offered a better yield, probably due to its higher FFA content. The process's limitations include the requirement of high-cost equipment, such as high-pressure pumps, strong durable reactors, and efficient control devices, energy consumption, and safety issues in the operation process. Hence, biodiesel production using this method is economically implausible on an industrial scale [22, 25].

Catalysis in Transesterification

Generally, feedstock oils (triglycerides) and alcohol are immiscible to form a single-phase reaction mixture. This results in reduced surface area for the transesterification; hence, the reaction rate is slow. The addition of a catalyst increases the contact area between the reactants, thus improving the reaction rate. Catalytic transesterification reactions use either chemical or biological catalysts. The chemical catalysts consist of homogeneous and heterogeneous catalysts. The homogeneous catalyst comprises an alkali or acid catalyst. The heterogeneous catalyst comprises solid acid, base, acid–base bifunctional, biomass waste-based, and nanocatalysts. Although homogeneous chemical catalysts can complete the reaction with higher conversions, it's challenging to recover the catalyst and purify the end product due to the soap formation [9]. Currently, enzyme catalysts are more attractive due to their substrate specificity, avoiding soap formation, and ease in the product's purification. Biological catalysts exist in two forms: free and immobilized lipase. Specifically, immobilized lipase on nanomaterial support is an attractive technology today [29]. The selection of any catalyst depends on the oil quality, quantity of FFA content in oil, operating conditions, catalyst activity required, cost, and availability [30].

Homogeneous Chemical Catalyst

The selection of the catalyst is a vital parameter to produce biodiesel as it can reduce production costs. The selection of the type of catalyst depends on the FFA content in the feedstock oils. The first conventional method used for biodiesel production is the utilization of homogeneous catalysts. Homogeneous catalysts are those which exist in the same phase as the reactants.

Homogeneous Alkali Catalyst

Homogeneous alkali catalysts are superior and commonly used in the industrial transesterification process for biodiesel production. Alkaline metal hydroxides such as NaOH and KOH and alkoxides such as CH_3ONa, CH_3OK, and $NaOC_2H_5$ are the most widely used industrial catalysts since the reaction is quick and the reaction conditions are moderate [31]. Homogeneous alkali catalysts provide better yield and purity when extra-pure virgin oils are used whose FFA content and acid values are less than 0.5% and 1 mg KOH/g, respectively. Otherwise, the soap formation occurs due to the high FFA, which leads to yield reduction and difficulty in product separation [32]. Dias et al. [33] studied different alkali catalysts for transesterification of virgin oils and waste cooking oils and found that the virgin oils produced 97% biodiesel yield, whereas waste oils could yield 92%. The catalyst's initial concentration, vegetable oil purity, feedstock oil to alcohol molar ratio, and temperature impact biodiesel purity and yield. An increase in catalyst concentration leads to soap formation, and subsequently, the biodiesel dilutes with glycerol, which increases the reaction time [34]. Initial catalyst loading of a 0.13 g NaOH catalyst yielded 70% biodiesel; further increasing the catalyst to 0.18 g gradually reduced the yield to 49% [35].

Heating and filtering the oil helps to remove unwanted deposits such as impurities, suspended solids, and inorganic materials in the oil. This step avoids unwanted by-product formation during the reaction. However, preheating oil above the boiling point is not recommended [36]. The addition of co-solvents to the reaction mixture improves the yield, prevents soap formation, and reduces reaction time. Jambulingam et al. [3] produced biodiesel using the waste beef tallow using methanol as a solvent and ethanol as a co-solvent system in the KOH catalyst. Ethanol effectively worked as a co-solvent, which improved the yield by 3.08% by working as a low polarity active ester exchange agent, reduced the reaction time by 61.11%, and avoided soap formation. Gu et al. [37] used a novel deep eutectic solvent and glycerol co-solvent to minimize the volatile solvent in biodiesel production and obtained a higher yield of 98%.

Significant advantages of homogeneous alkali catalysts are that they are cheap, produce a high-quality product in shorter periods, and are economically accessible [32]. Sodium-based catalysts are better than the KOH catalysts when methanol is used as a solvent because of their quick solubility in methanol and higher yields [9]. It was reported that the reaction rate of the base-catalyzed reaction is 4000 times faster compared to the acid catalyst [38]. This method has limited feedstock flexibility due to unwanted side reactions, such as soap formation if FFA and water content are > 0.5% and > 0.06 wt%, respectively. The formation of soap decreases the biodiesel yield's selectivity, inhibits the separation of the FAAE and glycerol, and forms an emulsion during the product washing. In the presence of high water content in the feedstock oil, particularly at higher temperatures, hydrolysis reaction occurs in which triglycerides convert to diglycerides and form FFAs [32]. Commercially approved base-catalyzed production involves edible, high-quality, extra-pure virgin oils that lead to food vs. fuel controversy. Another major drawback of this process is that the catalyst used can't be recovered; hence, it can't be reused. As a result, it must be neutralized and discarded as an aqueous salt waste stream. Additionally, a vast quantity of wastewater generates during the purification of biodiesel, which causes environmental problems [39].

Homogeneous Acid Catalyst

Altogether, the homogeneous alkali catalysts have some severe limitations, such as soap formation due to higher FFA content in feedstock oil and the use of high-quality extra-pure edible oils. These issues can be resolved using the homogeneous acid catalyst. Acid catalysts are not affected by the FFA content present in the feedstock oil, and they can catalyze esterification and transesterification reactions simultaneously. Hence, the cheap raw materials with high FFA content containing non-edible oils, waste cooking oils, and animal fats can be effectively used with acid catalysts [32].

Better access to the active sites of the catalyst can be achieved in the case of homogeneous catalysts. Bronsted acids, such as sulfuric acid (H_2SO_4), sulfonic acid (H_2SO_3), hydrochloric acid (HCl), and ferric sulfate ($Fe_2(SO_4)_3$) are less sensitive to the FFA. H_2SO_4 is most commonly used in this process because the reaction occurs at medium temperatures and atmospheric pressure. A 0.5% H_2SO_4 was used to convert *Chlorella pyrenoidosa* algae oil containing 90% of the water in the presence of methanol to biodiesel, and a yield of 93.2% biodiesel was achieved at 120 °C and 180 min. The presence of water content did not negatively affect biodiesel production [40]. Sagiroglu et al. [41] produced biodiesel using 1.85% HCl as a catalyst using various oils with methanol as the solvent. Safflower oil and soybean oil yielded 94.3% and 94.2% biodiesel at 100 °C after 1 h and 84.7% and 85.9% biodiesel at 25 °C after 3 h, respectively. Increasing the temperature has increased productivity by 11.3% and 9.7% of the biodiesel for safflower oil and soybean oil, respectively. As mentioned earlier, preheating helps with improving biodiesel yield. Sheet [42] preheated the waste cooking oil to 105 °C and produced biodiesel using an acid catalyst and found a 5% increase in the yield [36]. Biodiesel production from algal oil was studied using in situ transesterification with an acid catalyst. In this process, the algal lipids are simultaneously extracted and transesterified into methyl esters. Kim et al. [43] studied the in situ transesterification of algae oil with methanol as a solvent. HCl performed better under the same reaction conditions than the H_2SO_4 homogeneous catalyst, yielding 90% and 80% for HCl and H_2SO_4, respectively.

As this method can utilize cheap non-edible feedstocks, such as waste cooking oils and beef tallow, the production cost can be reduced. Karmee et al. [44] studied economic analysis using waste cooking oil and estimated a US$0.8 and US$0.9 per liter biodiesel using acid and alkali catalysts, respectively, compared to biodiesel's average price of US$1.01 per liter in Hong Kong. The problems associated with the formation of soap using alkali catalysts can be resolved using acid catalysts [45]. This process has another drawback of water generation during ester formation in the esterification process from the reaction of FFA with alcohol, inhibiting the transesterification reaction. The alcohol to oil molar ratio is the main factor that influences the reaction. So, the addition of excess alcohol speeds up the reaction and favors biodiesel production. Catalyst recovery is challenging from the biodiesel and glycerol layers after the reaction, which leads to contamination, corrosion problems, and difficulty in product separation and purification. During the product washing, a significant loss of biodiesel also occurs. Extra energy accumulation occurs while purifying the products, which consequently increases biodiesel production's overall cost [46].

