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REVIEW

A comprehensive review on biodiesel production from microalgae through nanocatalytic transesterification process: lifecycle assessment and methodologies

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Abstract
Biodiesel, a viable alternative fuel is a methyl esters of fatty acids that has gained considerable attention in recent years due to the increasing carbon emissions and exhausting conventional fossil fuels. The most significant criteria for effective biodiesel production are feedstock and catalyst selection. Microalgae is an ideal feedstock for biodiesel production due to its rapid growth and high lipid content. Nanocatalysts are increasingly applied in biofuel production due to its high surface area, catalytic activity and reusability. The present work is striving to explore the mechanism and application of nanocatalysts for biodiesel production through the transesterification process. The synthesis methods, spectral and structural properties using characterization techniques, regeneration and reuse of nanocatalyst are discussed. Along with nanocatalyst modification, the role of optimization parameters such as methanol to oil molar ratio, catalyst loading, reaction temperature and time in enhancing the biodiesel yield are offered. The physical properties of microalgae-based biodiesel through nanocatalytic transesterification were studied and compared with the conventional diesel based on international standards.

Keywords Microalgae · Biodiesel · Nanocatalyst · Transesterification · Lipid · Fatty acid methyl esters (FAME)

Abbreviations

FAME	Fatty acid methyl ester
FFA	Free fatty acid
TEF	Transesterification
MO	Methanol to oil

Introduction

The energy demand is soaring due to the increase in population, rapid industrialization, and transportation sector [1, 2]. It was also concluded that natural gas, oil, and coal reserves would be depleted within 60, 42, and 122 years, respectively. As a result, the focus on alternative renewable sources has been directed by researchers to mitigate petroleum-derived fuels [3]. There is an increased concern for conserving our planet, non-renewable natural resources due to various international agreements like the Paris agreement, Kyoto protocol, Montreal protocol, etc. [4]. There is a need to replace and find suitable alternatives for conventional petroleum-based fuels that comply with less pollution, economical, and producible in adequate amount to solve the energy crisis and reduce carbon footprints which are a major source of global warming. Thus, finding sustainable and renewable resources such as the hydrothermal, wind, hydrogen, organic, and solar energy is of at importance but energy derived from these sources should also be usable for transport within the existing infrastructure and vehicle assembly process. Biodiesel has remained as favorable and a good substitute for automobile engines which encouraged the researchers and investors worldwide to investigate more into the biodiesel production process and make it more economically viable, which results in the publication of a large number of articles, particularly in the last decade, as shown in Fig. 1.

Biodiesel has become a suitable substitute with various advantages over conventional fuel due to its non-toxic nature, environment friendly, lower carbon, sulphur, nitrogen emissions, lower persistent organic pollutants (POPs), low

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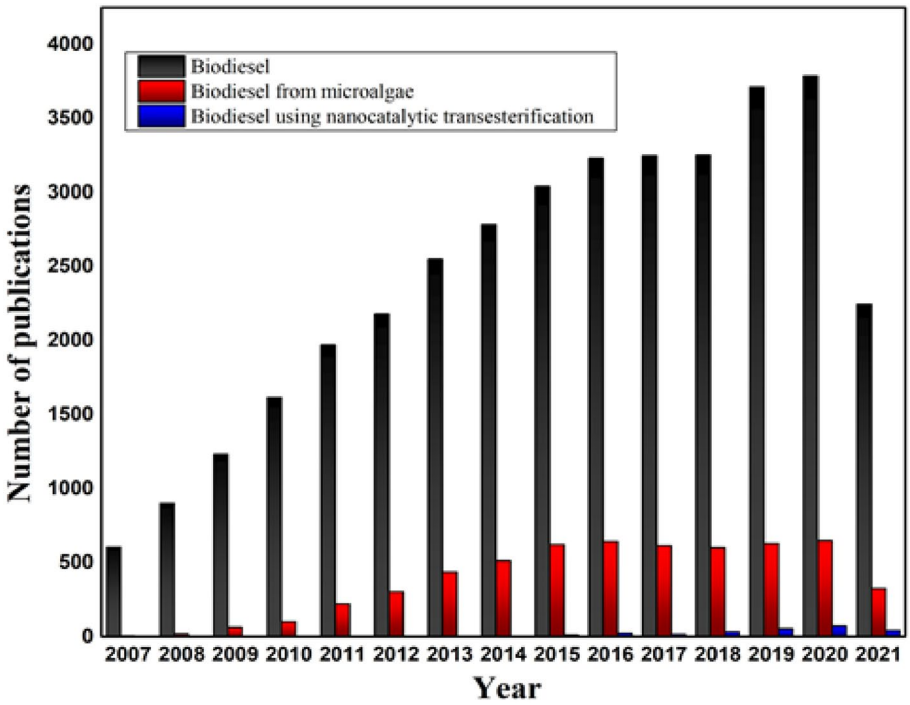


Fig. 1 Number of Publications from 2007 to 2021 (data from Web of Science)

particulate matter, aromatic hydrocarbons [5]. Biodiesel has more advantages over conventional diesel, such as higher cetane number [6], improved flash point, biodegradability, and lower exhaust emissions [7]. A variety of feedstocks can be used to produce biodiesel and thus classified into three generations. In the first-generation biofuel, biodiesel is produced using oil seeds and food-based crops as feedstock. The second generation-based biofuel is generally derived from non-food-based crops such as woody plants, forest residue, sugarcane, bagasse, jatropha, etc. The third-generation biofuels composed of microorganisms like microalgae, seaweeds and microbes. The percentage of oil content present in various feedstocks used to produce biodiesel is shown in Table 1.

Presently, biofuels account for nearly 10% of total global energy consumption, and the primary source of producing biodiesel is vegetable crops such as corn, soybeans, jatropha, sunflower, but due to its continuous demand, it is not competing for microalgae. Gendy and El-Temtamy analyzed that the biofuel produced from vegetable crops such as sugarcane, maize, soybean, sunflower, jatropha, peanut, etc., create pressure on food security, resulting in water scarcity contribute to deforestation. Hence, algal biofuels are generating significant awareness, and it is both scientifically and technically possible to produce energy products from algae [16]. Microalgae are unicellular species with the size ranging from a few micrometers to a few hundreds of micrometers, commonly found in marine and freshwater. It has been estimated that 2×10^5–8×10^5 species exist in which few of them are listed in Table 3. Biodiesel from microalgae is considered a third-generation biofuel with higher growth rate and can sequester CO_2, making it a carbon–neutral source of biodiesel production [17]. The microalgae has higher photosynthetic efficiency (6–8%) as compared to terrestrial plants (1.8–2.2%) due to their energy-conserving and simple cell structure as well as the presence of pigment called as *B-phycoerythrin* mostly found in red algae and cyanobacteria and has a much higher light-harvesting efficiency

Table 1 Oil content in various feedstocks for biodiesel production

Feedstocks	Oil content (%)	Feedstocks	Oil content (%)	Feedstocks	Oil content (%)
Sunflower oil [8–11]	25–35	Coconut oil [10, 11]	63–65	Karanja oil [10, 11]	27–39
Linseed oil [10, 11]	40–44	Castor oil [10, 11]	45–50	Canola oil [12]	40–45
Mustard oil [10, 11]		Rapeseed oil [13]	38–46	Neem oil [10, 11]	20–30
Rubber seed oil [10, 11]	45–70	Algae oil [10, 11, 14]	30–70	Rubber seed oil [10, 11]	53.74–68.35
Olive oil [10, 11]	45–70	Peanut oil [10, 11]	45–55	Soyabean oil [10, 11, 15]	15–20%
Palm oil [10, 11]	30–60	Jatropha oil [10, 11]	30–40	Chinese tallow seed oil [10, 11]	44.15

than other plants, that loses much of the remaining energy on growing roots. Amit and Ghosh observed that microalgae have a more significant advantage of availability, high lipid content, ease of cultivation and management, high cell density, reduction in CO_2 emission, and rapid growth [18]. Moreover, Akubude et al. studied that the microalgae grow at a high rate shows rapid biomass doubling time (1–6 days usually) and produces 10–20 times more oil than any other vegetable oil plant with a high photosynthetic rate of $6.9*10^4$ cells/ml/h and solar energy conversion capacity of about 4.5% [19]. Ansari et al. conferred that microalgae can be used in phycoremediation of wastewater as it consist of phytoplankton which is responsible for 90% of the photosynthetic activity with reduction of nitrogen, phosphorous and heavy metals concentration and energy production with a net profit of 16,885 US$·year^{-1} [20]. It is estimated that 1.8 kg of CO_2 is absorbed during photosynthesis which generates 1 kg of microalgae biomass [21]. Additionally, it offers another advantage that we can increase the lipid content of microalgae by controlling the environment of their cultivation condition like in photobioreactor, which is not possible for plants [22].

Microalgae can be used to generate various types of biofuels, such as biomethane, bioethanol, liquid oil, and biodiesel. Biomethane can be produced from microalgae by the process of anaerobic digestion [23], bioethanol can be produced by fermentation [24], biodiesel by TEF process [4]. A round of benefits of microalgae is shown in Fig. 2. Also, microalgae have various commercial applications such as cosmetics and play a key role in aquaculture and can also be used to extract vital products and supplements and enhance the nutritional properties of plants and animal feed [25]. Chen et al. observed that microalgae are also a source of chemicals, oils (omega-3, fatty acids) [26]. Other products include anti-viral, anti-fungal, anti-microbial, therapeutic proteins, drugs, pharmaceuticals, neuroprotective products,

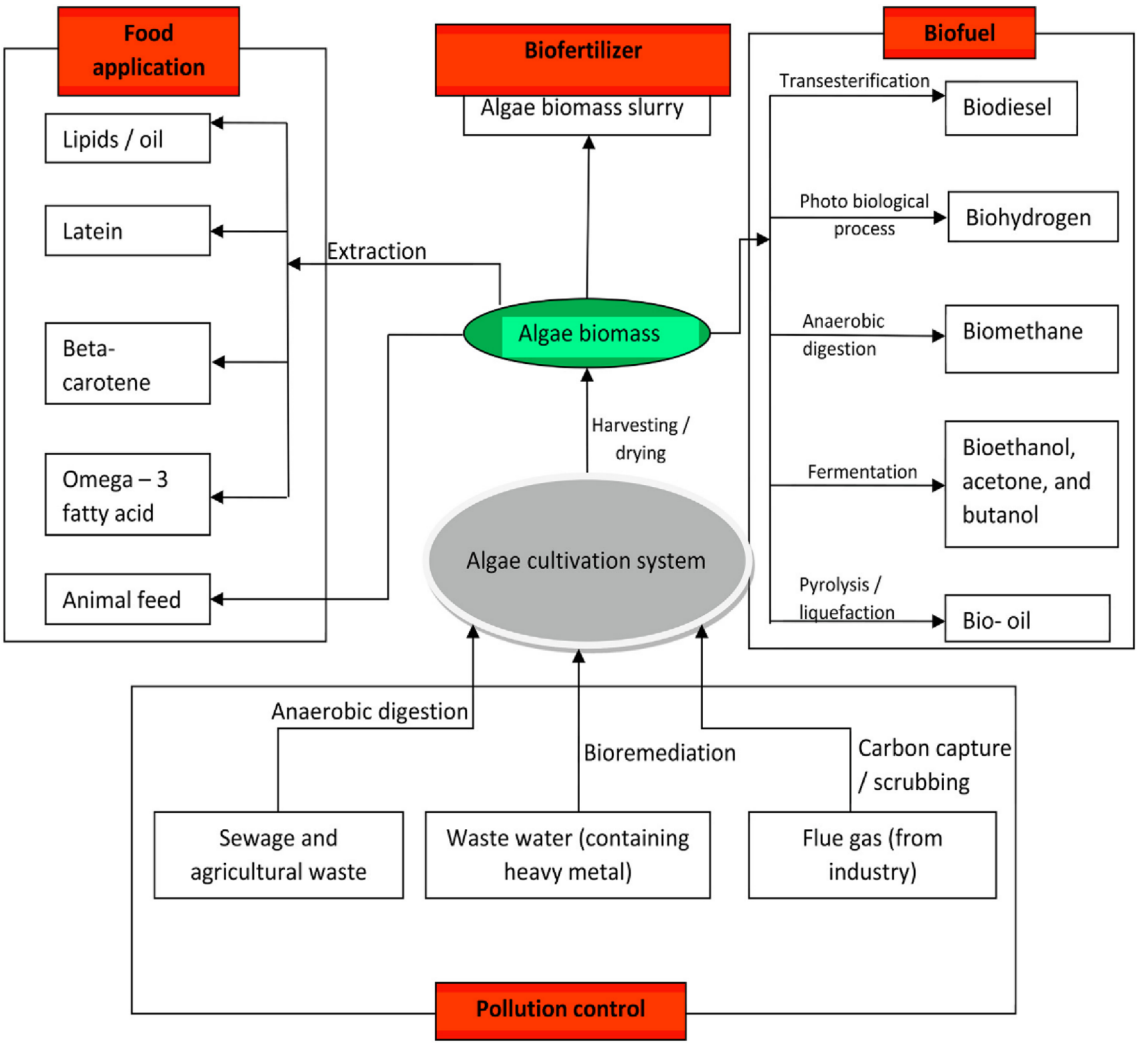


Fig. 2 Various benefits of microalgae. Reproduced with permission from Akubude et al. [19]

animal feed. High-value co-products such as proteins, lipids, pigments, vitamins, anti-oxidants, carbohydrates have been produced through biorefinery of microalgae [27].

