f

International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

Recent Advancements in catalysis used for biodiesel production: A review

Ayaz Ahmad[1], Muhammad Idrees Jilani*[2]

[1]Department of Chemistry, University of Agriculture, Faisalabad-38040-Pakistan.

[2]Department of Chemistry, The University of Lahore, Lahore, Pakistan.

Abstract

The rapid depletion of conventional energy sources necessitates a critical assessment of alternative options to meet growing global energy needs. Biodiesel emerges as a promising and financially viable solution among renewable resources. Catalysts play a pivotal role in biodiesel production, with interest in both heterogeneous and homogeneous approaches. Homogeneous catalysis yields faster reactions with lower catalyst loading, but a major drawback is the challenging and costly separation process, hindering the reuse of these catalysts. Ionic liquids as homogenous catalysts, offer faster reactions but pose challenges in reuse due to complex separation processes. Despite their efficiency, practical scaling of ionic liquids to industrial levels faces hurdles such as high cost, toxicity, and instability. Biocatalysts, though an alternative, are temperature and pH-sensitive and costlier. In contrast, heterogeneous catalysts operate in a separate phase, providing stability and easy removal without extensive cleaning. However, issues like organic deposition and catalyst deterioration limit their widespread use. The application of nanomaterial-based catalysts shows promise in reducing biodiesel production costs due to easy separation and a fast reaction rate. This research aims to provide a comprehensive overview of catalyst developments in biodiesel synthesis, emphasizing the types used and their roles, advancements and limitations.

Keywords: homogenous catalysts, ionic liquids, biocatalysts, heterogeneous catalysts, nanocatalyts.

Full length article *Ayaz Ahmad, e-mail: iamayazahmad48@gmail.com

1. Introduction

Pollution is damaging our world severely [1-3]. Energy is essential for survival, and optimizing finite resources has become an urgent necessity, given the escalating demand for energy sources. At present, global energy consumption is predominantly fueled by fossil resources, with petroleum at 35%, coal at 29%, natural gas at 24%, nuclear energy at 7%, and renewable energy at 5% accounting aimed at the major share [4]. The excessive reliance on fossil fuels contributes to air pollution, global warming, and the depletion of these finite resources. It is projected that by 2050, all the hydrocarbon deposits will be worn out. To address these pressing energy challenges, experts are actively exploring clean energy alternatives sourced from renewable options like solar, wind, tidal, geothermal, and biomass energy [5]. Innovative concepts in technology can significantly enhance renewable energy solutions, offering sustainable answers to the world's expanding energy needs in an environmentally friendly manner. Biodiesel emerges as one promising fuel that could reduce dependence on petroleum and coal, providing a potential avenue towards a more sustainable energy future [6]. Biodiesel is a non-explosive and safe substitute for petroleum diesel, exhibiting comparable characteristics. Its compatibility with standard diesel-powered vehicles contributes to a reduction in pollutants, smoke, and exhaust odors [7]. Illustrated in figure 1, biodiesel is produced through the trans-esterification reaction involving alcohol (CH_3OH /C_2H_5OH) and tri-glyceride, facilitated by catalysts [8]. With its versatile chemical and physical properties, biodiesel serves as a clean and environmentally friendly energy source, requiring minimal to no modifications for use in diesel engines. The successful replacement of petroleum diesel with biodiesel hinges on meeting two fundamental requirements: easy availability, environmental acceptability, and economic viability [9].

Currently, the cost of plant oils constitutes a significant portion, ranging from 60 to 80%, of the total production expenses of fatty acid methyl/ethyl ester (biodiesel) [10]. Consequently, scientists and industry players have discovered a diverse array of raw materials for the manufacture of biodiesel, categorizing them into four categories, i.e. (i)edible oils (ii)non-edible oils (iii) animal fats and (iv) algal lipids waste oils etc. as presented in the

figure 2 [11]. This multifaceted approach to feedstock selection underscores the industry's efforts to address both economic considerations and environmental sustainability in the quest for a feasible alternative to petroleum diesel. Analyzing and classifying a variety of sources offer valuable perspectives on the possibility of widespread acceptance of biodiesel as a feasible and eco-friendly energy choice [12].

Triglycerides react to the alcohols (mostly CH_3OH/C_2H_5OH) in the presence of catalysts, a process identified as trans-esterification to yield biodiesel. Catalyzed reactions can be homogeneous or heterogeneous, and the end product is fatty acid alkyl esters, which are mostly found as fatty acid methyl/ethyl esters. Transesterification, as seen in figure 1, is the process by which triglycerides are converted one after the other into diglycerides, monoglycerides, and finally glycerin (glycerol) with the production of one mole of biodiesel (fatty acid methyl easter) with each [13]. These are catalytic, sequential, and reversible processes. Production of biodiesel usually involves a single-step trans-esterification procedure using alkali catalysts. Nonetheless, a two-stage process could be required in situations with high amounts of water content and free fatty acid (FFA). This entails an esterification step, which is preceded by a trans-esterification phase, and is first catalyzed by an acid [14].