Two-Step Transesterification

Since single-step alkali or acid homogeneous-catalyzed transesterification has its advantages and limitations, researchers focused on a new, two-step method development in which both acid and base catalysts are used in two steps to produce biodiesel. This method increases the reaction rate and eliminates the saponification process. Since non-edible oils have higher FFA content, the pretreatment must reduce the FFA content to 0.5–1% using an esterification reaction with an acid catalyst. In the second step, the transesterification reaction is conducted with a base catalyst to increase biodiesel yield. Recently, a microreactor of the semi-industrial pilot scale was used to produce biodiesel. Initially, 1% H_2SO_4 was used to reduce the FFA content, and then KOH was used as a catalyst in the second step. The maximum yield of 97.2% in 1 min and 98.26% in 2 min of residence time was observed at the optimum condition of 9.4:1 methanol to WCO molar ratio, 1.16 wt% catalyst concentration, and 64.2 °C [47]. Thoai et al. [48] used a novel two-step transesterification process in which a homogeneous

Table 2 Two-step biodiesel production using various homogeneous catalysts for esterification followed by transesterification reaction and their optimum conditions for maximum biodiesel yield

Acid pre-treatment step						Transesterification reaction					
Catalyst	Catalyst loading (wt%)	Oil	Methanol and oil molar ratio	Temperature (°C) and time (h)	Acid value or yield	Catalyst	Catalyst loading (wt%)	Metha-nol and oil molar ratio	Temperature (°C) and time (h)	Yield (%)	Reference
H_2SO_4	5.5	WCO	10.5:1	60, 1	1.25*	NaOH	1.1	6.5:1	60, 1.08	87.7	[49]
CH_3ONa	0.32	Palm oil	5.48:1	55, 0.66	85 #	Amberlyst 15	12	10:1	115, 9	98	[48]
H_2SO_4	1	Chicken skin waste	3:1	65, 0.5	<0.5*	NaOH and KOH	1	3:1	60, 1	97.5	[50]
H_2SO_4	40	Waste lard	23:1	50, 2	94.20 #	KOH	2	9:1	50, 1	97.2	[51]
H_2SO_4	0.5% v/v	Neem oil	45 v/v	50, 0.75	<1*	NaOH	1	0.3:1	55, 1	90±2	[52]

Note: *, FFA value; #, biodiesel yield

base catalyst was used in the first step, and a heterogeneous catalyst was used in the second step with a final biodiesel yield of 98%. Various combinations of homogeneous acid and base catalysts used for biodiesel production in a two-step process are tabulated in Table 2.

The storage of oil seeds increases their FFA content. Rubber seeds (*Hevea brasiliensis*) oil's FFA content increased from 2 to 45 wt% upon the seeds' storage at room temperature for 2 months. Biodiesel was synthesized using a three-step method where high FFA containing oil was saponified, acidified, and esterified. In the saponification process, alcohol and NaOH were added to the oil at 68–70 °C for 30 min. In the acidification (second) step, the soap solution was treated with HCl catalyst to lower FFA acid oil. In the final step, FFA was converted to FAME by the acid-catalyzed esterification process [53]. Although the biodiesel yield can be increased with this process, the esterification rate is slow, and reaction times are relatively high. Another disadvantage of the two-step process is the extra separation steps involved to extract the catalyst in both stages.

Heterogeneous Chemical Catalytic Transesterification

Heterogeneous catalysts usually appear in solid form and act at different phases in the liquid reaction mixture. Over the last decade, a wide variety of solid catalysts have been employed for biodiesel production. Heterogeneous catalysts are gaining importance for biodiesel production because of the advantages of tolerance of FFA and water content in the feedstock. Due to the different phases, catalyst recovery from the reaction mixture is easy and can be reused for several cycles. The use of heterogeneous catalysts mitigates soap formation. The solid catalyst's reusability for several cycles makes biodiesel production economical [54]. Heterogeneous solid catalysts offer the flexibility of continuous biodiesel production in fixed bed reactors, making higher production possible on an industrial scale [55].

Heterogeneous Acid Catalytic Transesterification

State of the art in research related to catalysis is the development of new, sustainable heterogeneous catalysts for biodiesel production. Heterogeneous acid catalysts can synthesize biodiesel via esterification and transesterification, simultaneously replacing the homogeneous acid catalysts. Due to the presence of Brønsted and Lewis acid active sites on the heterogeneous solid acid catalysts, industrially, it is considered a significant catalyst over the homogeneous acid catalyst [56]. Compared to homogeneous acid catalysts, heterogeneous acid catalysts overcome the major problems associated with vessel corrosion and toxic effect. These catalysts are insensitive to the high FFA and water content in the feedstock oils, allowing low-quality, cheap feedstocks without acid pretreatment for biodiesel production [57]. The development of heterogeneous catalysts helps in continuous biodiesel production utilizing cheap animal fat, WCOs, and other waste-based oils to improve the process's economic feasibility [58].

Several solid acid catalysts, such as metal oxides, mixed oxides, sulfated metal oxides, sulfonated carbon materials, cation exchange resins, heteropolyacids, and zeolites, have been widely employed in biodiesel production [59]. The ideal heterogeneous acid catalyst should have a large pore size, high concentration of strong acid site, and hydrophobic characteristics [32]. Sulfonated metal oxide materials have high acidity; therefore, they are the promising heterogeneous acid catalysts for biodiesel production via esterification reactions. Among these, sulfonated iron oxides are of great importance due to iron oxides' efficiency and availability [60].

The magnetic catalyst exhibits excellent chemical and thermal stability and easy catalyst separation without complexities. A robust, magnetic core–shell SO_4/Mg–Al-FeO_3 heterogeneous catalyst was synthesized using stepwise co-precipitation, encapsulation, and surface functionalization methods. Transesterification reaction was conducted using the synthesized catalyst and obtained a maximum yield of 98.5% at the optimum conditions of methanol to WCO ratio of 9:1, 95 °C, and 5 h [61]. Wang et al. [54] synthesized a solid superacid catalyst, $S_2O_8^{2-}/ZrO_2$, using a new method, one-pot, with ammonium persulfate via vapor-phase hydrolysis biodiesel production using expired soybean oil. The 100% biodiesel yield was achieved using 3 wt% catalyst loading with methanol to oil ratio of 20:1 at 100 °C and 4 h reaction time. The formulated catalyst has shown high stability, and no sulfur leaching was observed.

Carbonaceous particles are under intensive catalysis study due to their physical and chemical properties, such as stable particles, high surface area, and thermal stability. One of the best carbon material features is their hydrophobicity to effectively absorb long-chain FFA and avoid water absorption [62]. A heterogeneous acid catalyst, carbon spheres, was sulfonated with hydroxyethylsulfonic acid (C_4-SO_3H) by hydrothermal carbonization. WCO was used to produce biodiesel using a C-SO_3H acid catalyst, and a maximum yield of 87% was obtained at 60 °C and 1 h. The catalyst showed good stability with only a 7% decrease of its activity after 5 cycles [58].

Although heterogeneous acid catalysts provide encouraging results under moderate conditions, they react slowly compared to heterogeneous alkali catalysts. In addition to this, higher temperatures, high catalyst loading, and higher methanol to oil ratio are required for these catalysts compared to heterogeneous alkali catalysts. However, there are some instances where the reaction rates are fast (0.5–2 h), and the reaction temperature is between 70 and 80 °C, but in that case, higher alcohol to oil molar ratio (20:1) was used to obtain the conversion > 90%. Leaching of catalyst sites may result in the deactivation of catalyst and causes product contamination.

Heterogeneous Alkali Catalytic Transesterification

Solid alkali catalysts have a higher catalytic potential than solid acid catalysts. Tremendous research was conducted to overcome the challenges that arose in biodiesel production with homogeneous alkali catalysts. Heterogeneous alkali catalysts are mostly alkaline oxides, alkaline earth metal oxides, hydrotalcite, metallic salt, anion exchange resins, and zeolites, supported over a large surface area of the catalysts [38, 63]. Among these catalysts, alkaline earth metal oxides are broadly used as solid alkali catalysts because of their low cost and high basic strength. In terms of catalytic activity, single metal oxides are effective for biodiesel production. The addition of dopants can help achieve higher catalytic performance due to increased surface area and catalyst properties [64].

Generally, CaO and BaO are stronger than MgO, but BaO is toxic and easily soluble in ethanol or methanol [65]. CaO is considered an excellent heterogeneous catalyst due to its selectivity, superior activity, availability, and less solubility in methanol and requires moderate reaction conditions. It is readily available and cheap. Further, it remains highly stable for longer times during industrial biodiesel production. Das et al. [66] produced biodiesel using a cobalt-doped CaO catalyst using *Scenedesmus quadricauda* algae oil. CaO was extracted from eggshells and calcined at 400 °C, 700 °C, and 900° C. The cobalt-doped CaO was prepared using the co-precipitation method. The maximum yield of 98.3% biodiesel was obtained with 1.5 wt% catalyst loading at 60 °C. The catalyst was reused for three cycles, with a 12% loss of biodiesel yield in the third cycle. This activity loss was due to catalyst poisoning. Jamil et al. [67] worked on different alkaline earth metals such as CaO, BaO, SrO, and MgO. Upon the addition of these metals to pristine carbon, CaO showed better catalytic activity for biodiesel production. The optimum yield of biodiesel achieved was 94.27%. The catalytic activity was holding still up to the sixth run; later, a decline in activity was observed. As these catalysts are highly suitable for continuous biodiesel production, solid calcium diglyceride (CaDG) was used for biodiesel production with 1.5 wt% catalyst loading, and a 90% yield was obtained in a semi-continuous reactor with a flow rate of 45 L/h at 50 °C and 4 h. The optimum methanol to oil ratio was found to be 4:1, which is close to stoichiometry is a notable advantage [68]. Due to the low mass transfer limitation (low solubility of the methanol in oil), the reaction rate is slow. This problem can be solved using the co-solvent in the reaction mixture, which is soluble in both the reactants (alcohol and oil) and increases the liquid–liquid interfacial area. Usually, co-solvents are organic solvents or ionic liquids. After the product formation, the co-solvent residues have to be completely removed from the reaction mixture because of the possibility of hazard risk and toxicity. To eliminate the recovery of the co-solvent step from the products, crude biodiesel can be used as a co-solvent. Todarovic et al. [69] produced biodiesel with sunflower oil with CaO catalyst using crude biodiesel (10 wt% to oil weight) as a co-solvent and obtained 99.9% biodiesel yield at 1.5 h. Salinas et al. [70] studied the potassium-supported TiO_2 (K/TiHT) catalyst for biodiesel production using canola oil. The optimum biodiesel yield of > 90% was found with the catalyst loading of 6 wt% and methanol to oil ratio of 54:1 at 55 °C and 5 h. Deactivation of the catalyst or leaching of the active species was observed. A total of 81 ± 6% of the yield was obtained after four repeated cycles without any treatment.