Moreover, the nano-catalytic processes and applications are profoundly involved in all the applications of microalgae for biodiesel production. The nanocatalyst can be utilized in the different stages of biodiesel production process from microalgae such as during the stages of cultivation, harvesting, lipid extraction and transesterification. However, the focus of our study is centered on the application of nanocatalyst during the transesterification process. The TEF process can be carried out using various type of catalysts categorized as homogeneous, heterogeneous and enzymatic catalysts that have some bottlenecks such as lower yield, difficulty in phase separation, mass transfer resistance, higher production cost and slow rate of reaction. Thus, biodiesel production by nano-catalyzed TEF is preferable as it addresses the challenges raised by using homogeneous, heterogeneous, and enzymatic catalysts such as NaOH, KOH lipases, zeolites, etc. because of its obvious advantage of higher specific surface area, high resistance to saponification and higher catalytic activity as observed by Akubude et al. [19]. According to the study of Deshpande Sarma and Anand, nanotechnology has wide application in various areas and services and has the potential to address some key challenges and develop various sectors such as health, energy, water, agriculture, environment, electronics, and textile [28]. It was also found that nanomaterials could increase lipid extraction efficiency without destroying or harming the microalgae. Nanomaterials could stimulate the metabolism of microorganisms [22]. Kumar and Ali analyzed that nanocatalyst has gained attention in recent times because of several advantages, such as the formation of uncontaminated products. It is recyclable and can be reused up to five times, has low sensitivity towards FFA and moisture content, and does not destroy reaction flask [29]. The main characteristics of nanocatalyst are high activity, high stability, the large and efficient surface to volume ratio, high resistance to saponification [10]. Furthermore, Mofijur et al. reported that nanocatalyst could be used in lower temperature approaches and, when used during the TEF process, speeds up the reaction process and is not affected by FFA and water content [30]. Because of the evident benefits of nanocatalysts, research has been shifted to the production of more and novel forms of nanocatalysts, particularly in the last decade, that can be employed in place of conventional catalysts. The list of some review articles on biodiesel production strategies in the last 10 years is summarized in Table 2.

The main purpose of this review article is to investigate the biodiesel production from microalgae using nanocatalysts. The benefits of the transesterification process were also carefully explored in comparison to other approaches. Furthermore, the effects of various parameters on the yield of biodiesel production were completely examined. In addition, the synthesis and characteristics of nanocatalyst in biodiesel production were entirely investigated. Finally, the physical properties of biodiesel produced using nanocatalysts were compared with international standards. According to the review articles cited in Table 2, no such in-depth work on biodiesel production from various feedstocks using nanocatalysts has been done previously. As a result, this review article would be a helpful resource for those interested in this arena.

Oil sources for biodiesel production

Biodiesel is defined as the mono-alkyl esters with a long chain of fatty acids derived through the process of transesterification of animal fats, vegetable oil, or waste cooking oil [7]. The biodiesel could be produced from various sources such as edible, non-edible and algal oils. The classification of various oil sources is shown in Fig. 3.

Edible oils

The edible oils have relatively less influence on humans and the environment as they burnt completely without organic compounds, less sulfide, and less particulate matter. The major concern for edible oil-based biofuels is food versus fuel as it is limited by natural conditions and leads to food security and water scarcity reasons [46–52]. Furthermore, the biodiesel produced through edible oils raised the cost of edible oil which ultimately increase the cost of biodiesel production [31]. Various nanocatalysts such as $Cs/Al/Fe_3O_4$ [53], $Ca[O(CH_3)]_2$ [4], Carbonated alumina doped by CaO[54], $SrO\text{-}CaO\text{-}Al_2O_3$ [55] were utilized to produce biodiesel from sunflower oil, soybean oil, canola oil, palm oil as feedstock with FAME yield of 94.8%, 98%, 98.8% and 98.16%, respectively, at an optimum condition. The biodiesel produced through nanocatalytic transesterification process has high methyl ester yield as compared to homogeneous or heterogeneous catalyst. The maximum conversion efficiency of 98.8% was achieved using Carbonated alumina doped by CaO from canola oil at an optimum condition of 15:1 MO ratio, 4 wt% catalyst concentration and 30 min reaction time.

Non-edible oils

The non-edible oils addressed the issues associated with the use of edible oils as there is no competition with food [52]. Several nanocatalysts such as Ni-doped ZnO [56], ferromagnetic zinc oxide [57], Li-CaO [5], $KF/CaO\text{-}Fe_3O_4$ [58], Mn-doped ZnO [59] were utilized to produce biodiesel from castor oil, jatropha and karanja oil, stillingia

Table 2 List of a review article on biodiesel production strategies in the last 10 years

Author	Year	Topic of review article	Remarks
Sajad Tamjidi et al. [31]	2021	Performance of functionalized magnetic nanocatalysts and feedstocks on biodiesel production: A review study	The performance of functionalized magnetic nanocatalysts in biodiesel production was discussed
Manojkumar Narasimha et al. [32]	2021	Heterogeneous nanocatalysts for sustainable biodiesel production: A review	Application of various heterogeneous nanocatalyst was only studied
Nabilah Atiqah Zul et al. [33]	2021	A review on the utilization of calcium oxide as a base catalyst in biodiesel production	Potential of CaO as a base catalyst in biodiesel production was analyzed
Digambar Singh et al. [34]	2020	A review on feedstocks, production processes, and yield for different generations of biodiesel	The pros and cons of various feedstocks used for different generation biodiesel production were primarily discussed
Moina Athar et al. [35]	2020	A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production	The various feedstocks, catalyst, and intensification techniques were mainly studied
Akubude et al. [19]	2019	Production of biodiesel from microalgae via nanocatalyzed transesterification process: A review	Application of nanocatalyst and its comparison with different class of catalyst was only reviewed
Suchit Deshmukh et al. [36]	2019	Microalgae biodiesel: A review on oil extraction, fatty acid composition, properties and effect on engine performance and emissions	Various extraction methods were explored
Minh Kim Nguyen et al. [37]	2019	Recent advanced applications of nanomaterials in microalgae biorefinery	Potential of nanoparticle in enhancing cell harvesting, disruption and extraction was studied
Indu Ambat et al. [10]	2018	Recent advancement in biodiesel production methodologies using various feedstock: A review	Various biodiesel production methodologies were explored
Jiaxin Chen et al. [26]	2018	The potential of microalgae in biodiesel production	The potential of microalgae as a feedstock for biodiesel production was examined
Dhawane et al. [38]	2018	Recent advancement and prospective of heterogeneous carbonaceous catalysts in chemical and enzymatic transformation of biodiesel	The potential of biomass derived carbon catalysts in biodiesel production were discussed
Chen et al. [39]	2017	Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts	Focus on application of solid catalyst for producing HMF, LA and FAME from biomass materials
Faried et al. [7]	2017	Biodiesel production from microalgae: Processes, technologies and recent advancements	The various cultivation, harvesting and extraction techniques for biodiesel production from microalgae were deeply studied
Baskar et al. [40]	2016	Trends in catalytic production of biodiesel from various feedstocks	Mainly focus on various catalytic technology for biodiesel production
Puneet Verma et al. [41]	2016	Review of process parameters for biodiesel production from different feedstocks	The influence of various process parameters on TEF reaction was reviewed
Young-Chul Lee et al. [42]	2015	Recent nanoparticle engineering advances in microalgal cultivation and harvesting processes of biodiesel production: A review	Nanoparticle engineering based developments for microalgae cultivation and harvesting were presented
Jia Luo et al. [43]	2014	Ultrasound-enhanced conversion of biomass to biofuels	The effectiveness of ultrasound in conversion of biomass to biofuels was reviewed
Zhang et al. [22]	2013	Biodiesel production from heterotrophic microalgae through transesterification and nanotechnology application in the production	The application of nanotechnology in lipid accumulation, extraction and TEF were reviewed
Ramachandran et al. [44]	2013	Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review	Advances in ultrasonic assisted TEF with the use of heterogeneous catalyst to produce biodiesel was discussed
Lin Lin et al. [45]	2011	Opportunities and challenges for biodiesel fuel	Development, environmental impacts and benefits of biodiesel was deliberated

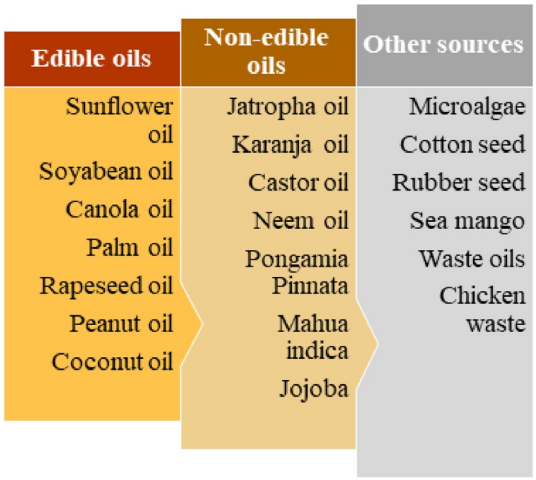


Fig. 3 Classification of various oil sources

oil and mahua oil palm oil as feedstock with FAME yield of 95.2%, 91%, > 99%, 95% and 97%, respectively, at an optimum condition. The maximum conversion efficiency of > 99% was achieved using Li-CaO from jatropha and karanja oil in 2 and 1 h, respectively, at 65 °C with catalytic loading of 5 wt% utilizing 12:1 MO molar ratio. Though non-edible oil-based fuels alleviate the concern raised by edible oils, because they are non-crop plants, they still have drawbacks as they are generally exotic or invasive species, and their cultivation can threaten the entire ecosystem [46]. Another obstacle with non-edible oil based fuels is a lack of mature or advanced technology and several technical barriers that make their production uneconomical [52].

Microalgal oil

Microalgae species are rich in oil content as lipid content which can convert to biodiesel. Microalgae oil appears to be the only biodiesel source capable of completely replacing petro-diesel because of numerous merits such as the low level of lignin content, richness in oil content, and rapid multiplication. Microalgae has a shorter growth cycle than that of energy trees and unlike the first-generation feedstock, it has no influence on food supply. Other advantages of microalgae include great lipid accumulation capacities, and the ability to grow in poor water quality. Also, microalgae have the highest capability to produce biodiesel and cost of microalgal-based biodiesel could be less or equal to other feedstock based biofuel [46, 60]. The composition of fatty acid of feedstock are essential factors in deciding the yield of biodiesel. Some algae species have over 50% lipid content, as shown in Table 3.

The different types of microalgal strains are used to produce biodiesel through nanocatalytic transesterification process. Various nanocatalysts such as Si/ZnO [65], Mn-ZnO capped with PED [66], TiO_2 [67], $Ca[O(CH_3)]_2$ [6], Fe_2O_3 [17] were utilized to produce biodiesel from microalgal strain of *Ulva lactuca*, *N. oculata*, *Synechocystis sp.* NN, *Nannochloropsis* sp, *Neochloris oleoabundans* as feedstock with FAME yield of 97.3%, 87.5%, 36.5 ± 8%, 99% and 81%, respectively, at an optimum condition. The maximum conversion efficiency of 99% was achieved by using $Ca[O(CH_3)]_2$ from *Nannochloropsis* sp. at an optimum condition of 30:1 MO ratio, 3 wt% catalyst concentration and 3 h reaction time. The high specific surface area (30 m^2/g) and large pore size (32.97 nm) facilitates the interaction

Table 3 Lipid content of microalgae species [19, 22, 61–64]

Microalgae species	Lipid content (dry wt%)	Microalgae species	Lipid content (dry wt%)
Anabaena cylindrical	4–7	Zitzschia sp	45–47
Chlorella emersonii	28–32	Dunaliellabioculata	8
Chlorella minutissima	57	Monallanthussalina	> 20
Botryococcusbraunii	25–80	Dunaliellaprimolecta	23
Chlorella sp	28–32	Cylindrothecasp	16–37
Nannochlorissp.	30–50	Isochrysissp	25–33
Neochlorisoleoabundans	31–68	Dunaliellasalina	6
Schizochytriumsp	50–77	Hormidiumsp.	38
Tetraselmismaculata	8	Euglena gracilis	14–20
Tetraselmissuecia	15–23	Dunaliellatertiolecta	35.6
Phaeodactylumtricornutum	20–30	Tetraselmissuecia	15–23
Crypthecodiniumcohnii	20	Scenedesmusobliquus	12–14
Porphyridiumcruentum	9–14	Scenedesmusdimorphus	16–40
Zitzschia sp	45–47	Pleurochrysiscarterae	30–50
Prymnesiumparvum	22–38	Schizochytriumsp	50–77

between catalyst and substrates, which effectively improved efficiency of transesterification. Due to mass transfer limitations, the three-phase catalytic reaction system slows down the TEF process in general, as shown in Eq. (2). However, some assumptions were made in this kinetic model, such as the rate of reaction not being dependent on methanol concentration and the reaction being considered as pseudo-first order. Secondly, the formation of intermediate species was expected to be negligible, and finally, all chemical reactions were estimated to take place only in the oil phase.