2. Catalysts Used for Transesterification

Catalysts are materials that accelerate the pace of the reaction, by altering the path of a reaction which raises the output of the process. As shown in figure .3 many catalysts have been there for the trans-esterification process that produces biodiesel [15]. It is possible to accomplish this catalytic process by using both heterogeneous and homogeneous catalysts. When opposed to heterogeneous approaches, the homogeneous catalytic approach usually produces quicker reactions with lesser catalyst loading. However, one significant disadvantage of homogeneous catalysts is that they are difficult to reuse due to their complex and often expensive separation procedure In addition, many washing stages are required to remove these catalysts from the finished product, which calls for the use of water—typically deionized water—and produces a weighty amount of effluent [16]. As homogeneous catalysts, Ionic liquids (ILs) have attracted considerable attention owing to their elevated catalytic efficiency and convenient extraction from the end product. Furthermore, ILs have the potential to increase the catalytic efficacy of complexes, metal ions, and ligands when used as co-catalysts [17]. However, their practical scaling to industrial levels is prevented by reasons including high cost, toxicity, and instability under extreme circumstances, which restrict their application[18]. In contrast, heterogeneous catalysts operate in a distinct phase from the reaction system, providing stability across varied conditions and allowing for the easy removal of the catalyst. These catalysts don't require a lot of cleaning before usage. However, problems with organic deposition from the reaction mixture, catalyst microstructure deterioration, and partial leaching of active sites prevent these catalysts from being widely used. As a result, creating heterogeneous catalysts that are efficient and reusable continues to be a major difficulty in the biodiesel synthesis industry [19].

The increasing application of catalysts based on nanomaterials is significant because it can considerably lessen the cost of the production of biodiesel and speed up the transesterification process. The investigation of transesterification procedures, which are critical to the synthesis of biodiesel, has mostly been carried out using different types of nano-catalysts. The main goal of this research is to give a thorough summary of current developments in catalyst studies, with an emphasis on the kinds used in the manufacture of biodiesel and their uses. We want to clarify the function of catalysts in influencing the biodiesel synthesis landscape by exploring their advancements and disadvantages [20].

2.1 Homogeneous Catalysts

Homogeneous catalysis pertains to a set of reactions catalyzed by substances existing in the same phase as the reaction system. Homogeneous catalysts, which are well-known for their ease of use and quick reaction completion, are among the preferred catalysts for biodiesel synthesis. This group includes catalysts for acidic and basic catalysts. Homogeneous catalysts are usually dissolved in a solvent that shares the same phase as all of the reactants to maximize their efficiency in the catalytic process. The main drawback of this type of catalysis is the non-reusability of the catalyst due to the difficulty of its separation from the product which increases the cost of the process and also the production of contaminated product [21].

2.1.1 Homogeneous alkali catalysis

These catalysts, which are mostly composed of alkaline liquids, perform well in the transesterification process, but they are sensitive towards the free fatty acid even in minute concentration. Catalysts that are often utilized include NaOH, KOH, CH_3OK, CH_3ONa, C_2H_5ONa, and other carbonates [22]. Historically, base catalysts have been used in the transesterification reaction of premium oils containing almost less than 1-percent concertation of free fatty acids e.g. vegetable oil. Figure 4 depicts the base catalysis mechanism [23]. Alkali metal methoxide has shown greater efficiency in comparison to Alkali metal hydroxides. The drawback of using methoxides is the significant amount of free fatty acids that are left behind as soap. Because of this, an additional catalyst must be utilized, and it is depleted during the soap-forming process [24]. Alkaline catalysts, while effective in transesterification, come with certain drawbacks such as saponification, slow reaction, and catalyst deactivation. Undesirable saponification occurs when the free fatty-acid concentration surpasses 2.5% in the reaction system, leading to the need for additional energy to address various technical issues. To mitigate this, the oil undergoes heating and filtration to eliminate abnormal deposits like suspended particles, inorganic contaminants, and pollutants. This process prevents the formation of undesirable byproducts during the reaction. However, it is advisable to refrain from heating the oil beyond its boiling point [25].

Saponification can be avoided by the introduction of co-solvent; it also increases the rate of reaction. In certain studies, researchers employed CH_3OH as a solvent and C_2H_5OH as a co-solvent and potassium hydroxide (KOH) catalyst for biodiesel production from residual cow tallow.