Although CaO is a promising solid alkali catalyst, the drawback of the CaO based catalyst is that Ca^{2+} leaching into methanolic solution is a significant concern during biodiesel production. The leached phase CaO forms soap reacting with FFA [63]. CaO catalyst gets easily deactivated by getting poisoned with CO_2 and water in the air. In contrast, MgO can't be leached easily and maintains considerable activity when reacted with higher water content in feedstock oil. However, pure MgO has less surface area; the catalytic activity can be increased using the support materials. Du et al. [65] synthesized a carbon-based MgO catalyst using the sol–gel method for the transesterification of castor oil. The MgO/UREA-800 exhibited impressive catalytic activity with 96.5% biodiesel yield with 6 wt% catalyst loading, with ethanol to oil molar ratio of 12:1 at 75 °C and 1 h. The catalyst durability test has shown that it can be used for five cycles without significant activity loss. Singh et al. [46] optimized biodiesel using a novel β-strontium silicate (β-Sr_2SiO_4) with a *Spirulina platensis* microalgae oil as a substrate. The optimum yield of 97.88% was obtained with the reaction conditions of the 2.5 wt% catalyst loading and 12:1 methanol to oil ratio, at 65 °C and 104 min. This catalyst showed consistency up to six cycles and then started decreasing the activity.

The heterogeneous alkali catalyst produces high yields with faster reaction rates. The processing cost can be significantly reduced through catalyst recovery and reusability after the reaction. Heterogeneous alkali catalysts are eco-friendly, less corrosive, and potentially cheaper. They can be used in the continuous process of biodiesel production. On the other side of the coin, there are several disadvantages associated with this process such as catalyst poisoning when exposed to air, the requirement of high methanol to oil molar ratio, sensitivity to FFA content due to its basic property, soap formation if FFA > 2 wt%, and leaching of the active site may contaminate the product [71].

Heterogeneous Acid–Base Bifunctional Catalytic Transesterification

Bifunctional heterogeneous catalysts are considered a promising source of catalysts. In the last few decades, bifunctional metallic oxide catalysts attracted the researchers' attention due to their high catalytic activity and stability. Bifunctional catalysts possess both acidic and basic active sites, supporting the chemical transformation that requires acid and basic catalysts [67]. They allow esterification of FFA and transesterification of triglycerides simultaneously with high conversion and selectivity. These catalysts are particularly suitable for low-cost feedstock oils such as waste cooking oil, non-edible oils, and tallow wastes [72]. In this catalytic process, primarily acid-catalyzed treatments reduce the FFA content $<0.1\%$ via esterification reaction and then transesterification with a base catalyst to produce high-grade biodiesel. Moreover, the heterogeneous bifunctional catalysts can be modified based on desired physicochemical properties. Hence, water or high FFA content does not adversely affect the transesterification process [73].

Jamil et al. [74] worked on calcium and copper-based metal–organic framework catalysts. Cu-MOF was used as an acid catalyst for esterification and Ca-MOF as an alkali catalyst for the transesterification reaction. Cu-MOF and Ca-MOF were synthesized using solvothermal and hydrothermal methods. When Cu-MOF and Ca-MOF were used alone as catalysts, 78.3% and 78% yields were obtained. However, a combination of the catalysts yielded 85% of the biodiesel yield. The catalyst was regenerated and reused three times in the reaction without much loss in the activity. Al-Saadi et al. [75] produced biodiesel using a novel acid–base bifunctional catalyst (SrO-ZnO/Al_2O_3) with corn oil and ethanol by esterification and transesterification reaction. The esterification reaction yielded 71.4% biodiesel at optimum reaction conditions of ethanol to corn oil molar ratio of 5:1, 70 °C, and 6 h. The transesterification reaction yielded 95.1% with corn oil to ethanol ratio of 1:10 at 70 °C and 3 h. A 10 wt% catalyst loading was used in both cases. Naturally available clay materials such as kaolin, zeolite, and bentonite can be synergized as a catalyst due to their heterogeneous composition, porosity, and low cost. Bentonite is an abundantly available clay with high porosity and absorption ability. A novel graphene oxide/bentonite bifunctional heterogeneous catalyst was used for one-pot simultaneous esterification and transesterification reactions. The acidic and alkali nature of GO-NaOH-bentonite improved the accessibility to the reactants with an increased pore size of the composite catalyst. Also, the presence of Na_2O enhanced the strength of active sites of the catalyst. The maximum biodiesel yield of 98.5% was obtained with a 6 wt% catalyst loading and methanol to rapeseed oil molar ratio of 6:1, at 60 °C and 4.5 h [76].

Heterogeneous Nanocatalytic Transesterification

Nanotechnology can be defined as engineering at the nanoscale of 1–100 nm. Specific characteristics of nanocatalysts provide the possibility to solve various problems associated with esterification and transesterification reactions. The key principle of nanotechnology is to validate scientific and engineering solutions in eco-friendly energy sources. The researchers worked on heterogeneous nanocatalysts to tackle the problems arising from the raw material cost and process time for biodiesel production. The nanocatalyst's nanodimensional pores on the surface provide high surface area and active sites for interaction with the substrates; hence, the production's efficiency can be enhanced. Thus, the focus is on finding nanomaterials that can produce higher yields, easier separation, reusability, and higher reaction rates. Nanomaterials' unique characteristics include a high degree of crystallinity, stability, durability, adsorption capacity, and efficient storage, which could enhance biodiesel production industrially [77, 78]. Nanocatalysts can be synthesized using various methods such as co-precipitation, self-propagating combustion, incipient wet impregnation, sol–gel, microwave combustion, hydrothermal, gas condensation, and chemical vapor deposition [79].

Singh et al. [80] synthesized biodiesel using a novel CoO-NiO-promoted sulfated ZrO_2 super acid oleophilic catalyst. The catalyst showed the supreme catalytic performance only with 0.2 wt% catalyst loading and produced a yield of 98.8% in 2 h at 65 °C with the methanol to WCO molar ratio of 3:1. This catalyst was reused for five cycles and has shown promising results, and the catalyst's reactivation could produce 96.8% biodiesel yield. Farrokhen et al. [81] synthesized magnetic nanocatalysts CaO/KOH-Fe_3O_4 and KF/KOH-Fe_3O_4 for biodiesel production using microalgae oil by electrolysis and reflux methods. The optimum biodiesel yield of 98.1% was achieved in electrolysis with KF/KOH-Fe_3O_4 magnetic nanocatalyst 1.5 wt%, methanol to oil ratio of 6:1 at 25 °C, and 6 h. In comparison, the reflux method produced an 80% yield with the same conditions except for the temperature of 60 °C. These catalysts' magnetic properties have high interaction with the reaction mixture and high catalytic surface area. Thus, this results in higher efficiency and reduced reaction time to achieve the maximum yield. Vahid and Haghighi [82] studied $MgO/MgAl_2O_4$ nanocatalyst for biodiesel production and obtained a yield of 95.7% with 3 wt% catalyst loading using methanol to sunflower oil molar ratio of 12:1, at 110 °C and 3 h. The catalyst has shown 83% of its initial activity after using for six cycles. Feyzi et al. [83] synthesized Cs/Al/Fe_3O_4 nanocatalyst and produced a biodiesel yield of 94.8% with a catalyst loading of Cs/S of 1.5:1 and Cs/Fe of 4:1 and methanol to oil ratio of 12:1, at 58 °C and 2 h. The catalyst was quickly recovered using an external magnet in less than 20 s, and it was reused for four cycles, with 88% of the initial activity.

The intrinsic properties, such as high surface area, hollow geometry, well-defined structure, and easily functionalize carbon nanotubes (CNTs), are attractive in recent years for biodiesel production. Ibrahim et al. [84] used N_2O-supported carbon nanotube (N_2O/CNTs) catalyst as a heterogeneous catalyst for the transesterification of WCO. The yield of 97% biodiesel was obtained with optimum reaction conditions of 3 wt% catalyst loading and 20:1 methanol to oil ratio at 65 °C and 3 h. The catalyst was reused three times, although some catalyst leaching or poisoning was observed. The nanocatalysts can achieve high biodiesel yield with mild reaction conditions and short reaction times. The catalysts' reusability is also good, and the activity can be retained for five or more cycles depending on the catalyst.