The application of nanocatalysts to produce biodiesel from various oil sources will be described in detail in Sect. 6, where Table 7 outlines the use of several nanocatalysts to produce biodiesel from various oil sources.

Lifecycle assessment of biodiesel production from microalgae

The process of biodiesel production from microalgae comprises microalgae cultivation, harvesting, extraction of lipid, and TEF [26]. There are various processes for cultivating and harvesting microalgae, lipid extraction, and TEF [1], as shown in Fig. 4. which play an essential role in deciding the quality and yield of biodiesel.

Microalgae cultivation

Microalgae cultivation is influenced by strain, light intensity, light/dark cycle carbon and nutrient cycle, temperature, and pH [68]. Microalgae cultivation approaches considerably affect the biomass productivity and biodiesel yield classified into a batch, fed-batch, continuous, semi-continuous, two-stage cultivation [69]. Hsieh and Wu investigated that the lipid productivity is highest in semi-continuous culture compared to batch and fed-batch cultivations [70]. The two-stage cultivation system (TSCS) is flexible, and its design can be changed as per requirement and enhances the lipid accumulation, but expenses associated with TSCS pose a challenge [69]. The most common cultivation methods are open cultivation and closed systems using bioreactors. The open cultivation system comprises natural ponds, circular ponds, raceway ponds, and inclined systems. Low construction cost, high biomass production, simplicity of the design are advantages of this system. Both favorable climatic conditions and adequate nutrients are required for the growth of microalgae. However, the open cultivation system is more susceptible to weather conditions and had no control over the culture conditions, and its success depends on regional climatic conditions [7]. Closed photobioreactors have gained considerable attention because they permit superior cultivation conditions than an open system [71]. A closed cultivation system includes various types of photobioreactors, including tubular, flat plate, column [26]. Photobioreactors have environmental (no chemical, decreased eutrophication, oxygen production) and economic advantages [72]. Closed photobioreactors are optimal for producing high-value long-chain fatty acids such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) [7]. Still, Narala et al. analyzed that hybrid cultivation yields exponential biomass production, lipid-rich microalgae, and simultaneously one or more efficient techniques can be carried out compared

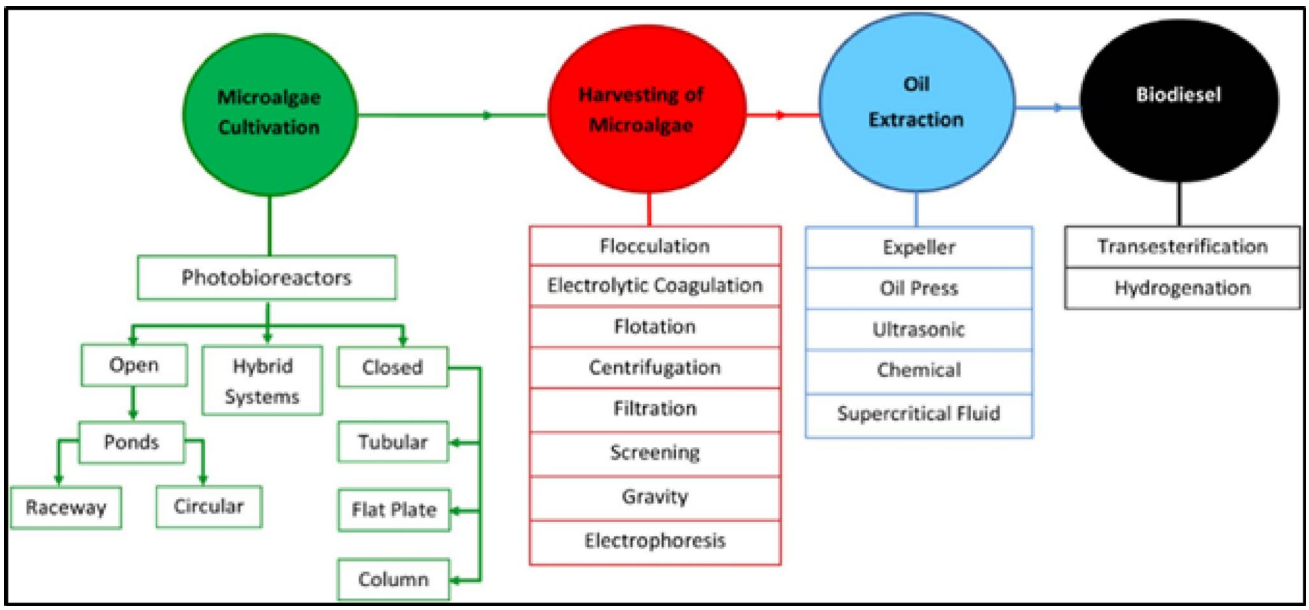


Fig. 4 Process flowchart for biodiesel production from microalgae. Reproduce with permission from Faried et al. [7]

to open or closed systems [73]. However, the higher capital and maintenance cost of the hybrid system can pose a severe challenge.

Harvesting of algal biomass

After the cultivation of microalgae, the microalgae biomass must be harvested [64]. Ortiz et al. observed that the separation of microalgae is challenging because of the small size of cells (5–20 μm) and their negatively charged cell wall, resulting in very small terminal settling velocity [74]. The leading technologies for microalgae harvesting include flocculation, screening, centrifugation, filtration, floatation, settling [26], ultrafiltration, air-floatation, auto floatation, and electrophoresis [75]. Ogbonna and Nwoba reported that bio-based flocculation had gained the attention of researchers due to its high efficiency, sustainability, and environmental conditions [76]. The advantages and disadvantages of various harvesting methods are summarized in Table 4.

Lipid extraction

As the water content of the biomass severely impacted the extraction process, drying has to be performed for further elimination of water. There are various methods for the lysis of microalgal cell and cell disruption mechanisms [7]. The organic solvent is most commonly and widely used to extract lipid at an industrial scale [26]. Lee et al. reported the various mechanical techniques (bead milling, ultra-sonication, grinding with mortar and pestle, oil expeller pressing), physical techniques (Microwave, Thermolysis, PEF, Osmotic shock, repeated Freeze–thaw), chemical techniques (acid/alkali, enzymes, detergent) which can be used for extraction of lipid from microalgae [81]. Various types of extraction solvents are used for the lipid extraction from microalgae, such as bio-derived solvents, supercritical fluid technology, ionic liquids, switchable solvents, deep eutectic solvents, fluorous solvents, supramolecular solvents [81, 82].

There are various conventional and modified methods such as Floch's method, Bligh and Dyer method [83], Soxhlet extraction [84], Accelerated solvent extraction (ASE) [85] was employed for higher-oil algal biomass. Kumari, Reddy, and Jha observed that the total lipid content obtained by Floch's method was several times higher than as obtained by Bligh and Dyer's method [86]. Chen et al. further analyzed that the extraction efficiency of Soxhlet apparatus and Accelerated solvent extraction is far better than conventional methods such as Floch's method, Bligh and Dyer's method. ASE and Soxhlet methods achieved total extraction of lipids from microalgae, unlike conventional methods [85]. Soxhlet apparatus using hexane is found to be less efficient than supercritical carbon dioxide ($SCCO_2$) extraction with lipid yield of 0.058 g lipid extract/g dried microalgae in 5.6* the required time [87]. Microalgae lipid extraction at lab scale is presently performed using chloroform, hexane, ethanol [64].

The effect of binary solvents mixtures on extraction efficiency was also discussed which is based on the principle of solvent extraction where ''like dissolves like'', the lower results produced by the 1:1 chloroform: hexane mixture with extraction efficiency of 0.98% could indicate that the algae contained smaller quantities of non-polar lipids, whereas when using 1:1 chloroform: ethanol mixtures the highest extraction efficiency of 11.76% was recorded that are indicative of larger quantities of polar and neutral lipids as shown in Fig. 5 [88]. Furthermore, the extraction behavior of the solvents when mixed depends not only on the result of intermolecular attractions, but also in discriminating between different types of polarities. The changes in viscosity will also affect the solubilities of the mixtures depending on their polarity and the van der Waals forces

Table 4 Advantages and disadvantages of various harvesting methods

Harvesting method	Benefits	Limitations
Coagulation/flocculation [64, 68, 75–78]	Simple and fast method, requires no energy	Chemicals may be expensive and toxic; recycling is limited
Bio-flocculation [64, 68, 76, 77, 79]	Inexpensive, non-toxic, no contamination issues	Cellular composition can be changed
Floatation [64, 68, 75, 77]	Inexpensive, less space requirement, short operation time, appropriate for commercial applications	Not feasible for marine microalgae, toxic due to use of chemicals, economically not feasible
Centrifugation [64, 68, 75, 79, 80]	Fast method, higher efficiency	Expensive, more energy consumption can rupture cells,
Filtration [68, 75, 77, 79]	Simplicity, inexpensive, easy to operate, high recovery efficiency	Possibility of fouling can increase cost, and maintenance cost is high
Gravity Sedimentation [68, 74, 75, 77]	Simple and inexpensive	Slow rate of settling, low biomass concentration, biomass can deteriorate
Electrophoresis [68, 75]	Suitable for all microalgae species, it does not require chemicals	High equipment cost, high-energy consumption

acting on them. Islam et al. observed that high-pressure solvent extraction under optimized conditions could be utilized for large-scale lipid extraction from microalgae, but its efficiency is strongly influenced by process temperature as increased temperature can speed-up the extraction process and improves the extraction yields and maximum lipid yield achieved at 90–120 °C at a sample dry biomass to water ratio (DBWR) of 50 and 75% [89]. Thus, there is a need for a reliable and functional lipid extraction technique. After the lipid extraction from microalgae, the lipid is transformed into biodiesel prepared from the process called TEF. TEF is the reaction where triglycerides are converted to FAME in the presence of alcohol (methanol/ethanol) with or without catalyst [4–6, 10].

The catalyst can be of different types such as homogeneous, heterogeneous, enzymatic, nanocatalyst (discussed in 5.1). The TEF process has a stable conversion efficiency of greater than 95% and is widely used in industrial processes for biodiesel production [26].

Biodiesel production methodologies

There are two types of approaches for the production of biodiesel; one is physical and another is chemical method. The physical method involves dilution or blending and microemulsion, whereas chemical methods includes pyrolysis or thermal cracking and transesterification process. However, there are some alternate production methods such as ultrasound-assisted transesterification process, reactive distillation technology, microwave radiation, in situ transesterification process, supercritical fluid methods.

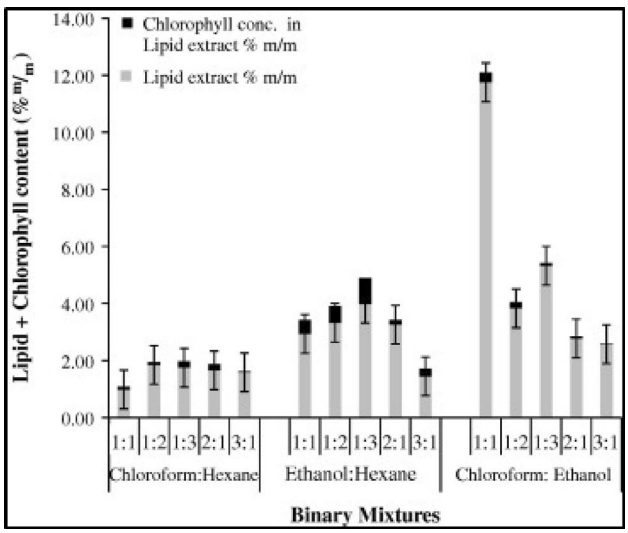


Fig. 5 Lipid extraction efficiency of various binary mixture of solvents. Reproduce with the permission from Ramluckan et al. [88]

The dilution process dilutes the vegetable oil by mixing the oil with a solvent or conventional diesel, and the mixing ratio can be expressed as B10, B20, B50, etc. The dilution process reduces the viscosity of oil and further decreases the utilization of diesel fuel [10, 90]. The micro-emulsion process is thermodynamically stable [91]. In the micro-emulsion process, the colloidal dispersion of 1–150 nm of isotropic fluid is formed [40] from the single or various amphiphiles and two immiscible liquids [10], and the high viscosity of vegetable oils or fats is reduced with the use of short-chain alcohols such as methanol, ethanol or 1-butanol [90]. Micro-emulsion is a simple process and can be used for high viscous oils [91]. However, the fuels obtained from this process have lower heat values due to the presence of alcohol, as analyzed by Aktaş et al. [90].