Ethanol acts as an active ester exchange agent with low polarity, proved to be a valuable co-solvent, contributing to a 3.08% increase in yield. Consequently, the reaction time was significantly reduced by 61.11%, and the formation of soap was successfully avoided. Homogeneous alkali catalysts offer notable advantages, including affordability, rapid production of high-quality goods, and ease of use. The performance of commonly used alkali catalysts has been elaborated in the table 2 [26]. Base catalyze transesterification is faster as compared to acid-catalyzed transesterification. The use of edible, premium, and extraordinarily pure virgin oils is a requirement of the commercially approved base-catalyzed manufacturing technique, which adds to the continuing discussion about the relative importance of fuel and food [27]. The non-recoverability of the catalyst, in this process makes it useless for further operations, which is another serious disadvantage. Thus, the catalyst has to be neutralized and disposed away as a waste stream consisting of aqueous salt. Furthermore, there are environmental issues because the procedure of cleansing biodiesel produces a substantial amount of wastewater [28].

2.1.2 Homogeneous Acid catalyst

Acid catalysts remain unaffected by the concentrations of free fatty acids (FFA) in the input oil and demonstrate efficient catalysis of both esterification and transesterification processes simultaneously. Consequently, acid catalysts work well with affordable raw materials that have a high FFA content, such as animal fats, leftover cooking oil, and non-edible oils. Better access to the catalyst's active areas is made possible by homogeneous catalysts. This category includes HCl, H_2SO_3 and H_2SO_4; which are frequently used for biodiesel production [29]. Figure 5 illustrates the acid transesterification pathway. Sulphuric acid is most commonly used as a catalyst due to it may catalyze reactions as compared to other acids at very low temperatures, H_2SO_4 is a frequently used acid catalyst. Table.3 provides info about the catalytic efficiency of H_2SO_4 catalytic. Even with 90% water content, *Chlorella pyrenoidosa* algal oil may be converted with a 93% yield using 0.5% H_2SO_4. Interestingly, there haven't been any documented negative impacts of water presence on H_2SO_4-based biodiesel synthesis [30].

By increasing the production of alkyl esters and lowering material costs, using acids as catalysts in the process lowers costs. But this method has disadvantages as well: it requires greater temperatures, operates more slowly, is more prone to corrosion, and is more expensive to purify and isolate. Reduced reaction rates are involved in the transesterification processes that acids catalyze. In accordance with the data given in Table.1 and Table.2, it can be estimated that the reaction rate catalyzed by an acid is much slower as compared to homogenous alkali catalysts. However, the higher energy needs and lengthier rate of reaction compared to base catalyzed reactions make this technique less viable commercially [31].

2.1.3 Two-step transesterification

In order to produce biodiesel, researchers have focused on a unique two-step process that uses both alkali and acid as catalysts. By speeding up reactions and skipping the saponification stage, this technique seeks to solve the disadvantages of single-step alkali/acid homogenous catalyzed biodiesel production. Because lower-quality oils contain high amounts of free fatty acid, the critical first step is to lower FFA levels to 0.5–1% using an acid catalyst in an esterification process. In the second stage, transesterification is aided by the use of a base catalyst, which results in an increased biodiesel output [32].

Recently, a semi-industrial-scale pilot-scale microreactor was employed for the synthesis of biodiesel. Initially, a 1% H_2SO_4 solution was utilized to decrease the concentration of free fatty acids (FFA). In the subsequent step, KOH served as the catalyst, with optimal yields of 97.2% achieved within 1 minute and 98.26% within 2 minutes of residence time at a methanol to waste cooking oil (WCO) molar ratio of 9.4:1, amount of catalyst was 1.16 wt.%, and a temperature of 64.2 °C. In this two-step process, a heterogeneous-catalyst was employed in the second phase following the use of a homogeneous base-catalyst in the first, resulting in a final biodiesel yield of 98% [33]. When oil is stored, the concentration of free fatty acids usually increases. For example, after two months of storage at room temperature, the fat content in rubber seed (*Hevea brasiliensis*) oil grew from 2 to 45 weight percent. To overcome this situation, biodiesel production was carried out in three steps. The oil was first saponified, which involved heating it to 68–70 °C for 30 minutes and adding alcohol and NaOH to it. After that, an HCl catalyst was used to lower the quantity of free fatty acids in the resultant solution. In the last stage, free fatty acids were esterified using an acid catalyst to produce Fatty Acid Methyl Ester. The described approach has drawbacks, such as a sluggish esterification rate and relatively prolonged reaction durations, despite yielding higher biodiesel quantities. The two-step procedure is made more complicated by the additional steps required to recover the catalyst used in both phases [34].