Biomass Waste-Based Catalytic Transesterification

Biomass refers to plant- and animal-sourced organic material. Various solid waste sources such as eggshells, snail shells, animal bones, and agricultural wastes have been extensively studied for biodiesel production to reduce the catalysts' synthesis cost. These catalysts can reduce overall biodiesel production costs [85]. The usage of carbon-based solid catalysts for biodiesel production has become popular in recent times due to various reasons, such as the carbon-based materials that are readily available and cheap. They can be prepared from simple protocol and show relatively higher stability [86]. So, the use of waste biomass is suggested as a highly stable heterogeneous catalyst. The development of the various methods to utilize waste biomass is being studied extensively. Niju et al. [87] synthesized the waste-based *Malleus malleus* shell heterogeneous base catalyst using the calcination–hydration–dehydration method for the transesterification of WCO. The maximum biodiesel yield of 93.81% was achieved with reaction operation conditions of 7.5 wt% catalyst concentration and methanol to oil ratio of 11.85:1 at 60 °C and 86.25 min. Due to the availability of surface functional groups, relatively high surface-to-volume ratio, and low cost, biochar has an incredible potential to be used as a support or carbonaceous catalyst in biodiesel production. Quah et al. [88] synthesized a novel sulfonated magnetic biochar catalyst from the waste palm kernel shell (PMB-SO_3H) using impregnation with Fe_3O_4 followed by the sulfonation process. The maximum biodiesel yield was obtained using response surface methodology. The maximum yield of 90.2% of biodiesel was achieved at the optimum operating conditions of methanol to used cooking oil molar ratio of 13:1, catalyst loading of 3.66 wt%, 65 °C, and 102 min. The catalyst deactivation was observed after 4 consecutive cycles. Currently, activated carbon loaded with different potassium salts grabbed great attention. Zhao et al. [85] prepared biomass waste pomelo peel and biochar-based catalyst using wet impregnation method and loaded with K_2CO_3 salt. The maximum biodiesel yield of above 98% was obtained at 65 °C and 2.5 h with optimum methanol to oil ratio of 8:1 and 6 wt% catalyst loading. Eighty two percent of biodiesel was obtained after reusing the catalyst eight times. The preparation methods of various heterogeneous acid, alkali, acid–base bifunctional, nano, and biomass wasted-based catalysts, and optimum biodiesel production conditions are summarized in Table 3.

Catalytic Supercritical Fluids

Several researchers have worked on biodiesel production using non-catalytic SCFs, as discussed. However, SCFs have some drawbacks, such as high-cost equipment, high pressure, and temperature. Researchers focused on reducing the severity of reaction conditions. The addition of a small quantity of catalysts and the use of co-solvent can reduce some reaction operating conditions, temperature, and pressures, compared to the non-catalytic supercritical biodiesel production conditions [101].

Aghilinategh et al. [102] produced the biodiesel using TiO_2 and $SrTiO_3$ nanocatalysts with *Chlorella vulgaris* algae oil and supercritical methanol. Water, diethyl ether, chloroform, and n-hexane were used as co-solvents for modifying the supercritical medium to increase the product yield. $SrTiO_3$ had shown the maximum activity when n-hexane was used as a co-solvent. The maximum yield of 16.65 mg/$g_{biomass}$ biodiesel was obtained at 270 °C, 9–10 MPa, and 1 h. The highest activity of n-hexane can be due to the very low dielectric constant of the n-hexane compared to other solvents used. The lower dielectric constant helps better dissolution of the biomass content and subsequent improvement of the mass transfer during the reaction. A continuous packed bed reactor was used to produce biodiesel using γ-Al_2O_3. The used catalyst has shown better activity for the supercritical esterification of oleic acid and methanol. A maximum yield of 26.91% was achieved in 1 min under optimum methanol to oil molar ratio of 20:1, at 275 °C, and 20 MPa. The catalyst hasn't shown any changes to the surface morphology and crystal structure. However, the catalyst deactivation occurred later due to carbon deposition on the catalyst's active surface area [103].

Kasteren and Nisworo [104] estimated the cost of industrial-scale biodiesel production from waste cooking oil using supercritical methanol. The study was conducted for three plant capacities, 125,000, 80,000, and 8000 tonnes of

Table 3 Biodiesel production using heterogeneous acid, alkali, acid–base bifunctional, nano, and biomass waste-based catalysts with preparation methods and optimum conditions for maximum biodiesel yield

Catalyst	Catalyst loading (wt%)	Preparation method and temperature (°C)	Alcohol and oil	Molar ratio	Temperature (°C)	Time (h)	Reusable cycles	Yield (%)	Reference
Heterogeneous acid catalyst									
rGO-SO_3H	3	Modified Hammer's, -	Methanol: soybean oil	20:1	80	2	5	99	[89]
RS-SO_3H	10	Sulfonation, T = 80	Methanol: WCO	20:1	70	6	8	90.38	[90]
S-TiO_2/SBA-15	1	Wet impregnation, -	Methanol: WCO	15:1	200	0.5	3	94.96	[4]
$MgF_x(OH)_{2-x}$	5	Sol–gel, T = 70	Methanol: WCO	30:1	150	5	3	75.29	[91]
H_2SO_4 Anidrol	5	Impregnation, T = 500	Methanol: oleic acid	15:1	120	4	2	100	[60]
Heterogeneous base catalyst									
CaO (CAM750)	4	Impregnation, T = 750	Methanol: palm oil	9:1	65	2	4	95.07	[63]
SrO-Carbon	4	Wet impregnation, T = 450	Methanol: coconut oil	15:1	65	1.5	6	94.27	[67]
β-Sr_2SiO_4	2.5	Microwave-assisted sintering, T = 800	Methanol: *Spirulina platensis* algae oil	12:1	65	1.7	6	97.88	[46]
MgO/ZSM-5	3	Impregnation and ultrasonic depression	Methanol: *Spirulina platensis* algae oil	15:1	75	1	5	92.1	[92]
Heterogeneous acid–base bifunctional catalyst									
GO-NaOH-bentonite	6	Impregnation, T = 110	Methanol: soybean oil	6:1	62	4.5	5	98.5	[76]
SrO-ZnO/Al_2O_3	15	Wet impregnation, T = 900	Ethanol: corn oil	10:1	75	5	2	95.7	[72]
Cu/Zn/γ-Al_2O_3	10	Wet impregnation, T = 820	Methanol: low-grade cooking oil	20:1	65	2	7	88.82	[64]
CaO/Al_2O_3	4	Co-precipitation, T = 750	Methanol: waste soybean oil	9:1	65	4	2	98	[93]
Heterogeneous nanocatalyst									
CaO/MgO	4.571	Calcination, T = 850–900	Methanol: waste edible oil	16.7:1	69.37	7.08	6	98.37	[94]
Ferric manganese doped sulfated zirconia	8	Incipient wetness impregnation	Methanol: tannery waste sheep fat	15:1	65	5	8	98.7	[78]
$CuFe_2O_4$	3	Co-precipitation and hydrothermal	Methanol: waste frying oil	18:1	60	0.5	5	90.24	[95]
HSO_3-/SnO_2	3	Self-propagating combustion, T = 600	Methanol: palm fatty acid distillate	9:1	100	3	5	93.8	[96]
CuO-nanoparticle	2.07	Drying, T = 110	Methanol: pig tallow	29.87:1	60	0.6	-	97.82	[97]

Table 3 (continued)

Catalyst	Catalyst loading (wt%)	Preparation method and temperature (°C)	Alcohol and oil	Molar ratio	Temperature (°C)	Time (h)	Reusable cycles	Yield (%)	Reference
Heterogeneous biomass waste-based catalyst									
Pequi fruit rinds	2.5	Wet impregnation, T = 800	Methanol: Pequi oil	18:1	60	1.66	10	99.4 ± 0.33	[98]
Mesua ferrea Linn seed	10	Carbonization, T = 500	Methanol: *Mesua ferrea* oil	6:1	55	2	-	99.57	[99]
Monk fruit seed based	4	Impregnation,T = 300–600	Methanol: palmitic acid	10:1	120	6	4	98.5	[100]
Coconut coir husk	10	Impregnation, T = 120	Methanol: waste palm oil	12:1	130	3	4	89.8	[86]

biodiesel per year. The methyl ester with the purity of 99.8% and glycerol 96.4% was attained. The biodiesel can be sold at US$0.17, US$0.24, and US$0.52 per liter if the plant can produce 125,000, 80,000, and 8000 tonnes of biodiesel per year, respectively. The supercritical fluid method is viable and can compete with the existing acid and alkali catalyzed processes. However, these methods have some drawbacks, such as harsh reaction conditions, pressure, and temperature. Also, severe reaction conditions have a negative impact on the yield and quality of biodiesel [105].