Baskar and Aiswarya reported that in pyrolysis or thermal cracking, the vegetable oils or fats are thermally decomposed to biodiesel in the absence of oxygen below its boiling point [40, 91]. The maximum liquid production occurs at a temperature of 350 and 500 °C [92], and no further separation or purification is required [91]. This is because different reactions occur at different temperatures in pyrolysis processes. Consequently, at higher temperatures, molecules present in the liquid and residual solid are broken down to produce smaller molecules which enrich the gaseous fraction. However, thermal cracking is an expensive process with high equipment costs and low biodiesel purity because of residue contamination [10, 91].

The ultrasound-assisted TEF process blends the oil and alcohol phases using cavitation and makes the mixing effective [40, 93]. Ho, Ng, and Gan reported that the ultrasound-assisted TEF process enriches the mass transfer characteristics with a high yield of biodiesel and thus reduces the reaction time and production cost [94]. Moreover, the consumption of power also reduces when ultrasound as auxiliary energy is used with the TEF process [95]. Ultrasound cavitation improves the mixing of reactants with either homogeneous or heterogeneous catalysts and enhances the biodiesel conversion compared to the conventional TEF process [94]. Acid-catalyzed TEF increases the biodiesel yield to greater than 98% at optimum conditions. However, base-catalyzed TEF is more popular as they are much faster and give a high yield of > 98% in a shorter time of 30 min than acid-catalyzed TEF, which takes a longer reaction time of 90–120 min [93]. Mahamuni and Adewuyi observed that the frequency of the ultrasound wave affects the reaction rate and biodiesel yield. High-frequency ultrasound of 581 and 1300 Hz has a minor effect on biodiesel yield, but an increase in ultrasound energy from 46 to 143 W increases the yield of biodiesel [96].

Reactive distillation is based on the concept of the multifunctional reactor where chemical reaction and distillation occur in single equipment [92]. The reactive distillation

process improves the conventional distillation process by integrating the chemical reaction and thermodynamic separation in a single unit [10]. Reactive distillation can be either catalytic or non-catalytic. Boon-anuwat et al. investigated that the utilization of reactive distillation along with homogeneous and heterogeneous catalysts is advantageous as compared to the conventional TEF process [97]. Homogeneous catalyzed (NaOH) reactive distillation improves the yield of biodiesel and eliminates the prerequisite of separation and purification of products relative to an ordinary approach that requires more methanol in the feed. Similarly, heterogeneous catalyzed (magnesium methoxide) reactive distillation proposes substantial benefits such as less energy consumption, less number of unit operations, etc., with a yield of 98 wt% biodiesel and glycerol as a byproduct with energy consumption of only 153kWh/t [97]. The process is advantageous as the final product is free of any contaminants due to the presence of a decanter, flash evaporator, and distillation column [40].

Microwave technology is a well-established technology that involves mixing reactants by supplying energy directly to reactants (oil, alcohol, catalyst) using a stirrer device [10, 98]. Microwave-assisted technology is an appropriate method for commercializing and reducing the cost of biodiesel. The utilization of microwave energy boosts the reaction rate and proposes a fast and easy route for biodiesel production [99]. Koech et al. observed that Microwave-assisted technology is a superior heating approach as it reduces the reaction time to 7 min compared to conventional heating, which requires up to 8 h and makes the separation process more accessible and simpler [100]. Moreover, using microwave-assisted technology, high quality biodiesel can be produced [98]. Furthermore, the biodiesel yield and production rate through microwave irradiation increases 1.3 times and 6 times than obtained via a two-step process using conventional heating [101].

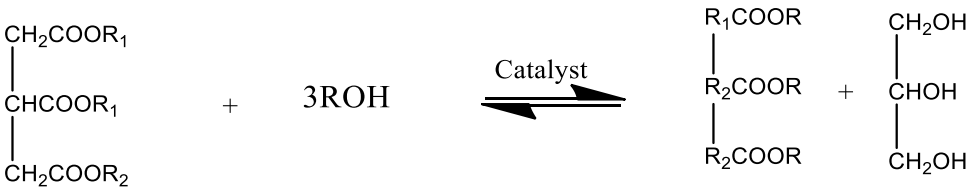
In situ TEF is the process of transforming oil seeds directly into biodiesel by reacting methanol with a catalyst [40]. In situ TEF is also referred to as reactive TEF, where the extraction of oil and TEF of oil into biodiesel takes place simultaneously without prior extraction of oil and thus eliminates the expensive solvent extraction step [100]. Ertuğrul Karatay, Demiray, and Dönmez reported that the In-situ TEF process provides the higher C16 and C18 FAME yield of 52% and 96.3%, respectively, and highest lipid accumulation [102].

The supercritical method or Saka method was developed in 2001 to avoid the use of catalyst and complete the TEF reaction in relatively less time [103]. Supercritical technology can be utilized at numerous stages of oil extraction, esterification, or TEF [104]. Ambat, Srivastava, and Sillanpää found that a substance is referred to as in the condition of supercritical fluid, which cannot be condensed anymore as its temperature and pressure are higher than critical temperature or pressure [10]. Under the supercritical condition, mass transfer greatly influences the reaction between oil and alcohol, and triglyceride can be well dissolved in methanol, and the mixture becomes a single phase due to the high miscibility of oil and alcohol [103]. Farobie and Matsumura observed that biodiesel production using supercritical technology devises a lot of benefits such as high reaction rate, less residence time, no requirement of pretreatment, does not require a catalyst and applicable to a variety of feedstocks, higher production efficiency with simpler separation and purification [105]. However, supercritical CO_2 is a perfect alternative to organic solvents for triglycerides and provides a processing temperature that is well within the optimum lipase requirements [104]. The high energy demand to achieve supercritical conditions can be a major obstacle to this process, including higher economic and technical expenses [10, 105].

The transesterification is the most popular and common method to convert oil/fats into biofuels or methyl esters. It is a reversible reaction where the reaction efficiency is directly influenced the various parameters. The most significant factors are the free fatty acid content, water content, ratio of the reactants (molar ratio of alcohol to oil), catalyst type, catalyst concentration, and the reaction conditions such as reaction temperature and duration, stirring speed. If the influence parameters are not optimized, then the process will be ineffective. The nanocatalyst use during transesterification is desirable as it has low sensitivity towards FFA and moisture content. There are many more benefits of using nanocatalyst in transesterification process such as high catalytic activity, effective surface to volume ratio, high stability and reusability [91].

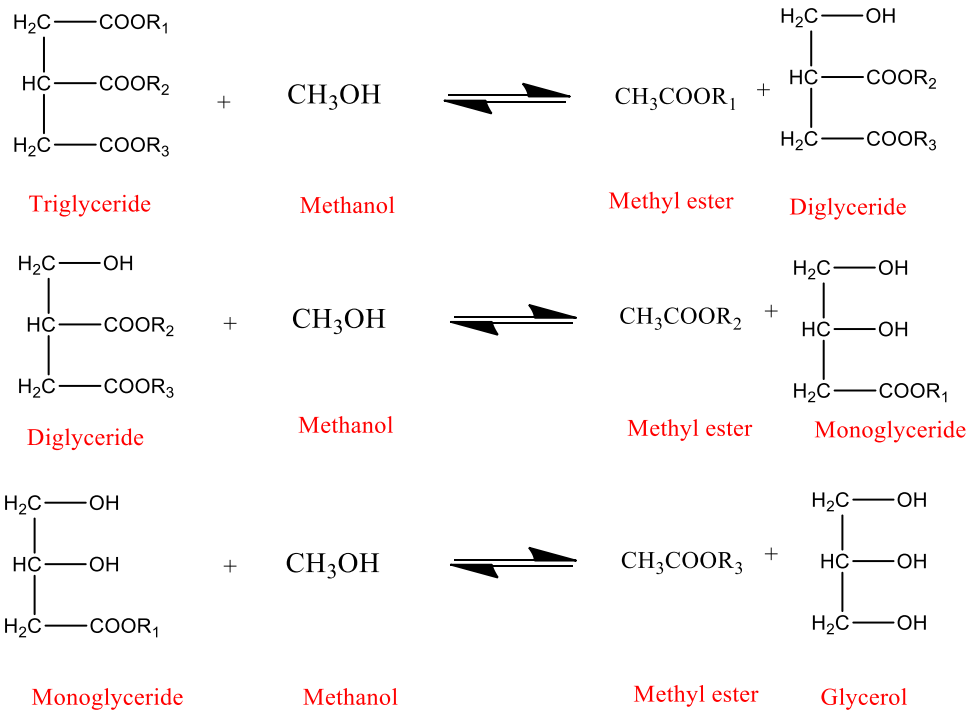
Stoichiometrically, TEF reaction requires 1 mol of triglycerides and 3 mol of methanol to produce 3 mol of methyl ester and 1 mol of glycerol [6]. As TEF process is a reversible reaction, adding excess methanol shifts the equilibrium toward the products so that triglycerides will be converted to FAME. However, excess methanol will increase the cost of biodiesel generation, but use of nanocatalyst and recovering methanol are the best options to improve the economics of the transesterification process as nanocatalyst can be regenerated and reused up to five times without deteriorating the biodiesel yield [30, 31]. The use of less amount of methanol decreases the rate of reaction which leads to the lower biodiesel yield due to the ineffective TEF process. In contrast, use of methanol beyond the optimal value increases the solubility of reactants, leads to saponification which makes the separation of product or glycerol difficult. On the other hand, the glycerol remaining in the solution shifts the equilibrium to the right side of the reaction, resulting in lower biodiesel yield. Therefore, an optimal amount of

methanol should be used in the TEF reaction. However, the detail discussion on effect of various reaction parameters in the TEF reaction done in Sect. 10. The chemical reaction through which triglycerides converts to FAME which ultimately leads to the formation of biodiesel and glycerol is shown in Eq. 1.



(1)

The triglycerides converts to monoglycerides in three sequential reversible reactions, as presented in Eq. 2 involves: (1) production of di-glyceride, (2) mono-glycerides formation, and (3) ultimate generation of the methyl ester (FAME), i.e., the biodiesel and glycerol [30].



(2)

Here, the R refers to the chain of saturated or unsaturated fatty acids from C16 to C22. Figure 6 depicts a generic diagram of the biodiesel production using the transesterification process. Thus, TEF process is the most reliable and effective approach because of direct and simple conversion process, short reaction time, low temperature and pressure requirements and high conversion yield.

The advantages and disadvantages of various biodiesel production methodologies are summarized in Table 5.

Catalytic processes for the production of biodiesel

Various types of catalysts are used in the TEF process, categorized as homogeneous, heterogeneous, and enzymatic catalysts, as shown in Fig. 7. The presence of catalyst increases the rate of reaction and ultimately increases the yield of biodiesel [10, 40]. TEF can be carried out under supercritical conditions to avoid using any catalyst, which we have already discussed [103].

Homogeneous catalysts are most often employed to carry out the transesterification (TEF) process because of their simplicity, greater activity, and little cost. There are two types of homogeneous catalysts used for the production of biodiesel as homogeneous acid catalysts and homogeneous alkali catalysts. The acid-catalyzed TEF process is carried out using sulfuric, sulfonic, hydrochloric, phosphoric acids [106], whereas alkali-based TEF process is carried out using metal oxides, metal alkoxides, alkaline earth oxides, or hydrotalcite, such as NaOH, KOH which are relatively cheaper and widely available [105]. The

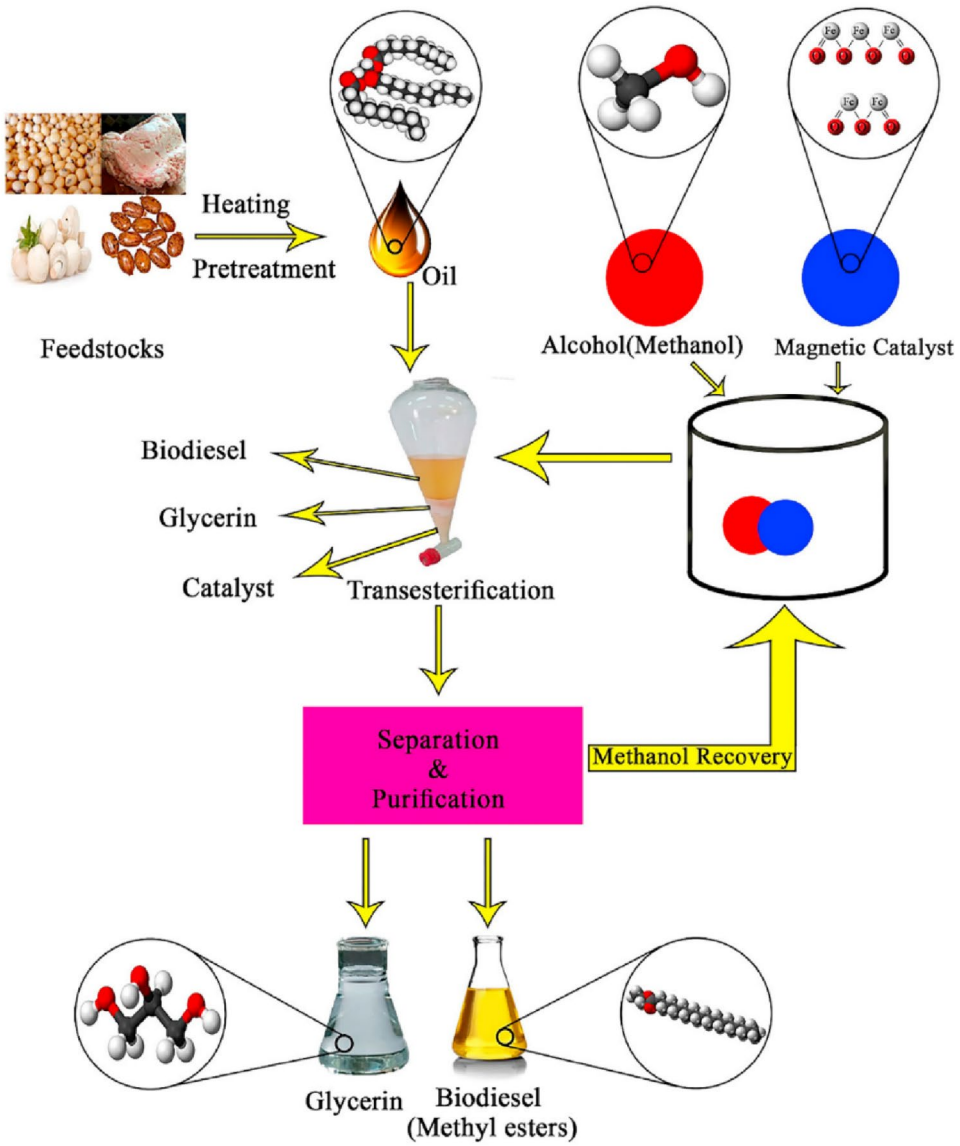


Fig. 6 Biodiesel production using transesterification process. Reproduce with the permission from Tamjidi et al. [31]