2.2 Ionic liquids catalysts

For the transesterification step of biodiesel synthesis, a variety of different catalysts can be employed; however, ionic liquids (ILs) have gained popularity due to their remarkable stability, high catalytic activity, and facilitated product separation. As co-catalysts, ligands, complexes, and metal ions can all be added to ILs to boost their catalytic activity [35]. The names and structures of frequently used ionic liquids are included in the table.3. However, several obstacles stand in the way of the commercial use of ILs as of yet. These difficulties include the paucity of studies on the use of ionic liquids in the production of biodiesel and the lack of detailed physical properties like conductivity and viscosity. There are still more obstacles to overcome, such as lowering costs and improving the reusability of ionic liquids. As of right now, ionic liquids continue to be more expensive than traditional catalysts [36].

It is crucial to remember that the total process costs will decrease the more times these catalysts are utilized. Thus, studies concentrating on lowering these ionic liquids' manufacturing costs and improving their reusability might improve this system's usefulness. Ionic liquids with basicity or Brønsted acidity are particularly interesting, as the literature points out. They not only have a little chance of

contaminating the environment, but they also convert vegetable and animal fats into biodiesel at high yields in a short amount of time and with moderate reaction conditions [37]. Furthermore, without needing an earlier oil preparation for moisture removal, Brønsted acidic ionic liquids may effectively convert both free fatty acids and triglycerides to biodiesel. They are a viable option for biodiesel production because of this feature, which simplifies the process and lowers expenses [38].

2.3 Biocatalysts

Biocatalysts have surfaced as a potentially viable option to facilitate the sustainable synthesis of biodiesel within the catalytic category. The necessity to address and reduce greenhouse gas emissions linked with traditional petroleum or fossil fuels makes the employment of biocatalytic technology in the manufacture of biodiesel imperative. Usually, lipases catalyze the transesterification process, which is a key stage in the creation of biodiesel. Because lipases have great physiological and biochemical properties, they are excellent catalysts for converting feedstocks into biodiesel. This enzymatic method provides a technique to lessen the adverse environmental impact of conventional diesel fuels while also being in line with sustainability objectives [39]. The enzymatic activity of lipases derived from bacteria and fungi leads to the generation of methanol and ethanol, with concentrations varying between 70% and 95%. The final result of this procedure is biodiesel, which is mostly made up of fatty acid alkyl esters. The precise composition is dependent upon the kind of alcohol used in the synthesis. This emphasizes how flexible biodiesel synthesis is and how the type of alcohol used may affect the end product's properties [40].The difficulties presented by acid and alkali-based-catalyzed processes can be overcome by using the biocatalytic synthesis method for biodiesel production. Biocatalysis, in contrast to conventional techniques, reduces issues related to contaminants and unwanted byproducts. Because they can create biodiesel from cheaper oils even with a high ratio of free fatty acids, they have several positive effects on the economy as well as the environment. Notably, the biocatalytic method produces pure and extremely valuable glycerol, produces the least amount of effluent, operates under gentle reaction conditions, and prevents soap (free fatty acid) development [41]. This demonstrates the biocatalytic biodiesel synthesis's effectiveness and long-term sustainability, establishing it as a competitive option in the biodiesel production space. Low energy consumption results from easing the biodiesel manufacturing process by simply removing biocatalysts from the reaction solution and lowering the danger of contamination. Advances in biomaterial catalysts, such as xylanase, glucosidase, laccase, cellulose, and cellobiose, have greatly increased the robustness and efficiency of catalytic processes [42]. Due to high manufacturing costs, lengthy reaction periods, and difficulties with usage and reusability, biocatalysts are inefficient. One major problem with biocatalysts, and particularly lipases, is that methanol, the acyl acceptor in transesterification deactivates them. The amount of alcohol that can be present during the reaction is limited by this restriction. aggregation of enzyme molecules may result from the non-specific interaction of solvent molecules with the protein, which can cause permanent deactivation. Furthermore, solvent molecules have the ability to non-covalently bind to the substrate binding site of the enzyme, so impeding competition. It is essential to comprehend the process and provide technological solutions in order to properly handle these limits [43].

Many supports, including granular substances, glassy and metallic substrates, nanotubes of carbon, polymeric supports, colloidal supports, and porous and non-porous materials including mesoporous silicates and meso-cellular foam, can be used to immobilize enzymes. Mesoporous materials have the potential to entrap proteins and other biomolecules inside their internal pores by entrapment and on their exterior surface through covalent attachment, which increases stability when alcohol is there. Metabolic engineering, cell-surface display technologies, and whole-cell biocatalysts are further strategies for the microbial production of biodiesel [44].