Enzyme Catalyst

In the last few years, biocatalysts have become the central focus in the discussion of biodiesel production. The use of enzymatic biocatalysts for biodiesel production is an emerging technique compared to conventional chemical methods. The enzymatic catalyst eliminates the problems that arise during biodiesel production via alkali or acid catalytic processes. The enzymatic biodiesel synthesis allows (i) use of cheap and low-quality with high FFA content containing raw materials, (ii) avoids soap formation, (iii) produces high yield and purity of the biodiesel and glycerol by-products, (iv) facilitates simple production processes, (v) tolerates water content of the oil and increases yield, (vi) has low energy consumption as the reaction occurs at lower temperatures, (vii) easy immobilized enzyme recycling and (viii) allows easy separation and purification of the products. By minimizing the wastes generated during biodiesel production, the enzymatic transesterification meets the necessities of green chemistry, reducing the environmental complications [106].

Lipases (triacylglycerol acylhydrolases, EC 3.1.1.3) are ubiquitous enzymes found in animals, plants, fungi, and bacteria. They catalyze the hydrolysis of triglycerides to FFA and glycerol at the water–lipid interface. Lipases can also catalyze esterification, interesterification, alcoholysis, acidolysis, and aminolysis reactions [107]. Lipases are classified into extracellular and intracellular based on the nature of the release. Intracellular enzymes are produced inside the cell or in the cell wall, whereas extracellular enzymes are produced outside the cell (in the fermentation media). Among other sources, microbial lipases are widely used because most microbial lipases are extracellular. Extracellular enzymes are easy to extract from the fermentation medium. These enzymes exhibit good enantioselectivity, regioselectivity, and chemoselectivity, and they have a wide range of substrate specificity [108].

Lipases belong to the α/β hydrolase family. The active site of lipase consists of three amino acid residues, serine or cysteine as a nucleophile, histidine as a base, and aspartic acid as an acid. Lipase exists in an open or closed form and has a property called interfacial activation. A polypeptide chain called a lid covers the enzyme's active site, which is in closed form. The lid moves away to give the substrate access when lipase is exposed to the hydrophobic environment [2]. Lipases can act at the interface of organic and aqueous media. Increasing the water content increases the interfacial area; the optimum water content for lipase activity is 2–5%. However, some recent studies produced higher biodiesel yields with higher water content [109, 110]. Lipases are potential catalysts for industrial biodiesel production due to their non-toxicity, tolerance to organic solvents, insensitivity to feedstock FFA, and reusability [39].

Traditional Immobilized Lipases

In most industrial applications, lipases are used in free liquid formulations or as immobilized forms. Immobilization refers to the enzymes that are physically confined or localized in a certain region of space retaining their catalytic activity. Immobilization enhances the stability of the enzyme under both storage and operational conditions. Immobilized lipase is not affected by an abrupt change in temperature or pH. It makes the separation process easy, avoids product contamination, and yields high-quality and pure products [6]. Immobilization of lipases on solid support allows the catalyst to be reused several times. It also provides an opportunity to modify lipase to withstand the reaction conditions and inhibit temperature, pressure, pH, and organic solvent effects. The immobilization of enzymes improves enzyme stability and protects the enzyme from denaturation [111].

By looking at the latest literature on biodiesel production, it is evident that the research is focused on the immobilization of the lipase, owing to enhanced catalyst activity and reusability. An immobilized enzyme system's essential factors are the enzyme, support matrix, and attachment mode on the support. The selection of the immobilization technique dramatically influences the physical and chemical properties of the enzyme. Reduction in the enzyme activity and diffusion limitations due to the mass transfer limitations depend on the immobilization method and the support material used [112]. The common immobilization techniques involved are carrier binding, cross-linking, encapsulation, and entrapment, as represented in Fig. 4. The enzyme is attached to the carrier matrix support called carrier bonding, such as physical adsorption, ionic bonding, affinity bonding, covalent bonding, chelation or metal bonding, and disulfide bonding. The interaction between the support matrix and the enzyme is further classified into reversible and irreversible techniques. In a reversible (physical) immobilization technique, the enzyme can be detached from the carrier matrix with mild conditions, such as physical adsorption, encapsulation, and entrapment. In an irreversible technique, the enzyme cannot be detached from the support matrix without destroying the enzyme's biological activity or the support, such as covalent bonding and cross-linking. These methods are currently mostly used [8, 113]. The carrier matrix choice depends upon the mechanical strength, thermal stability, microbial resistance, chemical durability, hydrophilic/hydrophobic nature, loading capacity, regeneration, availability, and cost. Some immobilized lipases are currently commercially available, such as Novozyme 435, Lipozyme RM IM, Lipozyme TL IM, and Lipae P-SC. The significant parameters affecting biodiesel production via enzymatic transesterification are choice of lipase and its immobilization method, choice of substrate and its concentration, pH, water content, and temperature [79].

Physical Adsorption

The immobilization of lipase by adsorption is a physisorption process. It is a common and the oldest method for preparing immobilized enzymes in which the adsorbate (lipase) and adsorbent (support matrix) involve low

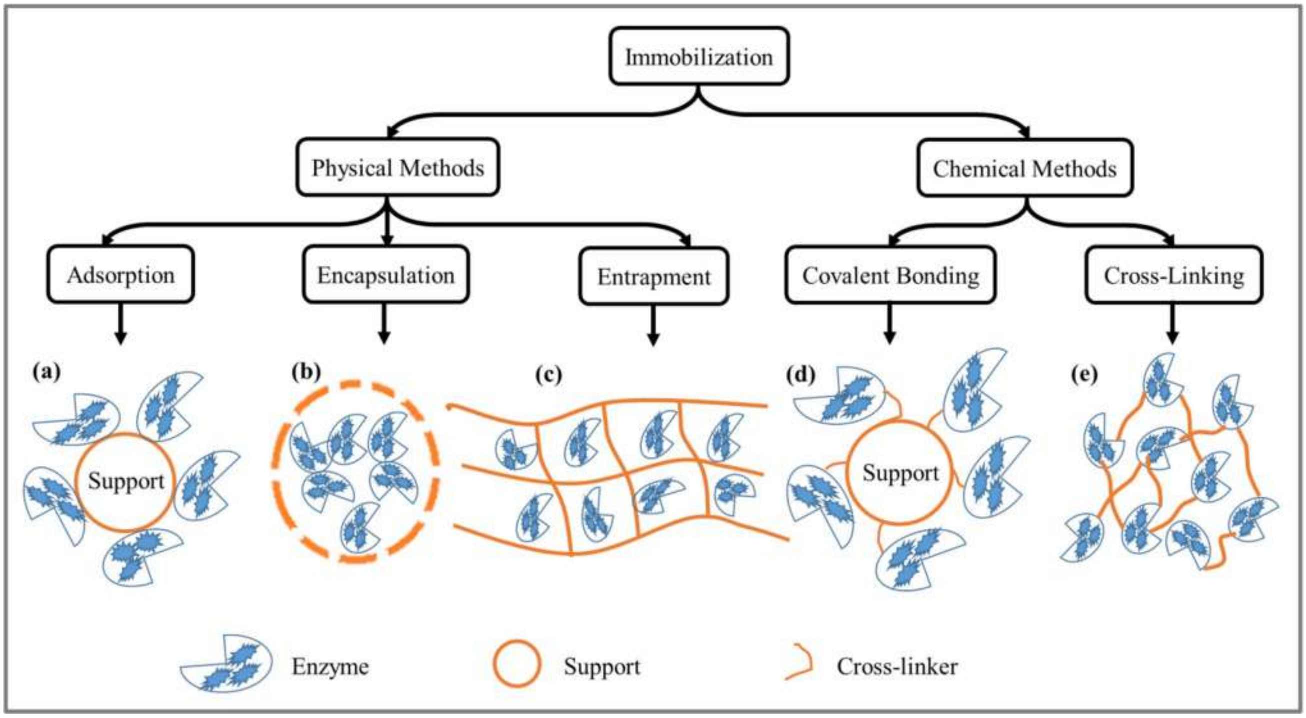

Fig. 4 Schematic representation of common enzymatic immobilization techniques used in biodiesel production. **a** Physical adsorption. **b** Encapsulation. **c** Entrapment. **d** Covalent bonding. **e** Cross-linking

energy bonds via acid–base bonding, hydrogen bonding, ionic bonding, and van der Waals forces within the exterior of the supporting material. The reversibility of this method makes it the most widely used immobilization technique. The support matrix's porosity and surface area are important for adsorption [114]. The pore diameters tending towards the molecular scale , microporous (<2 nm) materials are not large enough to successfully accommodate protein molecules whose size ranges from 2 to 10 nm on the carrier matrix. Macroporous materials (>50 nm diameter) have been extensively employed for immobilization. In recent years, emphasis is growing on mesoporous (2–50 nm diameter) supports. The mesoporous materials can achieve a surface area of greater than 800 m^2/g, and about 290 mg protein per gram support material can be loaded [115]. The commonly used adsorption carriers include anionic and cationic resins, acrylic resins, silica gels, ceramics, alumina, controlled pore glass, polyurethane foams, activated carbon, and biochar [113].

Yagiz et al. [116] investigated biodiesel production using the immobilized lipase (Lypozyme TL IM) by physical adsorption on hydrotalcite and four different zeolites (13-x, 5A, FM-8, and AW-30) from the waste cooking oil. The amount of protein adsorbed was higher in the hydrotalcite 13 mg/g matrix than the zeolites 9 mg/g. After the seventh cycle, the enzyme retained 36% of its initial activity at 45 °C and 15% at 55 °C. Almeida et al. [114] immobilized a *Burkholderia cepacia* lipase on guava seed biochar, a new, effective alternative support material. The maximum yield of 48% biodiesel was achieved at the optimum conditions of 40 °C, 7:1 ethanol to coconut oil molar ratio, and 96 h using the immobilized catalyst.