Table 5 Advantages and disadvantages of biodiesel production methodologies

Techniques	Advantages	Disadvantages
Dilution [10, 90]	Simple and low production cost	Incomplete combustion, high viscosity, high level of FFA, higher engine wear and maintenance cost
Micro-emulsion [10, 40, 90, 91]	Simple and can be used for high viscous oil, lower emissions and less waste formation	Incomplete combustion, poor stability, and volatility
Pyrolysis [10, 40, 91, 92]	Simple, pollution-free, no need for separation and purification	Expensive, low purity of biodiesel, requires high temperature
Transesterification [6, 10, 40]	Byproduct(glycerol) can be utilized, unreacted feedstock can be recycled	Expertise required, complex equipment and product separation is difficult

mechanism of alkali-based and acid-based TEF process is shown in Fig. 8a and b, respectively. The mechanism of alkali-based TEF process includes alkoxide and protonated catalyst production, the formation of tetrahedral intermediate after the nucleophilic attack on the carbonyl atom of triglyceride that reacts with alcohol to revive anion. The process is repeated two more times to produce biodiesel (methyl esters) and glycerol [10, 105]. In an acid-catalyzed TEF

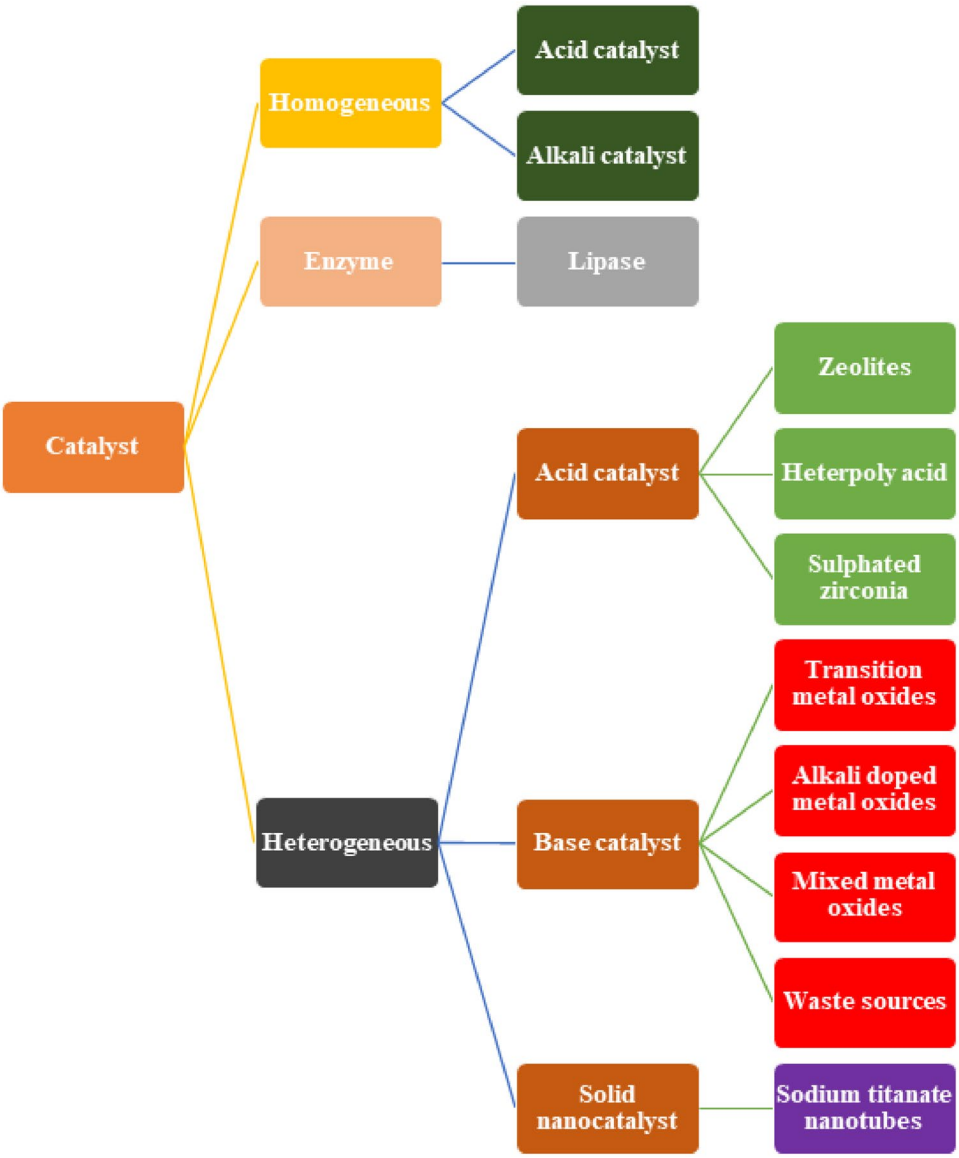


Fig. 7 Catalytic techniques for biodiesel production

reaction, protonation of a carbonyl group results in carbocation, which is then exposed to the nucleophilic action of alcohol to generate a tetrahydral intermediate. With the aid of a tetrahydral intermediate, the glycerol is removed, the ester is produced, and the catalyst is restored [10, 105]. The major advantage of using a homogeneous catalyst is that it entails mild operating conditions, consumes less time, and is less sensitive to free fatty acid (FFA) content [107]. However, on an industrial scale, it consumes a lot of catalyst and entails a number of washing and purifying stages, making it a costly process [40].

Galadima and Muraza explored the utilization of heterogeneous catalysts to address the complications accompanied with homogeneous catalysts. It consists of solid acids (zeolites, sulfated zirconia, heteropoly acids, nafion, etc.) and solid bases (basic zeolites, oxides, and carbonates of calcium and magnesium) [108]. Aransiola et al. investigated that Heterogeneous catalysts lessen the material and processing costs as they can be easily separated, regenerated, and reused up to several times. However, because of phase separation between the alcohol and oil, it has diffusion limitations and can leach active catalyst sites, resulting in product contamination. It also takes longer time and high temperatures to react, making it an energy-intensive process [104].

Enzyme-catalyzed transesterification, especially lipase based is a green method that addresses the unfriendly environmental nature of the chemical-catalyzed transesterification process, and further, it simplifies the purification process with a higher purity of products, avoids saponification, and consumes less energy [109]. Farobie and Matsumura reported that the economic viability of enzyme-based transesterification is hindered by a number of shortcomings,

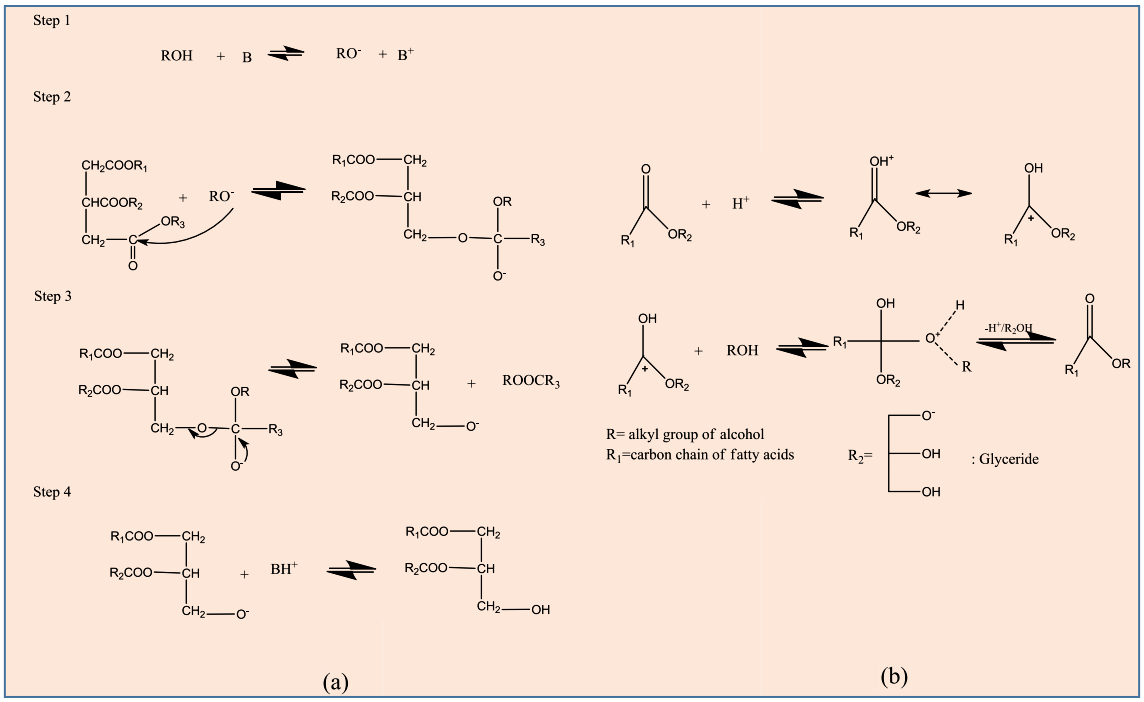


Fig. 8 **a** Mechanism of alkali-based transesterification process [10, 105]. **b** Acid-based transesterification process

including a slow rate of reaction even slower than acid-catalyzed, higher lipase production costs, and restricted reuse and regeneration of catalyst [105]. The merits and demerits of homogeneous, heterogeneous, enzymatic TEF are summarized in Table 6.

Application of nanocatalyst in biodiesel production

In recent times, nanocatalyst has gained special attention due to its high catalytic efficiency. Nanocatalyst mediums possess high surface area and large pore size that facilitates the interaction between catalyst and substrates, which in turn amplifies the efficiency of the nanocatalyst when compared to conventional catalysts. Many researchers from all around the world have observed at the use of nanocatalysts in the

Table 6 Merits and demerits of various catalytic transesterification processes

Catalyst	Merits	Demerits
Homogeneous catalyst [10, 40, 105, 106, 110]	Economical High reactivity Good selectivity Faster reaction at mild condition Esterification and transesterification occurs simultaneously Very fast reaction rate of alkaline based	Catalyst cannot be reused High cost for product purification Catalyst separation is problematic Soap formation decreases the yield Acid based transesterification causes corrosion
Heterogeneous catalyst [10, 40, 91, 104, 106, 108, 110–113]	Reduces the difficulty of separation of catalyst and product Catalyst can be regenerated and reused Non-corrosive Catalyst has a longer lifespan	Time-consuming Low yield Diffusion limitation Reduces overall catalytic efficiency
Enzyme catalyst [10, 40, 104, 105, 109, 114]	No side reaction requires less downstream operations highly efficient consumes less energy high-purity biodiesel	Expensive extremely slow reaction,

production of various types of biodiesel. The mechanism of the transesterification reaction utilizing nanocatalysts is depicted in Fig. 9. The conversion of Lewis acid sites to Bronsted acid sites is caused by the adsorption of water or hydroxyl groups on Fe, Ti, and/or S sites. Methanol is supposed to be adsorbed on Lewis acids (Fe^{+3} and Ti^{+4}), resulting in Bronsted acidity. Due of the weaker Fe-sulphate bond, alcoholic groups approach Fe-sulphate sites more favorably than Ti-sulphate sites. As illustrated in Fig. 9, the acidic sites of the catalyst contribute to methanol activation by producing a methoxide anion by coordinating methanol oxygen with the Fe^{+3}/Ti^{+4} site. The Lewis site of the catalyst activates the keto group of triglyceride, and subsequent methoxy nucleophile attack on the carbonyl carbon leads