2.4 Heterogeneous catalysts

The various phases of heterogeneous solid catalysts provide facile catalyst recovery from the reaction system, hence permitting many cycles of reuse. A vast range of solid catalysts have been employed for the production of biodiesel within the past years. The fact that heterogeneous catalysts can tolerate the presence of free fatty acid and water in the feedstock is one factor contributing to their increasing significance in the biodiesel manufacturing process. Moreover, less soap is formed when heterogeneous catalysts are used. The multicycle reuse of solid catalysts increases biodiesel production's economic viability. Larger industrial production levels are made possible by the flexibility provided by heterogeneous solid catalysts, which also enables the continuous manufacture of biodiesel in fixed-bed reactors [45].

3.4.1 Heterogeneous Base Catalysis

Heterogeneous base catalysts are essential for overcoming a number of obstacles, especially in procedures such as saponification when glycerol cannot be separated from the methyl ester layer. When compared to alternatives, these catalysts have clear benefits, such as simple recovery and reusability, little effect on waste materials, non-corrosiveness, selectivity, and tolerance for elevated concentrations of moisture and free fatty acids (FFA). They also encourage ecologically friendly practices and are reasonably priced. Research suggests that solid-base catalysts may be modified to improve their lifetime, activity, and selectivity. Alkali-earth metal-oxides including CaO, MgO, BaO, SrO, BeO, and RaO as well as transition-metal oxides are a few examples of efficient solutions [46]. Ion exchange resins, alkali metal compounds based on alumina [47], mixed metal oxides [48] $CaTiO_3$, $CaZrO_3$, $Ca_2Fe_2O_5$ [49], and $CaMnO_3$ [49] are also important. The solid-base transesterification catalysts include, but are not limited to, CaO, Li/CaO, MgO, KNO_3/ Al_2O_3, KF/Al_2O_3 KF/ZnO, K_2CO_3/Al_2O_3, and SrO [50]. Moreover, basic hydrotalcites such as Mg/Al, Li/Al, Na/NaOH/- Al_2O_3, [51]anion exchange resins, base zeolites, hydrotalcite, calcium carbonate rock, Li/CaO, and MgO/KOH are effective [52]. In the transesterification process, oxide catalysts exhibit great

yields and stability. The mechanism of heterogeneous base catalyzed transesterification is explained in the figure 6 [53]. One notable feature of the heterogeneous alkali catalyst is its capacity to produce large yields at increased reaction speeds. The possibility for significant processing cost savings through catalyst recovery and repurposing following the reaction is a noteworthy benefit. Heterogeneous alkali catalysts are less harmful to the environment, less corrosive, and maybe more affordable. Furthermore, they may be easily included in the ongoing biodiesel synthesis process. However, the drawbacks of heterogeneous alkali catalysts include their propensity to absorb moisture during storage, their vulnerability to air exposure that can cause poisoning, the requirement for a higher alcohol-to-oil molar ratio, their sensitivity to free fatty acid content because of their intrinsically alkaline nature, the possibility of soap formation in the presence of FFA exceeding 2 percent by weight, and the risk of active site leaching [54].

2.4.2 Heterogeneous acid catalysis

These types of catalysts show less worries about the environment, fewer toxic effects, as well as less corrosion as compare to their homogenous counterpart. They have a variety of acidic sites that range in Lewis's acidity. They appear to show slower reaction rates than basic catalysts, even if they yield promising results under mild reaction conditions. Certain conditions are necessary for these catalysts, such as a high-catalyst loading, a high-temperature, then a long time of reaction. Furthermore, for the purpose of producing biodiesel, solid acid catalysts enable the concurrent transesterification of oils with a large concentration of free fatty-acid content [55]. More specifically, fatty acid esterification is accelerated by solid acid-catalysts with organosulfonic groups includes Nafion and Amberlyst. The transesterification technique uses a special mesostructured catalyst that has been treated with sulfonic acid; conversion rates of up to 100% have been recorded [56]. While heterogeneous acid catalysts demonstrate promising outcomes under moderate conditions, their reaction rates are comparatively sluggish when juxtaposed with heterogeneous alkali catalysts. Additionally, these catalysts often necessitate elevated temperatures, high catalyst-loading, and a higher alcoho-to-oil ratio in contrast to their alkali counterparts. Nevertheless, certain instances exhibit accelerated reaction rates (0.5–2 hours) at temperatures ranging between 70 and 80 °C, albeit requiring a higher alcohol to oil ratio (20:1) to achieve a conversion rate exceeding 90%. It is imperative to note that leaching of catalyst sites may occur, leading to catalyst deactivation and potential contamination of the product [57].