Physical adsorption has several advantages compared to the other immobilization methods, such as (i) no chemical additive requirement, (ii) relatively low cost of support material and immobilization process, (iii) easy regeneration of carrier material, and (iv) easy operation at mild conditions [8]. The drawbacks are that the enzyme's leaching occurs due to the weak bonding between the carrier matrix and the enzyme. The water–oil interface increases the enzyme's deactivation, which in turn reduces the stability of the enzyme. This method also has the limitation of sensitivity towards the temperature and alcohol concentration [117]. The thermal stability or sensitivity towards the alcohol concentration of the immobilized enzyme depends on the source of the enzyme and the support matrix. The study conducted by Miao et al. [118] on *Candida antarctica* lipase immobilized on aminopropyltriethoxysilane-Fe_3O_4 showed the maximum activity at 45 °C and methanol to rapeseed oil molar ratio of 6:1, and *Pseudomonas fluorescens* lipase immobilized on $Co_2{}^+$-chelated magnetic nanoparticles showed the maximum activity at 50 °C and methanol to WCO molar ratio of 4:1 [119].

Entrapment/Encapsulation

Entrapment is another physical immobilization method in which the enzyme is locked within the polymeric network, such as organic polymers allowing the substrates and products through the membrane, but still, the enzyme is retained. Encapsulation refers to the enzyme capture within the gel polymer, such as beads and capsules, whereby the molecules can pass through the permeable membrane [117]. Encapsulation protects the lipase from direct contact with the reaction medium. Hence, the enzyme deactivation due to the methanol concentration is reduced. Entrapment allows the enzyme's free movement within the hollow microscopic polymer networks inside relatively larger polymers, unlike the carrier binding lipases. This method allows the enzyme to run for longer reaction times with high stability and does not require an extra step of catalyst extraction from the products [120, 121]. This method of immobilization is relatively simple and fast and used in small-scale applications. Immobilization of lipase in hydrogels such as alginate, pectin, and gelatin is advantageous because of their swelling behavior, maintaining three-dimensional structures of enzymes and holding a large amount of water [122]. Other materials used for entrapment are polyacrylamide, polyurethane, collagen, silicone rubber, and polyvinyl alcohol [123].

Candida rugosa lipase was immobilized on polyvinyl alcohol (PVA) alginate sulfate beads via entrapment. The immobilized beads were used in the transesterification of palm oil mill effluent with an initial palmitic acid concentration of 43.5% w/w and oleic acid with an initial concentration of 40% w/w. Maximum biodiesel yields of 65% and 44% were obtained for palm oil and oleic acid, respectively, with the optimum methanol to oil ratio of 6:1 at 5 h and 300 rpm [124]. Whole-cell immobilization improves cost-efficiency as it can be easily separated by simple filtration after the reaction for catalyst reuse [125].

Entrapment can increase thermal stability and minimize leaching. The enzyme does not chemically react with the polymer matrix; therefore, denaturation does not occur. The disadvantage of this method is that the practical use is limited due to the mass transfer limitations. Entrapment is not very successful in large-scale industries because of the mass transfer resistance to substrates and products as the substrates do not diffuse deep into the gel matrix. If the pore size is too large, the enzyme's leakage occurs, loading capacity reduces, and abrasion of the support material occurs during the usage [111, 123].

Covalent Bonding

Covalent bonding, one of the most commonly used chemically irreversible techniques, is a covalent attachment of the enzyme to the carrier matrix. Carriers commonly used for covalent bonding in the immobilization techniques are sand, cellulose, porous glass, ceramic, synthetic polymers, and metallic oxides. Glutaraldehyde is the commonly used chemical compound as an activation agent that provides a covalent bond between the support and enzyme [117]. The chemical reaction between the carrier matrix's active functional group and the enzyme's active amino acid residues is the basic mechanism involved. The enzyme functional group is usually binding via side-chain cysteine (thiol group), lysine (ε-amino group), and aspartic acid, and glutamic acid (carboxylic group). The leaching of the enzyme and the carrier significantly reduces because of the strong bond between them [123, 126]. This method provides enzymatic stability and attachment between the support and the lipase, guaranteeing rigidity. The enzyme maintains an unaffected structure against denaturation agents such as organic solvents, heat, and pH due to its rigidity [113]. However, this method has some drawbacks, such as the loss of activity during immobilization and the preparation procedure is rigorous. Yet, some coupling reagents are toxic [121].

Carvalho et al. [127] studied *Burkholderia cepacia* lipase immobilization using covalent bonding with novel support, treated silica xerogel with protic ionic liquid, and bifunctional agents glutaraldehyde and epichlorohydrin. Three different oils, sunflower, colza, and soybean oils, were used for transesterification. The maximum conversion of ethyl esters of 98% was achieved with colza oil using treated silica xerogel without protic ionic liquid. Transesterification of soybean oil and sunflower oil yielded 93% and 92% biodiesel, respectively, with treated silica xerogel and protic ionic liquid.

Cross-Linking

The cross-linking immobilization of enzymes involves the formation of intermolecular cross-linkages by adding bifunctional or multifunctional cross-linking agents to connect the enzyme molecules into three-dimensional cross-linking aggregates. Enzyme immobilization by cross-linking is an irreversible process. This method of immobilization technique joins the enzymes to each other into a three-dimensional structure. This technique is usually support-free. Cross-linking enzyme aggregates (CLEAs), and cross-linking enzyme crystals (CLECs) are the two cross-linking immobilization approaches [8]. The preparation of CLEAs is considered a very simple procedure that involves enzyme precipitation, which does not need to be purified, whereas the preparation of CLECs requires highly purified lipases which involve multistage purification before crystallization. CLEAs/CLECs are generally prepared by aggregating an enzyme with precipitants such as organic solvent (n-butanol) or salt (ammonium sulfate) and subsequently cross-linking by bifunctional reagents like glutaraldehyde. Cross-linking occurs between lysine residues on the surface of a neighboring enzyme molecule and glutaraldehyde via Schiff's base reaction. Lysine residues are essential in the formation of CLEAs/CLECs. Lipases containing less accessible lysine residues are supported with additional amino acid residues such as bovine serum albumin and glutaraldehyde. This technique is called proteic feeding [117, 120]. The microporous density assembly and catalyst density of CLEAs show high catalyst activity, operational stability, long shelf life, and reusability. They also provide cost-efficiency compared to the matrix-associated immobilized lipase approaches. Cross-linking immobilization results in both stabilization and immobilization of the enzyme without dilution of activity. The intermolecular contacts and cross-links between enzymes in the crystal lattice of CLECs stabilize the enzyme and prevent denaturation [128].

Some researchers recently studied the effect of immobilization with a two-step process, adsorption followed by cross-linking. Physical aggregates are held together by physical adsorption (non-covalent bonding) without worrying about their ternary structure. The subsequent cross-linking of physical aggregates renders them permanently insoluble while maintaining their activity by maintaining their pre-organized structure [129]. Binhayeeding et al. [130] used a combination of two immobilization methods to prepare a robust catalyst, such as adsorption followed by cross-linking of the *Candida antarctica* lipase on an immobilized matrix. Initially, lipase was adsorbed on PHB beads, followed by cross-linking with glutaraldehyde. This immobilized lipase retained its 80% activity for 2 h in 30–60 °C incubation temperature and 30 days at 4 °C. The maximum lipase activity of 50% could retain after using for 14 cycles. The same authors produced biodiesel using the mixed lipases (*Candida rugosa* and *Rhizomucor miehei)* immobilized on PHB followed by cross-linking with glutaraldehyde. The transesterification of waste cooking oil and methanol obtained a maximum yield of 96.5%, and the recycled catalyst was reused for six cycles, after which the catalytic activity reduction was observed. The biodiesel produced with this catalyst met the international specification for EN14214 and ASTM D 6751 standards [11].

Lipase Immobilization on Nanoparticles

In order to make the process more economical, recycling and reusability of the lipase are recommended to be immobilized on a solid support material; thus, the concept of heterogeneous biocatalysis comes into existence. The lipase immobilization on nanosupport materials is the key factor for efficient biodiesel production, enhancing the surface area, porosity, and the nature of hydrophilicity/ hydrophobicity that catalyze a targeted reaction. The support must also enhance and facilitate the substrate molecule to active site attachment, and it should have a different morphology to minimize the diffusional limitations [131]. Compared to the traditional immobilization materials, nanomaterials have emerged as promising novel support materials as they possess high enzyme loading, good dispersibility, and low mass transfer resistance, making them sustainable biocatalyst supports for biodiesel production. Traditional nanomaterial supports such as magnetic nanoparticles, nanometal particles, nanosilicon, and some novel nanostructured forms, nanoflowers, nanofibers, nanocarbon tubes, and metal–organic frameworks have been extensively used for enzyme immobilization [132].