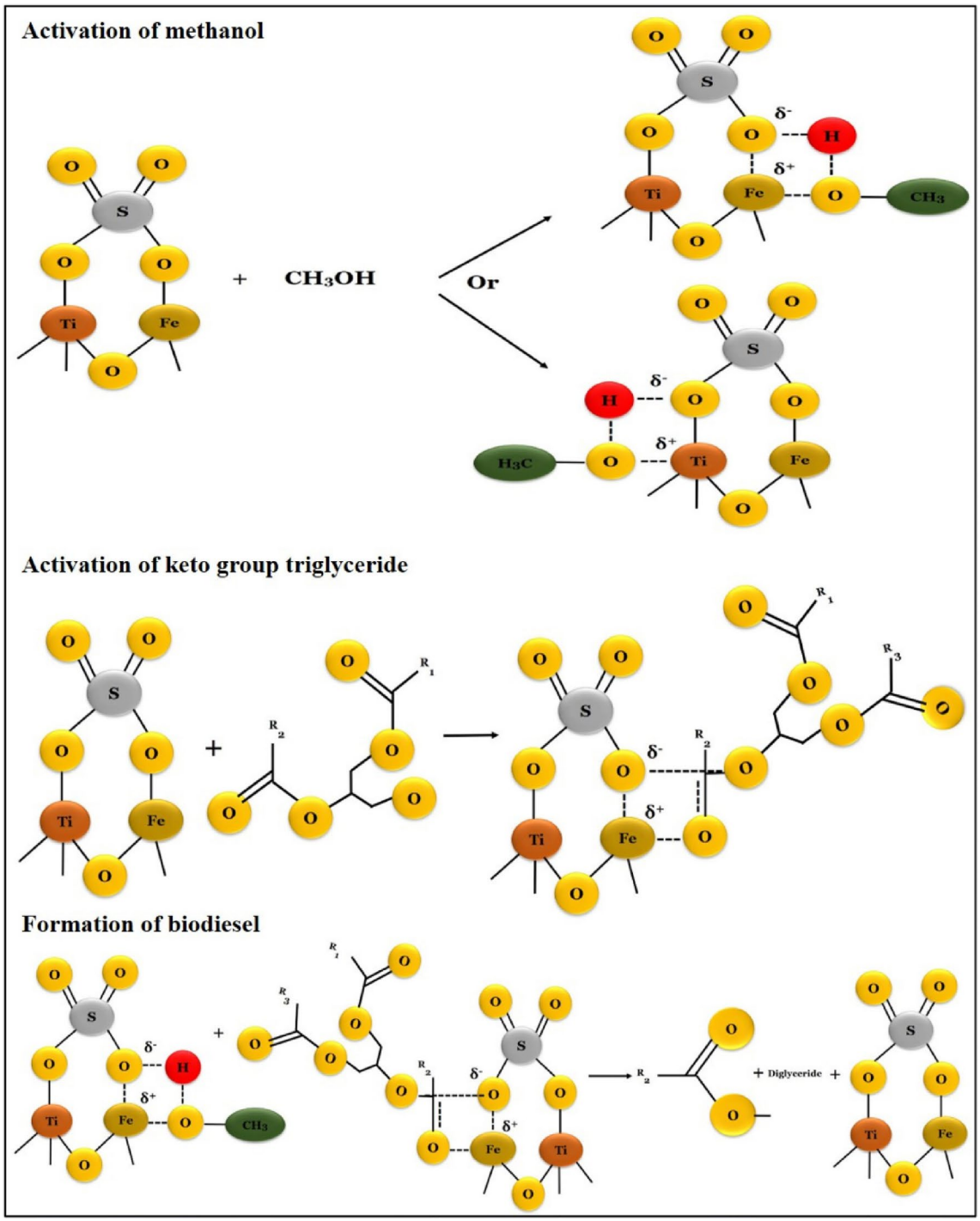


Fig. 9 Mechanism of transesterification reaction using nanocatalyst. Reproduce with the permission from Mofijur et al. [30]

the formation of ester and diglyceride. The same mechanism operated here and results in the formation of fatty acid methyl ester and glycerol [115]. Akubude et al. studied that biodiesel production using nanocatalyst increases the rate of reaction and combines the positive characteristics of both homogeneous and heterogeneous catalysts, and eliminates their respective limitations [19]. The most important characteristics of nanocatalyst, such as large surface area, elucidate various complications related to the TEF for biodiesel production [40]. The various nanocatalysts have been used in TEF reaction as shown in Table 7.

Baskar, Aberna Ebenezer Selvakumari, and Aiswarya utilized the heterogeneous Ni-doped ZnO nanocatalyst for TEF of castor oil, which gives the biodiesel yield of 95.2% under the optimum condition of 1:8 MO ratio, 11% (wt/wt) catalyst loading at 55 °C for 60 min [56]. Kaur and Ali carried out the TEF of jatropha and karanja oil using lithium impregnated calcium oxide as a nanocatalyst which gives the yield of > 99% in 2 and 1 h, respectively, at 65 °C with catalytic loading of 5 wt% utilizing 12:1 MO molar ratio [5].

Saber et al. conducted the Bio-oil production from microalgae *Nannochloropsis through* hydrothermal liquefaction (HTL) process and investigated the applicability of nanocatalyst (nano-Ni/SiO_2), an acid catalyst (zeolite) and alkali catalyst (Na_2CO_3) to increase the bio-oil yield at low temperatures (210 °C, 230 °C, 250 °C) and found that nano-Ni/SiO_2 offered the yield of 30 wt% at 250 °C that was higher as compare to acid catalyst (zeolite) and alkaline catalyst (Na_2CO_3) with nanocatalyst recovery of 2–3 times [116]. Teo, Islam, and Taufiq-Yap produced the calcium methoxide nanocatalyst by the hydrothermal synthesis route and obtained the highest FAME yield of 99.0% from algae *Nannochloropsis* sp. over 3 wt% of $Ca(OCH_3)_2$ catalyst loading at 30:1 MO molar ratio with the reaction time of 3 h at 80 °C [6].

Fe_2O_3 nanocatalyst aided TEF improves the yield of biodiesel up to 81%, which is higher than that attained from NaOH (48%) and HCl (64%) when biodiesel is produced from *Neochloris oleoabundans* microalgae where Fe_2O_3 nanoparticles were synthesized from extract of *Hibiscus rosa-sinensis* by green procedure [17]. Feyzi, Hassankhani, and Rafiee prepared the nanocatalyst Cs/Al/Fe_3O_4 through a novel synthesis method and showed the highest catalytic activity with the biodiesel yield of 94.8% under optimum conditions at 58 °C for 120 min with molar ratio 14:1 and catalyst loading Cs/Al = 2.5/1 [53]. The ultrasound assisted extraction of oil from autoclaved algal biomass was found effective with maximum biodiesel yield of 97.3% was achieved by using zinc oxide as a nanocatalyst for biodiesel production from *Ulva Lactuca* marine microalgae under optimized conditions at 8% catalyst loading, 9:1 MO ratio, 55 °C reaction temperature and 50 min of reaction time where [65]. Baskar and Soumiya achieved the FAME yield of 91.0% in 50 min at 55 °C and 14 wt% catalyst loading with 12:1 MO molar ratio by using ferromagnetic zinc oxide nanocomposite as catalyst prepared by the co-precipitation method for TEF reaction from castor oil [57]. Furthermore, Vinoth Arul Raj et al. obtained the yield of 87.5% from *N. oculata* species using Mn-ZnO nanocomposite capped with Poly Ethylene Glycol (PEG) at 15:1 MO molar ratio, 3.5%

Table 7 Various nanocatalysts used for biodiesel production

Catalyst	Feedstock	Molar ratio (methanol/oil)	Catalyst loading (wt%)	Temperature (°C)	Time (min)	Yield (%)
Ni-doped ZnO [56]	Castor oil	8:1	11	55	60	95.2
Li-CaO [5]	Jatropha oil	12:1	5	65	120	> 99
Li-CaO [5]	Karanja oil	12:1	5	65	60	> 99
Ni/SiO_2 [116]	Microalgae (*Nannochloropsis)*			250		30
Ca[O(CH_3)]$_2$ [6]	Microalgae (*Nannochloropsis* sp)	30:1	3	80	180	99
Fe_2O_3 [17]	Microalgae (*Neochloris oleoabundans)*					81
Cs/Al/Fe_3O_4 [53]	Sunflower oil	14:1	2.5/1	58	120	94.8
Si/ZnO [65]	Marine microalgae (*Ulva lactuca*)	9:1	8	55	50	97.3
Ferromagnetic zinc oxide [57]	Castor oil	12:1	14	55	50	91
Mn-ZnO capped with PED [66]	Microalgae *(N. oculata)*	15:1	3.5	60	240	87.5
Li-CaO [29]	Cottonseed oil	12:1		65	45	
KF/CaO-Fe_3O_4 [58]	Stillingia oil					95
Carbonated alumina-doped by CaO [54]	Canola oil	15:1	4		30	98.8
TiO_2/$PrSO_3H$ [118]	Used cooking oil	15:1	4.5	60	540	98.3
TiO_2 [67]	*Synechocystis sp.* NN					36.5 ± 8.3 mg

(wt/wt) catalyst loading and reaction temperature of 60 °C for 4 h by response surface method (RSM). The response surface methodology is a statistical and mathematical procedure used to develop a functional relationship between various input variables and the response of interest [117]. The significant advantage of utilizing RSM is that it produces the necessary statistics in fewer experimental runs and thus reduces process time and process variability [66]. The nanocrystalline Li^+ impregnated CaO was used as a heterogeneous catalyst for TEF from cottonseed oil and took 45 min for complete TEF at 65 °C and 12:1 molar ratio when FFA and water content was 0.31 wt% and 0.26 wt%, respectively, concluded that Li^+ impregnated CaO nanocatalyst has an ability to convert the cheap feedstock with high FFA into biodiesel to reduce its production cost [29]. Hu et al. obtained the FAME of greater than 95% using nanomagnetic catalyst KF/CaO-Fe_3O_4 prepared by the facile impregnation method under optimal conditions with catalyst reusability up to 12–14 times without much deterioration in catalytic activity [58]. Nayebzadeh et al. synthesized the nanocatalyst by the microwave combustion method (MCM) and attained the biodiesel yield of 98.8% from microwave assisted TEF of canola oil using carbonated alumina doped by calcium oxide as a nanocatalyst at optimum conditions 270 W microwave power, 15:1 MO ratio, 4wt% catalyst concentration and 30 min reaction time [54]. Jawaharraj et al. enhanced the biomass, lipid and biodiesel productivities by response surface methodology-genetic algorithm (RSM-GA) approach and attained the highest conversion of 36.5 ± 8.3 mg FAME/g from TEF of *Synechocystis sp.* NN by using titanium oxide as a heterogeneous nanocatalyst coupled whole-cell TEF method [67]. The Genetic algorithm (GA) is a potent non-linear global optimization tool, which could be utilized to predict the optimal conditions of the model predicted by RSM. Gardy et al. synthesized the solid acid nano-catalyst TiO_2/$PrSO_3H$ by the post-synthetic grafting of propyl sulfonic groups onto a mixed phase of a TiO_2 approach and obtained the 98.3% of FAME yield from TEF of used cooking oil at 4.5 wt% catalyst loading, 15:1 molar ratio, 60 °C reaction temperature and 9 h of reaction time [118].

Methods for synthesis of nanocatalyst

Nanocatalysts can be produced using various techniques for biodiesel production as shown in Fig. 10. Gas condensation, co-precipitation, vacuum deposition and evaporation, mechanical attrition, chemical vapour deposition, impregnation, sol–gel techniques, and electrochemical deposition are the most prevalent techniques [10, 119].

The gas condensation was the first technique used to produce nanocrystalline metal and alloys. Regulated

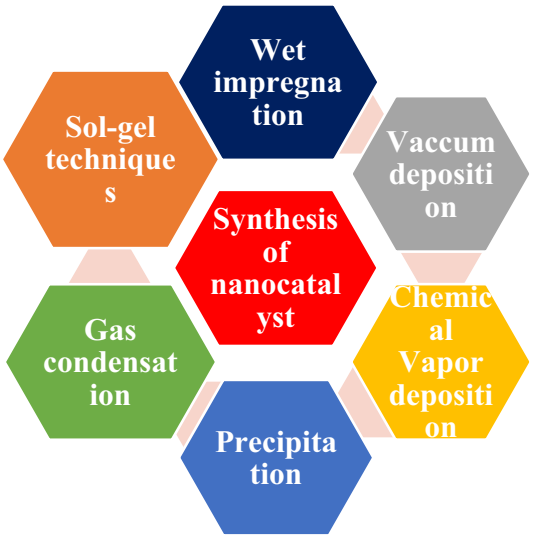


Fig. 10 Several approaches for nanocatalyst synthesis

evaporation and condensation is the primary mechanism involved. Evaporated particles strike with molecules of gas in an inert state in this process. This decreases the total kinetic energy, resulting in the output in the vacuum of nano-sized particles or detached small fine particles. By connecting the collector to the evaporation unit, the resultant particles may be collected, and stored in liquid nitrogen at a low temperature. A compaction section is also present, which is utilized to aggregate the energy generated. The system's primary drawback includes a mismatch between context and source, a discrepancy in evaporation rate and temperature options, and a long process time. The resulting particles can be collected by connecting the collector to the evaporation unit, stored with liquid nitrogen at a low temperature. There is also a compaction portion that is used to combine the power generated. The primary drawbacks of the system are the mismatch between context and source, the difference in the rate of evaporation and temperature choices, and lengthy process time [10, 119–121].