2.5 Nano-catalysts

Cutting-edge investigations into innovative and cost-effective nanomaterials for diverse applications, including carbon nanotubes, nanoclays, nanofibers, nanocomposites, porous nanomaterials, nanowires, and nanoparticles, have been conducted by researchers over the past few decades. Nanoparticles, characterized by pseudo-spherical or spherical shapes with a diameter below 100 nm, have proven utility in various catalytic processes. This represents one of the pioneering applications of nanotechnology. These catalysts are recognized for accelerating the transesterification reaction by eliminating unnecessary steps and reaction byproducts. They support simple recovery, reusability, and an economical procedure. These catalysts also have several benefits, such as the capacity to tolerate an elevated number of free fatty-acids molecules and moisture, which is important in some sensitive elevated temperatures and high-pressure scenarios [58].

These catalysts may be tuned for the highest yield of reaction products by modifying elemental composition, surface efficiency, and atom count. They also have great stability, efficient surface areas, and enhanced resistance to saponification. Various techniques, such as vacuum deposition, vaporization, coprecipitation, electrochemical deposition, self-propagating elevated temperature synthesis, microwave-assisted ignition, hydro-thermal and solvo-thermal methods, impregnation, and sol–gel technology, are employed in the fabrication of these catalysts. The nanoparticles that make up these catalysts range in size and shape from less than 100 nm. Both homogeneous and heterogeneous catalysts present significant benefits in the form of reusability; selectivity; activity and efficiency. In the realm of biodiesel synthesis, there are two main categories of nanocatalysts: non-magnetic and magnetic [59].

2.5.1 Nonmagnetic Nano-catalysts

Numerous nonmagnetic nanocatalysts are commonly employed in biodiesel production, including hydrotalcite, zeolites, metal-oxides, sulfated-oxides, and zirconium oxide [60]. ZrO_2 based on mesoporous silica show extraordinary catalytic activity even after the fifth catalytic phase. The mechanism of transesterification using ZrO_2 based on the mesoporous silica is shown in the figure 7 [61]. According to studies, ZnO nanorods produced biodiesel from olive oil with a yield of 94.8% [62], somewhat higher than the typical ZnO output of 91.4% [63]. Co/ZnO nanoparticles at 2.5 weight percent, 60°C for three hours, and an alcohol-to-oil ratio of 9 were used to achieve 98.03% [64]. By the alteration of the surface of $NaAlO_2/\gamma\text{-}Al_2O_3$, the maximum output of 97.65% has gained out at 64.72°C, 10.89 weight percent catalysts, and alcohol to oil ratio O of 20.79:1 [65]. Nanomaterials encapsulated with calcium, in particular, represent alkaline earth metal compounds that function as non-magnetic catalysts for biodiesel production. MgO/TiO_2 [66], Mg-Al hydrotalcite [67], KF/CaO, Mg/Al, Li/CaO, MgO [68], MOFs (metal-organic frameworks) [69], zeolite, and hydrotalcite are notable instances of these nonmagnetic catalysts [70]. Due to their expansive surface-area, excellent catalytic-activity, then efficient charge carriage pathways, nanocatalysts are gaining significant attention for their applications [71]. The intrinsic properties of carbon nanotubes (CNTs), such as their enormous surface area, hollow-geometry, and well define structure, and ease of functionalization, have made them more appealing in the production of biodiesel.N_2O-supported carbon nanotubes (N_2O /CNTs) are a heterogeneous catalyst used in the production of fatty acid methyl ester (biodiesel) from waste cooking oil (WCO). A 97% biodiesel yield was obtained under ideal reaction conditions, which included a 3% catalyst loading, a 20:1 alcohol (CH_3OH) to oil ratio, and 3 hours at 65 °C. The catalyst showed reuse-ability for up to three cycles, despite occasional leakage or poisoning [72].

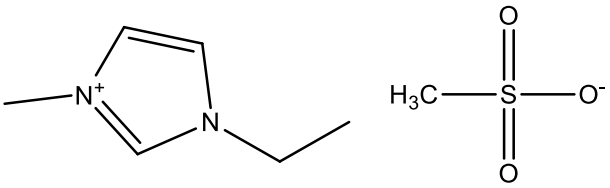
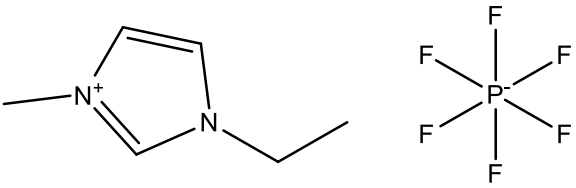
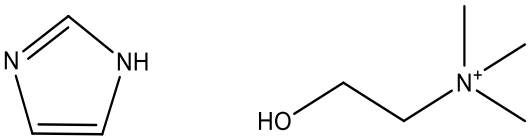
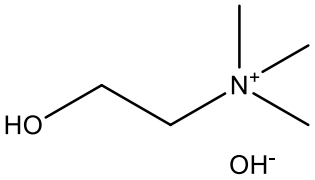
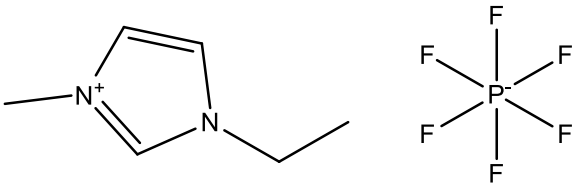
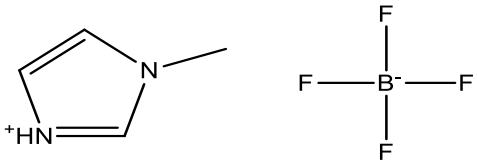
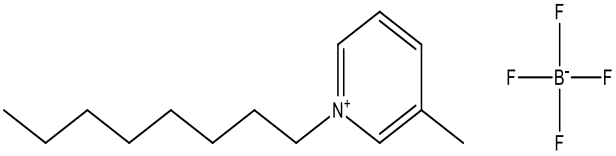
Table 1. Efficiency of commonly used alkali catalysts with the different oils.