Enzyme molecules adsorbed on the non-porous nanomaterials hinder the internal diffusion compared to the porous immobilized nanomaterials. In recent times, magnetic nanoparticles based on Fe_3O_4 have been extensively studied due to their easy and rapid recovery with a magnetic field. Magnetic nanoparticles also have high stability and low toxicity. Magnetic Fe_3O_4 nanoparticles have to be coated with chemically active substances to provide functional groups to immobilize enzymes [133]. Badoei-Dalfard et al. [134] synthesized magnetic Fe_3O_4 functionalized with 3-aminopropyltriethoxysilane to acquire amino activated functional group. CLEAs of lipase were mixed with 3-aminopropyltriethoxysilane-functionalized magnetic graphene oxide and formed a maGO-CLEA-lipase nanocomposite and used for biodiesel production using *Ricinus communis oil*. The maximum yield of 78% was obtained at the optimum reaction conditions of 3:1 methanol to oil molar ratio, 0.2 wt% enzyme loading at room temperature, 160 rpm, and 24 h. The enzyme could retain the activity up to 5 cycles but continuously started decreasing. Several conventional and nanomaterial supports used for lipase immobilization in biodiesel production with optimum biodiesel conditions are summarized in Table 4.

EnzymoCore is a leading biodiesel company in Israel founded in 2007. It holds several biodiesel plants around the world. They developed solid organic resin-supported modified-immobilized enzymes, producing biodiesel with high methanol resistance. EnzymoCore's cutting-edge technology produces high-quality ASTM and EN grade biodiesel from all types of vegetable and animal fat-based feedstock, especially which contain high FFA content and waste cooking oils. The catalyst can be used either in the batch or continuous reactors in commercial scales [140].

Free/Liquid Lipase Formulations

Most of the researchers focus on lipase immobilization on the various supports as a catalyst. Due to inappropriate support material selection, the shear breaking of the catalyst into small particles, deactivation of the enzyme because of the glycerol accumulation on the carrier matrix, catalyst leaching, and the higher cost of immobilization, the soluble/liquid/free formulations are rapidly growing. Liquid lipases (*Candida antarctica* lipase B, US$140 / kg) are cheaper than immobilized lipases (immobilized Novozyme 435, US$2,273/kg). These lipases have some unique characteristics, substrate-specific, highly active, pH, and thermally stable. Novozymes launched a commercial enzyme, liquid lipase formulation called Eversa Transform 2.0 (Callera Trans L). The enzyme being an amphiphilic molecule acting on the oil–water interface remains concentrated after separation by gravity in an emulsion between FAAE and glycerol. The reuse of the liquid lipases is possible after recovery from the reaction medium by simple decantation [141]. Lv et al. [142] used liquid-formulated lipase NS81006 for methanolysis and ethanolysis reactions using WCO. The transesterification reaction was conducted at 45 °C and 1000 rpm in a 250-mL three-necked round bottom flask. The molar ratio of methanol to oil and ethanol to oil was 4.2:1 and 5:1, respectively. The FAME and FAEE yields of 90% were obtained. However, the reaction rate of methanolysis (8 h) was faster than the ethanolysis process (17 h). The acid value and monoglyceride, and diglyceride values were significantly reduced when the water content was reduced from 20 to 3%. Upon reusing the lipase five times, the yield reduced from 90 to 84% in the fifth cycle in both cases. Kuo et al. [143] used *Candida antarctica* lipase for biodiesel production, and a maximum yield of 95.3% was obtained in the presence of 50% water content. The liquid catalyst was able to keep the catalyst activity of 53% after reusing it three times for 6 days. In another study conducted by Nguyen et al. [10], the water content in the reaction medium favored the reverse reaction. Liquid lipase was used for the esterification of FFAs with methanol using the response surface methodology technique to obtain the maximum biodiesel yield. The maximum yield of 96.73% biodiesel was obtained at the optimum reaction conditions methanol to the oleic acid molar ratio of 3.44:1 and catalyst loading of 11.98%, at 35.25 °C. The superabsorbent polymer was used as a water-absorbing agent to remove the excess water from the reaction mixture to increase biodiesel yield. Liquid lipase formulations have better miscibility with the reactants, which reduces the mass transfer limitations and increases the reaction rate. Hence, liquid lipase formulations can be an effective alternative catalyst for biodiesel production [109]. Lipases from various microbial sources have been extensively investigated for the production of

Table 4 Biodiesel production using immobilized lipase on conventional and nanomaterial supports and optimum operating conditions for maximum yield

Source	Support	Preparation technique	Catalyst loading (wt%)	Alcohol and oil	Molar ratio	Water (wt%)	Temperature (°C)	Time (h)	RPM	Reusable cycles and activity retained (%)	Particle size (nm)	Yield (%)	Reference
Conventional methods													
Pseudomonas cepacia	Sodium alginate and PVA	Entrapment	10	Methanol: Karanja and castor oil	6:1	0	50 ± 1	24	120	9, 52	-	78	[6]
Pseudomonas cepacia	Hybrid bio-support	Entrapment	10	2-propanol: castor oil	6:1	-	50 ± 1	24	120	6, 70	-	78	[135]
Burkholderia	Silica xerogel	Covalent bonding	20	Ethanol: colza oil	7:1	-	40	72	80	-	-	98	[127]
Candida antarctica Lipase B	Modified polyporous magnetic cellulose beads	Cross-linking	15	Methanol: yellow horn seed oil	16:1	15	60	2	-	5, > 70	-	92.3	[136]
Candida rugosa and *Rhizomucor miehei*	Polyhydroxybutyrate (PHB)	Adsorption and cross-linking	1	Methanol: WCO	6:1	5	45	24	250	6, 60	-	96.5	[11]
Candida rugosa	Tosylated cloisite	Covalent bonding	0.1 g	Methanol: waste frying oil	15:1	10	50	8	200	10, 61.3	-	97.1 ± 1.1	[126]
Immobilization on nanoparticles													
Thermomyces lanuginosus (Lipozyme TL IM)	Magnetic rice straw	Adsorption	-	Methanol: soybean oil	6:1	10	45	48	-	10, 80	50–60	83	[137]
Candida rugosa	Mg modified Fe_2O_4	Adsorption	30	Methanol: olive oil	4:1	-	45	48	200	4, > 80	11–16	98 ± 1.6	[138]
Rhizomucor miehei	Aminopropyltriethoxysilane-Fe_3O_4	Covalent binding	5	Ethanol: (babassu oil)	1:1	-	40	6	200	-, -	3.9	81.7 ± 0.7	[139]
Pseudomonas fluorescens lipase	Co_2^+-chelated magnetic	Adsorption	7.5	Methanol: WCO	4:1	5	50	12	200	10, 83	22–28	95	[119]

Table 4 (continued)

Source	Support	Preparation technique	Catalyst loading (wt%)	Alcohol and oil	Molar ratio	Water (wt%)	Temperature (°C)	Time (h)	RPM	Reusable cycles and activity retained (%)	Particle size (nm)	Yield (%)	Reference
Lipase	Aminopropyltriethoxysilane-Fe_3O_4	Covalent bonding	300 mg	Methanol: *Aspergillus niger* lipid oil	4:1	1 mL	45	4	200	5, -	20 ± 5	84	[29]

biodiesel. Some of the free lipases from the literature used for biodiesel production with optimum conditions are summarized in Table 5.

Lipases are sensitive to the high concentration of methanol or ethanol depending on the source of lipase. *Candida antarctica* lipase showed the maximum activity at 4:1 methanol to waste frying oil [109], and *Candida rugosa* lipase showed the maximum activity at 3:1 methanol to *Jatropha curcas* oil [143]. So the stepwise alcohol addition is recommended to preserve the catalytic activity. Firdaus et al. [144] studied biodiesel production using *Thermomyces lanuginosus* (Eversa Transform) liquid lipase. As the enzyme is sensitive to a high alcohol concentration, the methanol was added in three steps to obtain a maximum biodiesel yield above 90%.

Biodiesel production using microalgal lipids is becoming a new trend in recent years due to their less space occupation, faster growth, high photosynthetic efficiency, and high biomass yield. Microalgae can probably synthesize 30 times more oil per hectare than terrestrial plants. The lipid content depends on the specific algal strains and their growth conditions. Most microalgal strains are rich in lipids, which account for 20% to 30% of the dry biomass weight [146]. Kabir et al. [147] screened 41 microalgae strains from freshwater and wastewater. *Chlorella vulgaris* and *Scenedesmus obliquus* have produced the highest lipid as 30.4 ± 0.3% and 27.9 ± 0.4%, respectively. A novel three-phase partition (TPP) method was used to extract the microalgal lipids from *Chlorella vulgaris* sp. in which salt was added to the microbial solution. In the next step, the organic solvent was added to this salty microbial solution. Then three layers are formed, and the upper organic layer is taken out, consisting of lipid extract of 15.9%. The extracted lipid was transesterified with methanol and obtained a yield of 12.05% [148]. The lipid was extracted from the *Nannochloropsis oculata* strain with maximum biomass content of 4.38 g/L and total fatty acid content of 1.55 g/L in two extraction cycles using ethanol. The lipid ethanol mixture was directly used to produce biodiesel using free lipase from *Thermomyces lanuginosus* and obtained a maximum yield of 90.25% [13].