The vacuum deposition is another technique for the synthesis of nanocatalyst. In the vacuum deposition process, the compounds are vaporized by the application of a heat source to evaporate various materials at a pressure of less than 0.1 Pa and in a vacuum level of 10–0.1 MPa [10, 120, 121]. Mechanical attrition is another unique process that produces nanoparticles by structural breakdown of coarse-grained structures with the help of high-energy mills such as planetary ball mill, attrition ball mill, low-energy tumbling mill, high-energy ball mill, and vibrating ball mill at room temperature [10, 120].

Chemical vapour deposition (CVD) is an expensive technique used for the production of nanocatalyst, mostly in electronic industries. The chemical vapour deposition (CVD)

involves the deposition of the target materials by a chemical reaction on the surface of a substrate. With elevated temperatures or plasma, this reaction can be caused in two ways. For a temperature-induced chemical reaction, an overhead temperature of 900 °C is required, whereas the temperature is lower in plasma-activated CVD, between 300 and 700 °C [120]. The advantages of this method include the employment of appropriate deposition coatings without the need of any high vacuum, and the availability of a wide range of precursors. The by-products of CVD, on the other hand, are dangerous to one's health [10, 120].

The required component containing liquid comes into contact with the solid during the wet-impregnation technique of nanocatalyst production, and the liquid is deposited on the solid's surface as a consequence. Species polymerization/depolymerization ensues at different rates throughout the impregnation process, and adsorption occurs at varying rates due to various forces such as Vanderwall forces, hydrogen bonds, or coulomb forces [119, 121]. Several nanocatalysts prepared by the wet impregnation method are calcium methoxide [6], Mo sulfide loaded over graphene oxide (MoS_2/GrO) [122], KF/CaO-Fe_2O_3 [58], Li-CaO [29].

There are various nanocatalysts prepared by co-precipitation method such as Si-doped ZnO[65], CoO-NiO promoted sulfated ZrO_2 (CN/SZ) [123], Ca-Mg–Al catalysts [124], iron(II) doped ZnO [57], Mn-doped ZnO [59], Mn-ZnO capped with PEG [66]. In this method, nanocatalyst is synthesized by the reaction of solvent components where dopant is added before the precipitation reaction in the main solution and surfactant is added to maintain the separation between the particles and nanoparticle is separated by centrifugation, washed and vacuum dried [120].

Nanocatalysts such as calcium oxide [125], $NaAlO_2$ [126], CaO-MgO [127] prepared by sol–gel technique requires lower temperature, and the process is much simpler and flexible. Das et al. observed that the sol–gel involves the formation of colloidal suspension (sol) and gelation from the network in the continuous liquid phase (gel). Sol–gel formation involves four phases as hydrolysis, condensation, growth of particles, and agglomeration of particles [10, 120].

The synthesis of nanomaterials by electrodeposition can overcome various challenges, but its potential and application are unexplored as their films are mechanically strong, uniform, and offers a combination of increased hardness and wear resistance [120]. The various synthesis methods for the nanocatalyst in biodiesel production are summarized in Table 8.

Characterization of nanocatalyst using various techniques

The nanocatalyst can be characterized by various techniques for evaluating the different properties or aspects of nanocatalyst, such as nature, surface area, and composition. The total surface area, total pore volume, and average pore size of the catalyst were investigated using Barrett Joyner Hlenda (BJH) and Brunauer Emmett Teller (BET) at − 196 °C temperature of liquid N_2, and it reveals that nanomaterials are capable of providing a large surface to volume ratio [6]. Generally, the pore diameter of each nanocatalyst was in the range of 2 nm (micropore) and 50 nm (macropore) and hence called a mesoporous catalyst which has been widely used for the production of biodiesel in recent times. The $Ca(OCH_3)_2$ catalyst surface consist of mesopores of range 2–5 nm [6]. Besides, small pore sizes of nanomaterials enhance reactant diffusion rate to the active sites of catalyst and thus accelerate the TEF reaction [22]. The particle size, morphology, or topology of catalyst surface and precursor was observed by employing scanning electron microscopy (SEM) [53]. Generally, the pore diameter of each nanocatalyst was in the range of 2 nm (micropore) and 50 nm (macropore) and hence called a mesoporous catalyst which has been widely used for the production of biodiesel in recent times [53]. Baskar and Soumiya reported that nanoparticles

Table 8 Various synthesis methods for nanocatalysts in biodiesel production

Synthesis method	Nanocatalyst
Impregnation method	RHC/K_2O-20%/Ni [128], $Ca(OCH_3)_2$ [6], Mo sulfide loaded over graphene oxide (MoS_2/GrO) [122], KF/CaO-Fe_2O_3 [58], Li-CaO [29]
Co-precipitation	Mg_4Al_2 [124], Iron(II) doped ZnO [57], Mn-doped ZnO [59], Mn-ZnO capped with PEG [66]
Precipitation	Cs/Al/Fe_2O_3 nanoparticles [53]
Impregnation and co-precipitation	CoO-NiO promoted sulfonated ZrO_2 (CN/SZ) [123]
Deposition–precipitation	Nano MgO supported on Titania [10]
Ball milling	CaO and MgO supported over Al_2O_3 [108]
Sol–gel technique	Calcium oxide [125], $NaAlO_2$ [126], CaO-MgO [127]
Super-critical sol–gel method	Cs-MgO [10]
Impregnation and sol–gel method	$CsH_2PW_{12}O_{40}$/Fe-SiO_2 [10]

were generally spherical in shape, and agglomeration was observed for iron(II) doped ZnO [57]. Vinoth Arul Raj et al. analyzed the SEM of Mn-ZnO capped with PEG, which reveals the irregular hexagonal agglomerated shape of nanocatalyst with different morphologies and found to be heterogeneous [66]. The FESEM image of Fe_2O_3 nanoparticles shows the diameter of particles in the range of 150–200 nm [17]. A flower-like cluster arrangement was witnessed in the SEM image of $Ca(OCH_3)_2$ [6]. Transmission electron microscopy (TEM) can be used to determine the morphology and particle diameter of the nanocatalyst. Kumar and Ali discovered a TEM study of the same particle, which revealed that these particles are clusters of smaller particles, indicating that the catalyst is present in nanoparticle form [29]. Banerjee et al. demonstrate the TEM image of Fe_2O_3 nanoparticles of size ~200 nm [17]. Kumar and Ali discovered a TEM study of the same particle, which revealed that these particles are clusters of smaller particles, indicating that the catalyst is present in nanoparticle form [29]. The TEM of $Ca(OCH_3)_2$ found the nanoparticles in cubical shape [6]. The phase structure, composition, and crystallinity of the nanocatalyst were determined using X-ray diffraction analysis [4]. The nanocatalyst exhibited the usual ZnO hexagonal wurtzite structure in the XRD study of Mn-ZnO capped with PEG [66]. A strong diffraction peak at $2\theta = 35°$ in XRD analysis of Mn doped ZnO reveals the hexagonal structure of the nanocatalyst [59]. The Fourier Transform Infrared spectroscopy (FTIR) was used to characterize the composition of species adsorbed by surface [54]. Gardy et al. revealed that the FT-IR spectrum for $TiO_2/PrSO_3H$ nanocatalyst shows multiple additional peaks compared to the TiO_2 NPs spectrum [118]. The particle size and average roughness of the surface were characterized by using Atomic Force Microscopy (AFM) [57], whereas to determine the decomposition or breakdown nature of the catalyst Thermogravimetric analysis (TGA) has been employed [6]. The features of various characterization techniques are summarized in Table 9.

Regeneration and reusability of nanocatalyst

The budget of biodiesel production generally depends on the feedstock and the catalyst used in the process reaction. The mode of cultivation, harvesting, dewatering method, lipid extraction method, TEF process efficiency includes in the estimation process [26]. Moreover, Sun et al. reported that the costs are inter-related among the stages meaning thereby if the cultivation stage attains higher biomass productivity, then the price of harvesting and extraction will ultimately reduce [46]. The reusability of the catalyst is a key economic factor, because it makes the process more inexpensive and sustainable. To evaluate the reusability of nanocatalyst, nanocatalyst has to separate from the glycerol and fatty acid esters. To reuse catalyst, the used catalyst must be washed thoroughly with methanol and hexane and then dried overnight in an oven after each experiment [6]. Hu et al. found out that nanomagnetic catalyst $KF/CaO\text{-}Fe_2O_3$ exhibits good catalytic activity up to 14 times; however, catalyst loses its activity after 16 times of usage [58]. The solid acid nanocatalyst $TiO_2/PrSO_3H$ can reuse up to four times without significant loss of catalytic activity [118]. Kalavathy and Baskar observed that the biodiesel yield of Si/ZnO nanocatalyst has not reduced for the first few cycles but reduced to 34% after the third and fourth cycle due to the accumulation of organic matters active sites [65]. Feyzi, Hassankhani, and Rafiee maintained the activity of the $Cs/Al/Fe_3O_4$ nanomagnetic catalyst up to four times, but further usage reduces the biodiesel yield to 88.3% [53]. The iron(II) doped ZnO catalyst activity remains stable for four-cycle of 90%, but after the fourth cycle, the conversion was reduced to 87% [57]. The $Ca(OCH_3)_2$ nanocatalyst was reused for TEF reaction up to five times with FAME yield of 92–96%; further usage will reduce the FAME yield to 67.2% [6]. The $KF\text{-}CaO/Fe_3O_4$ has good durability, high recovery, and sustained its activity even after 14 reusability cycles with a catalyst recovery rate of more than 90%. However, after 16 times of use, the catalyst seriously loses its activity but recovery of catalyst still reaches to 84% even after 20 times of use [58]. The catalytic

Table 9 Features of various characterization techniques [6, 53, 54, 57]

Characterization technique	Features
SEM	Observe the particle size, morphology, and topology of the catalyst surface
TEM	Examine the morphology and particle diameter of nanocatalyst
XRD	Determine the phase structure, composition, and crystallinity of catalyst
FTIR	Characterize the composition of species adsorbed by surface
BET	Investigate the total surface area, total pore volume, and average pore size of the catalyst
AFM	Evaluate the particle size and average roughness of the surface
TGA	Determine the decomposition or breakdown nature of the catalyst

activity of Mn doped ZnO nanocatalyst remains stable for five cycles with biodiesel yield of 91% but decreased after 5th cycle due to deactivation of active sites of catalyst [59]. Vinoth et al. analyzed the reusability of PEG encapsuled Mn-doped ZnO nanocatalyst and found that no significant loss in biodiesel yield for few cycles but decreases to 85.8% in 5th cycle and 73.5% in 6th cycle from 87.5% [66].

Effect of main reaction parameters on biodiesel yield

The most important operating parameters on the biodiesel production include reaction temperature, methanol to oil molar ratio, reaction time, and the catalyst loading as detailed in the following.

Methanol to oil molar ratio

The methanol to oil molar ratio is a critical factor that affects the yield of biodiesel production significantly. The high fatty acid content requires more alcohol to proceeds further as the molar ratio depends on the nature of oil and catalyst. Bano et al. observed that the higher MO ratio results in the greater conversion of esters in short duration but at the same time more the molar ratio, greater the complexity of separation and purification processes [91, 129] which not only increase the cost of the process but also no longer affects the biodiesel production positively. Hence, the optimum ratio of MO ratio is required to increase biofuel production. Kalavathy and Baskar examined the impact of MO ratio in the presence of heterogeneous nanocatalyst waste clay doped with ZnO at (3:1, 5:1, 7:1, 9:1, 11:1 and 13:1) and found out that by increasing the MO ratio from 3:1 to 9:1 ended up improving the biodiesel yield from 51.48 to 93.52%, marking the 9:1 MO ratio as optimal. However, there is no significant increase in yield on further increase in MO ratio which might be due to accumulation of methanol on the catalyst surface of the nanocatalyst [65]. Likewise, Gardy et al. analyzed the impact of MO ratio (6:1 to 18:1) using solid acid nanocatalyst TiO_2/$PrSO_3H$ and noted that the highest FAME yield of 98.1% was obtained when the molar ratio of MO was steadily increased to 15:1 but further increasing the MO molar ratio to 18:1 decreases in FAME yield [118].