Catalyst	Wt.%	Raw material	Molar ratio of alcohol/oil	T (°C)	Time (min)	Yield
Potassium hydroxide	1	*Pongamia pinnata*	10:1	60	90	92%
Sodium hydroxide	1	Canola oil	6:1	45	15	98%
Potassium hydroxide	1	Rapeseed	6:1	65	120	95-96%
Sodium hydroxide	1	Sunflower oil	6:1	60	120	97.1%
Potassium hydroxide	1	Vegetable oil	6:1	25	40	51-87%
Sodium hydroxide	1	Cotton seed oil	6:1	60	60	97%
Sodium methoxide	0.6	Soybean oil	6:1	60	60	97%
Potassium hydroxide	1.5	Roselle Oil	8:1	60	60	99%
Sodium hydroxide	1	Frying oil	7.5:1	50	30	96%
Potassium hydroxide	1	Vegetable oil	6:1c	25	40	51-87%
Potassium hydroxide	1	Duck tallow	6:1	65	180	83.6%
Potassium hydroxide	1	Waste cooking oil	12:1c	60	120	72.5%%

Table 2. Performance of H_2SO_4 as catalyst with different type of raw material

Catalyst	Wt.%	Raw material	Mole ratio(alcohol/oil)	T(°C)	Time (min)	Yield
Sulphuric acid	2.5	Tallow	30:1	60	1440	98.3%
Sulphuric acid	3	Soybean oi	30:1	60	2880	98%
Sulphuric acid	1-2	Tobacco seed	24:1	60	25	91%
Sulphuric acid	2	*Zanthoxylum bungeanum*	18:1	60	80	98%
Trifluoroacetic acid	2 M	Soybean oil	20:1	120	300	98.4%
Sulphuric acid	0.5	*Chlorella pyrenoidosa*	20:1	65	120	90%

Table 3. different types of ionic liquids catalysts used for biodiesel production

Name	Structure	Ref.
[BMIM][CH3SO3] (1-Ethyl-3-methylimidazolium methanesulfonate)		[73]
[BMIM][PF6] (1-Ethyl-3-methylimidazolium hexafluorophosphate)		[74]
ChIM (choline imidazolate)		[75]
ChOH (Choline hydroxide)		[76]
[EMIM][PF6] 1-ethyl-3-methylimidazolium hexafluorophosphate		[77]
[HMIM][BF4] 1-methylimidazolium tetrafluoroborate		[78]
[OmPy][BF4] 1-octyl-3-methylpydridinium tetrafluoroborate		[79]