Andrade et al. [149] investigated annual biodiesel production's economy using liquid lipase (Eversa Transform) without reusing and immobilized lipase (Novozyme 435) with reusing on a 250,000 tons capacity. Methanol and castor oils were used as raw materials. The cost of immobilized lipase is US$1000/kg immobilized beads, whereas liquid lipase is 65 times cheaper than immobilized lipase. Although liquid lipase is cheaper than immobilized lipase, the process capital cost is higher due to the complex steps involved in biodiesel separation. The liquid lipase-catalyzed process resulted in a US$0.78/kg biodiesel production cost, corresponding to a profit of US$51.6 million/year. Due to the higher cost of

Table 5 Free/liquid lipase formulated catalysts for biodiesel production with optimum biodiesel yield conditions

Biocatalyst	Lipase loading (wt%)	Alcohol and oil	Molar ratio	Water (wt%)	Temperature (°C)	Time (h)	RPM	Yield (%)	Reference
Eversa Transform	1 v/v	Methanol to rapeseed oil	4.5:1	3	35	24	350	96.7	[144]
Candida rugosa lipase	160 U	Methanol: *Jatropha curcas* oil	3:1	50	37	48	250	95.3	[143]
Candida antarctica lipase	5.5	Methanol: waste frying oil	7:1	16.6	30	22	400	94.6 ± 1.4	[109]
Thermomyces lanuginosus lipase	0.3	Methanol: residual chicken oil	4:1	2	35	36	200	93.16	[145]
Callera Trans L	1.45	Methanol: tallow mixed soybean oil	4.5:1	9	35	8	300	84.6	[110]
Free lipase NS81006	1.5	Methanol: WCO	4.2:1	5	45	8	1000	90	[142]

immobilized lipase, it should be reused at least 300 cycles to get a profit similar to liquid lipase. Hence, the liquid lipase-catalyzed process is the most economical in this scenario.

The lipase-catalyzed transesterification reactions require only 50% of the actual stoichiometric ratio's excess methanol to reach 95% of the biodiesel yield compared to the alkali catalyst, which requires 100% excess methanol [150]. However, liquid lipases have a better mass transfer with reactants; the recovery and reuse are limited. The presence of excess alcohol and glycerol leads to enzyme deactivation [149]. The advantages and challenges of various types of catalysts for biodiesel production are summarized in Table 6.

Future Prospectives

Due to energy security and other environmental concerns, biodiesel production is increasing worldwide. According to the International Energy Agency, the global biodiesel production dropped from 41 billion liters in 2019 to 37 billion liters in 2020 due to the COVID-19 pandemic, and it is expected to reach 46 billion liters in 2025. Indonesia is the leading producer of biodiesel, with 7.9 billion liters, followed by the USA and Brazil with 6.5 and 5.9 billion liters in 2019. Germany and France are holding fourth and fifth place with 3.8 and 3 billion liters. Many countries like Indonesia, Canada, Brazil, Argentina, Chile, China, and India are implementing mandatory policies to use biodiesel blends with conventional fossil fuels. In the coming years, biodiesel demand will increase considerably due to government mandates switching to renewable energy, increasing prices for crude oil, and increasing environmental pollution.

The appropriate feedstock oil selection is a critical factor for cost-effective biodiesel production. The selected feedstock oil should not compete with food crops. Presently, biodiesel production with feedstock oils such as non-edible, *Jatropha*, *Karanja*, and animal fats is studied extensively as these oils will not cause competition on human food. Especially, *Jatropha* plants can grow well on poor and infertile soils and can withstand all types of climate. The *Jatropha* seeds also contain high oil content up to 50%. Recently, microalgae are being explored as an alternative to vegetable oils. Microalgae also absorb CO_2 and help to reduce greenhouse gases. The oleaginous microalgae have gained much attention as a new source of feedstock for biodiesel production. In the future, research should be focused on the microalgae lipid feedstock as a potential raw material for biodiesel production.

Heterogeneous catalysts and immobilized enzyme catalysts are superior to the conventional homogeneous catalysts in biodiesel production. The usage of heterogeneous catalysts, such as waste biomass-based and nanocatalysts, is increasing rapidly because of their cost-effectiveness. Also, the immobilization of lipase on nanocatalysts is a growing field by which enzyme stability can be improved. Heterogeneous catalysts and immobilized enzyme catalysts can be easily separated from the reaction mixture, recovered, and reused, leading to high efficiency and low production cost.

Continuous research is going on to improve the process economics using enzyme catalysts to implement on an industrial scale. EnzymoCore developed solid organic resin-supported modified-immobilized enzymes to produce biodiesel with high FFA containing oils on a commercial scale. Some immobilized lipases are currently commercially available, such as Novozyme 435, Lipozyme RM IM, Lipozyme TL IM, and Lipae P-SC. In the near future, enzyme catalysts can replace homogeneous catalysts on an industrial scale.

Table 6 Advantages and challenges of various types of catalysts for biodiesel production

Method	Advantages	Disadvantages
Non-catalytic Supercritical fluids	Faster reaction rates (0.1–1.5 h) No catalyst involved	Requires high temperatures (250–350 °C) and pressures (10–35 MPa) Safety issues High-cost equipment requirement
Homogeneous alkali	High catalytic activity Widely available and cheap No corrosion Ideal catalysts for refined oils with low FFA and low water content	Soap formation Not suitable for feedstock oils with high FFA (> 0.5%) and high water generation Not reusable Generates high wastewater during product washing
Homogeneous acid	High catalytic activity Suitable for any feedstock oils No soap formation	Causes vessel corrosion Difficulty in product separation and not reusable Slower reaction rate (> 1.5 h) compared to the alkali catalysts (0.05–1 h)
Heterogeneous acid	Esterification and transesterification occur simultaneously Higher FFA containing oils can be used Insensitive to FFA and water in the oil Easy catalyst recovery from the product Catalyst can be reused	Requires high reaction temperature (60–275 °C), alcohol to oil molar ratio (up to 40:1), and long reaction time up to 20 h Catalyst synthesis is costly Catalyst leaching may contaminate the product
Heterogeneous alkali	Mild reaction conditions (60–70 °C, < 2 h, < 4 wt% catalyst loading) Relatively faster reactions compared to the heterogeneous acid catalyst High possibility of regeneration and reuse Safe and cheaper Effluent generation can be minimized	Catalyst poisoning on exposure to ambient air Sensitive to FFA acid and forms soap (FFA > 2%) Soap formation reduce biodiesel yield and cause problems during purification Leaching of the catalyst may contaminate the product High cost of catalyst synthesis
Heterogeneous nanocatalyst	High surface area, high catalytic activity Mild reaction conditions Reusability	High cost of catalyst synthesis
Free/liquid lipase	Insensitive to FFA and water content in the oil Mild reaction conditions	Complicated enzyme recovery from the reaction mixture High cost for industrial use Sensitive to methanol and causing enzyme deactivation
Immobilized lipase	Improved lipase stability, easy product separation, reusability, easy glycerol recovery Mild reaction conditions (sometimes < 6:1 alcohol to oil molar ratio, < 50 °C) High-quality products Catalyst can be reusable	Possibility of shape change within the support material or getting detached drops activity High immobilization cost Loss of enzyme activity during immobilization Slow reaction rate up to 60 h
Lipase immobilized on nanocatalyst	High enzyme loading High surface area and increases catalyst stability Less mass transfer limitations Catalyst can be reused	High cost of catalyst synthesis

Conclusion

Transesterification of lipids and methanol with a suitable catalyst is a widely accepted method for biodiesel production. Homogeneous catalysts have already been developed on an industrial scale as they provide faster reaction rates and higher yields. But, they are associated with various drawbacks such as an extra neutralization step, tedious purification process, wastewater generation, and non-recoverability of the catalyst. In contrast, heterogeneous catalysts are more promising than their homogeneous counterparts as they can be easily separated from the products and reused for several cycles reducing overall production cost. The heterogeneous catalysts showed potential to overcome the challenges of homogeneous catalysts and replace them on an industrial scale.

Enzyme catalysts are proliferating due to the usage of low-quality feedstock oils such as WCO and animal fats with high FFA content at lower reaction temperatures and lower oil to alcohol molar ratios. Lipase immobilization on a nanocatalyst increases its activity and surface area and offers the advantages of easy catalyst recovery and reuse for multiple cycles. Liquid lipase formulations for biodiesel production are rapidly growing due to their better miscibility with the reactants, reducing the mass transfer limitations and increasing reaction rates. However, biodiesel production using lipase on an industrial scale is still a challenge to overcome due to its higher cost.

Abbreviations FAAE: Fatty acid alkyl ester; FAME: Fatty acid methyl ester; FAEE: Fatty acid ethyl ester; FFA: Free fatty acid; WCO: Waste cooking oil; SCF: Supercritical fluid; $scCO_2$: Supercritical carbon dioxide; PVA: Polyvinyl alcohol; CLEAs: Cross-linking enzyme aggregates; CLECs: Cross-linking enzyme crystals; PHB: Polyhydroxybutyrate

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Declarations

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