Catalyst loading

The catalyst content or loading plays a crucial role for optimizing the transesterification process as it affects the reaction rate while contributing to hydrolysis and soap formation. As the concentration of catalyst increases, the conversion of triglyceride and ester content increases, ultimately the production of biodiesel increases [130]. On the other hand, high catalyst weight can cause agglomeration, which reduces the interaction of active sites create mass transfer limitations [91]. Siow Hwa Teo et al. inspected the impact of catalyst loading using $Ca(OCH_3)_2$ nanocatalyst where the concentration of catalyst varied from 0 to 15 wt%. The maximum FAME yield of 92.0% was obtained at catalyst loading of 12 wt%. However, as the catalyst loading was increased to 15 wt%, the yield began to reduce to 61.6%, which might be attributed to inadequate diffusion between the methanol–oil–catalyst systems when catalyst overloading occurs in the TEF reaction process [6]. Thus, because of the increased surface area availability on the catalyst, any increase in catalyst dosage leads to better biodiesel production efficiency. Similarly, as Baskar et al. increased the iron(II)-doped ZnO nanocatalyst loading from 2 to 14 wt%, the FAME yield increased from 4 to 90%, respectively. However, as the catalyst concentration was increased beyond 14 wt%, there is slight reduction in the conversion, because slurry becomes viscous and emulsified [57].

Reaction temperature

The TEF process is generally carried out at a temperature (50–60 °C) below the boiling temperature of alcohol as reaction temperature plays an important role in determining the yield of biodiesel. The increase in temperature increases the reaction rate and ultimately decreases the reaction time, and hence optimum temperature is desirable for higher conversion [91, 130, 131]. Mandeep Kaur et al. conducted the TEF reaction of Karanja and Jatropha oil at room temperature (35 °C) by using nanocatalyst 1.75Li-CaO but time required longer duration for the completion of the reaction, i.e. 6 and 7 h for karanja and jatropha oils, respectively. Therefore, when the temperature of reaction increased from 35 to 65 °C, the time reduces from 6 to 1 h for karanja oil and 7 to 2 h for jatropha oil [5]. Also, Banerjee et al. investigated the effect of reaction temperature on biodiesel production using Fe_2O_3 nanocatalyst in the range of 35–75 °C, where maximum biodiesel yield of 84% achieved at 65 °C. The increase in biodiesel yield as the temperature increases from 35–65 °C is due to a decrease in algal oil viscosity, which allows better interaction of algal oil with the methanol. One more reason is that at higher temperatures, glycerol separates and settles out faster causing increased reaction rate and hence higher FAME content and biodiesel yield. However, increasing the reaction temperature beyond the optimal level (at 75 °C) can be attributed to the faster side reactions (for example hydrolysis of fatty acid methyl esters to corresponding acid and alcohol) as compared to transesterification resulting decrease in biodiesel yield [17].

Reaction time

The reaction time depends on the nature of the catalyst, but nanocatalyst usually requires a lesser time (1–2 h) for conversion. The increase in reaction time leads to greater conversion of fatty acid, but further increase in reaction time can deteriorate the yield and leads to more production of glycerol [91, 130]. Vinoth Arul Raj et al. while producing biodiesel from microalgae *Nannochloropsis oculata,* using Mn-ZnO capped with PEG varied the reaction time from 2 to 6 h. A maximum biodiesel yield of 87.5% was achieved after 4 h of transesterification reaction [66]. However, on further increase in the reaction duration beyond 4 h, the biodiesel yield decreased either due to the conversion of triglycerides to other compounds rather than esters or reverse reaction occurs as transesterification is a reversible reaction. Also, Baskar et al. produced the biodiesel from Mahua oil using Mn-ZnO nanocatalyst and observed that biodiesel yield was increased to 97% as the reaction time was increased from 20 to 50 min, indicating that increase in time increases the conversion but longer exposure of catalyst and methanol can reduce the yield [59].

Characterization and properties of biodiesel

The biodiesel can be characterized by various chromatographic (GC–MS, HPLC) or spectroscopic (NMR, FTIR) analysis techniques. The most common and accurate method for analyzing FAME is gas chromatography grouped either with mass spectroscopy (GC–MS) or with flame ionization detector (GC-FID) [10, 40]. The yield of biodiesel can be calculated by estimating the FAME percentage where C16 and C18 are the most common and suitable fatty acids for biodiesel production. GC may be utilized to calculate the percentage of FAME. The following equation can be used to determine biodiesel yield. [132]:

$$\begin{aligned}&\text{Biodiesel yield}\,(\%)\\&= \text{FAME}(\%)\,\text{result from}\,GC \times \text{Volume yield},\end{aligned} \tag{3}$$

whereas volume yield of biodiesel can be calculated using the following equation [132]:

$$\text{Volume yield}(\%) = \frac{\text{Volume of product}}{\text{Volume of feed}} \times 100. \tag{4}$$

Tariq, Ali, and Khalid reported that high-performance liquid chromatography (HPLC) is less engaged in the determination of FAME, but the analysis time is shorter than GC [107]. Furthermore, HPLC is an advantageous technique as it can be used for different feedstocks [40]. HPLC can be used to measure the total amount of mono-, di- and tri-glycerides [113]. The triglyceride conversion to FAME in percentage can be calculated using the following equation [133]:

$$\text{TG}(\%) = \text{TG(oil)} - \text{TG(sample)}/\text{TG(oil)} \times 100, \tag{5}$$

where TG denotes, the percentages of triglycerides converted, TG (oil) is the total triglyceride HPLC peak area in the diluted oil, and TG (sample) is the total triglyceride HPLC peak area in the biodiesel sample.

Madhuvilakku and Piraman observed that thin-layer chromatography (TLC) is a rapid method taken for the confirmation of conversion of triglycerides to fatty acid esters. TLC is the systematic method for qualitative analysis of oil and methyl ester content in the mixture [134].

The NMR can be used for the determination of blend level and to monitor the conversion of oil to FAME [10]. In this technique, the conversion is evaluated from the peaks corresponding to the different ppm ranges [40]. The percentage of biodiesel conversion was measured by the following equation [107, 134]:

$$C = 100 \times \frac{2A_{\text{ME}}}{3A_{\text{CH2}}}, \tag{6}$$

where C defines the percentage of conversion of triglycerides to FAME, A_{ME} denotes the integration value of methyl ester, and A_{CH2} denotes the integration value of methyl protons.

Another approach for assessing the TEF of oils/fats is Infrared spectroscopy (IR), where fatty acids and triglycerides are denoted by peaks and shoulders, respectively [10, 40, 107].

Amit and Ghosh investigated that the quality of biodiesel depends on the properties of biodiesel which can be calculated from FAME profile as presented in Eqs. (7) to (15) attained from GC–MS examination. The fatty acids profile significantly affects the various properties of biodiesel such as iodine value (IV), cetane number (CN), oxidative stability (OS), density, kinematic viscosity (KV), saponification value (SV), high heating value (HHV), cold filter plugging point (CFPP), long-chain saturation factor (LCSF) [18, 135]. A high cetane number is required for better engine efficiency and good cold start properties with less smoke [136]. Both viscosity and cetane number increase as chain length increases and the saturation degree of fatty acid [36, 137]. As overnight temperatures reach − 10 to − 15 °C poor cold flow properties such as wax settling and filter plugging occurs and more the saturation level is, poorer the cold flow property is [138]. Oxidative stability also requires better saturation degree of fatty acids [136]. Similarly, calorific value depends on saturation degree; greater the saturation degree, higher the

calorific value and polyunsaturation level remains proportionate to density [21, 26, 36].

$$\mathrm{IV} = \sum 254\mathrm{DB} \times \%\mathrm{FC} \div M, \tag{7}$$

$$\mathrm{CN} = 46.3 + 5458 \div \mathrm{SV} - (0.255 \times \mathrm{IV}), \tag{8}$$

$$\mathrm{OS} = 117.9295 \div (\mathrm{wt}\%C18 : 2 + \mathrm{wt}\%C18 : 3) + 2.5905, \tag{9}$$

$$\mathrm{Density} = 0.8463 + 4.9 \div \sum M + 0.0118 \times \sum \mathrm{DB}, \tag{10}$$

$$\ln(\mathrm{KV}) = -12.503 + 2.496 \times \ln\left(\sum M\right) - 0.178 \times \sum \mathrm{DB}, \tag{11}$$

$$\mathrm{SV} = \sum 560(\%\mathrm{FC}) \div M, \tag{12}$$

$$\mathrm{HHV} = 49.43 - 0.041(\mathrm{SV}) - 0.015(\mathrm{IV}), \tag{13}$$

$$\mathrm{CFPP} = (3.417 \times \mathrm{LCSF}) - 16.477, \tag{14}$$

$$\mathrm{LCSF} = (0.1 \times C16) + (0.5 \times C18), \tag{15}$$

where M is the molecular mass of each fatty acid, DB is the number of a double bond, and FC is the % of each fatty acid component. The comparison of various properties of conventional diesel and microalgal biodiesel is summarized in Table 10.

Current challenges associated with the use of nanocatalyst and future prospects.

In this section, some limitations of the current-state-of-the art research on biodiesel production from microalgae through nanocatalyst-based TEF process are reviewed as well as suggestions for future development are discussed.

(1) The economic viability of the microalgae biodiesel endeavor remains pitiable because of the high production costs, particularly the lipid extraction procedure. As a result, microalgae biodiesel is less cost-effective than alternative fuels like commercial diesel. To address this problem, nanomaterial might be introduced to the culture medium, which alters lipid metabolism and, therefore, escalates lipid accumulation. Thus, it proposes a focused strategy with well-defined targets, executable initiatives, and a comprehensive policy structure to stimulate the successful and sustainable development of biodiesel.

(2) The utilization of nanocatalyst in producing biodiesel offers certain advantages compared to other catalysts, such as high catalytic activity, better yield, and regenerability, but it is still in the suckling stage. However, for effective transesterification and better yield, additional alcohol is necessary and preparing appropriate catalysts might be expensive. To address existing difficulties, it is important to develop efficient and cost-effective catalysts that are also environmentally friendly. As a result, a catalyst with such properties that have been developed for effective TEF would be a watershed moment in the fuel industry.

(3) Nanocatalysts have certain difficulty responding to the transesterification process, despite their many advantages. The main disadvantage of nanocatalysts is the sintering of nanoparticles. In many catalytic processes,

Table 10 Comparison of microalgal biodiesel and conventional biodiesel [7, 10, 26]

Parameters	Units	Microalgal biodiesel	Conventional diesel
Density	Kg/L	0.864	0.38
Viscosity	mm^2/s at 40 °C	5.2	1.9–4.1
Flash point	°C	155	60
Boiling point	°C	–	180–340
Solidifying point	°C	− 12	− 50 to 10
Cloud point	°C	–	− 15 to 5
Pour point	°C	− 12	− 35 to − 15
Cetane number		–	51
Cold filter plugging point	°C	− 11	− 3.0
Higher heating value	MJ/kg	41	
Acid value	mg KOH/g	0.374	0.5 max
H/C ratio		1.81	1.81

metal atoms become unstable at high temperatures in the reactive environment, resulting in significant changes in the size and form of metal nanoparticles. Unwanted consequences such as non-uniformity, selectivity loss or reversal, and catalytic discontinuance result from such structural alterations. As a result, unless precautions are followed, sintering in nanocatalysts may limit their use to low-temperature and short-term applications [109].

(4) During the recovery stage, several metal-based nanocatalysts have some difficulties. In fact, in the transesterification reaction, lattice oxygen species form hydrogen bonds with methanol and glycerol, thus increases the viscosity of glycerol and form solids in a suspended form with some nanocatalyst types, which is difficult to recover [109].

(5) Apart from the category of feedstock utilized and appropriate catalyst, the commercialization of biodiesel from laboratory scale to commercial level poses a challenge, with heat and mass transfer issues being key stumbling blocks. Hence, developing a viable alternative technology to facilitate TEF is more conspicuous in terms of mass, heat, mixing intensity over the reaction.

Conclusion

Production of biodiesel from microalgae is considerably important when reserves of petro-diesel are depleting and vegetable oil-based fuels lead to food scarcity. Moreover, the rapid growth of microalgae and its high lipid content render it an ideal feedstock to produce biodiesel. The review argues various biodiesel production methods where transesterification is the most effective method to produce biodiesel. The nanocatalysts are of utmost favorable due to their large and competent surface-to-volume ratio, reusability, higher activity, yield, stability and resistance to saponification. The use of nanocatalysts can drastically reduce energy consumption and waste production which was associated with the use of other catalysts that are generally uneconomical, time and energy consuming. Moreover, nanocatalyst are non-toxic, and environmentally friendly and can be used as a suitable option for biodiesel production. Currently, the use of nanocatalyst is limited to a laboratory level but their use on an industrial scale will be of great importance. However, there are few complications associated with the use of nanocatalyst on industrial scale as it could be deactivated either by the blocking of active sites from impurities, soap and glycerol or leaching of the active species. Thus, before using nanocatalyst on industrial scale, it endorses a framework with precise objectives and novel technologies examined from the environmental and economic point of view as nanocatalyst can prepare and produce more efficient, stable, and renewable products.

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Declarations

Conflict of interest The authors have no conflict of interest.

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