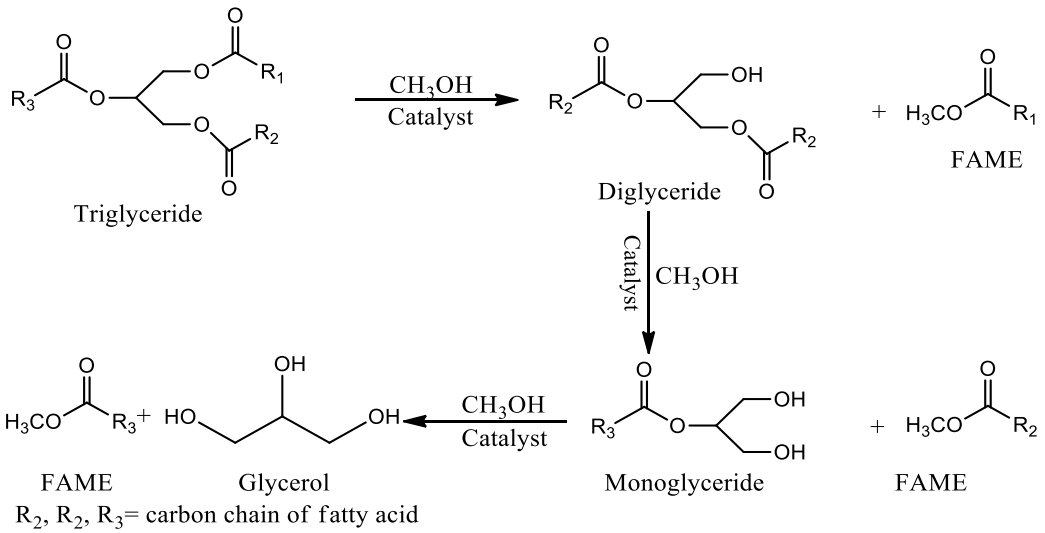


Figure 1. Transesterification reaction for biodiesel (FAME).

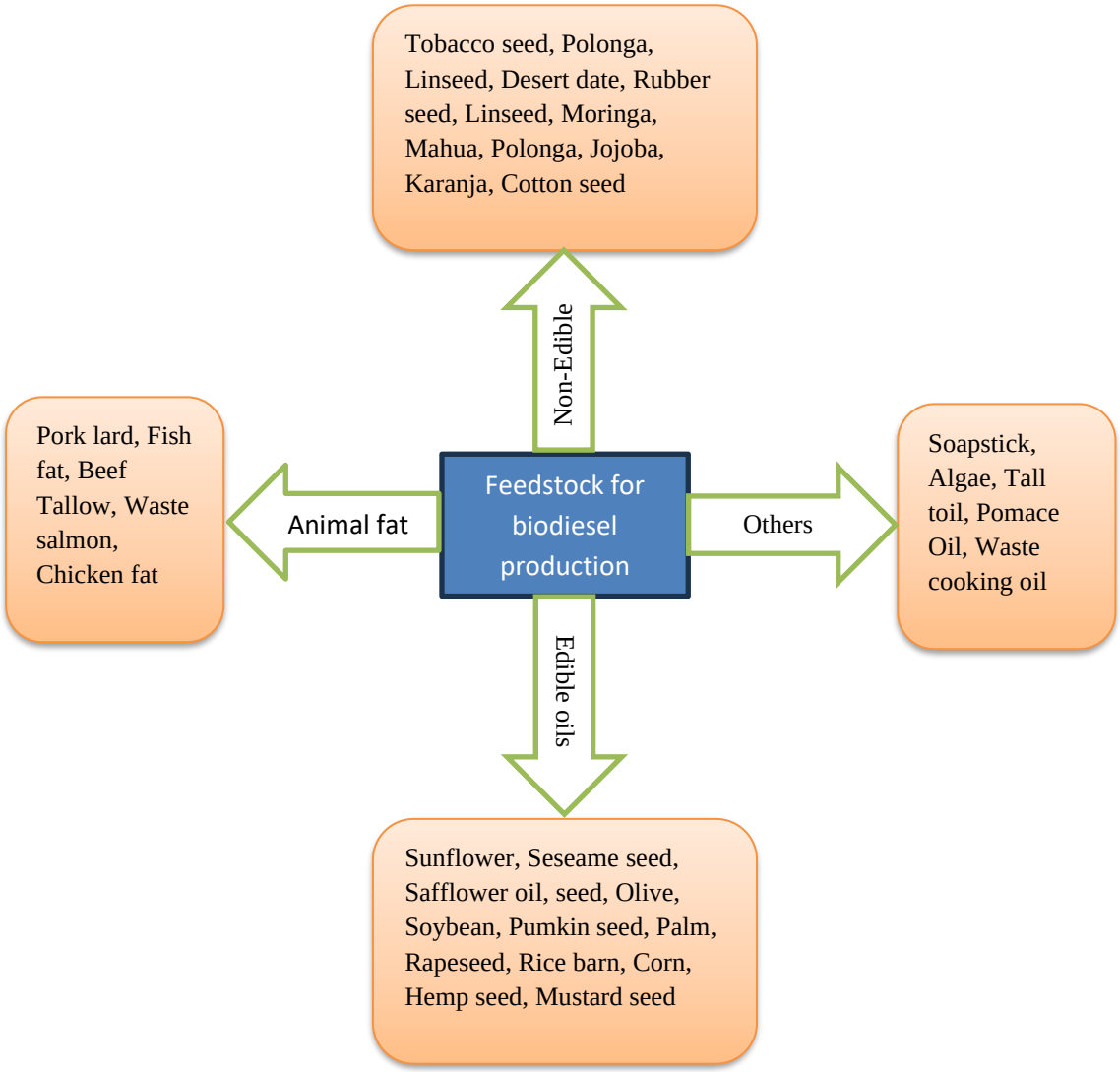


Figure 2. Different types feedstocks used for biodiesel production.

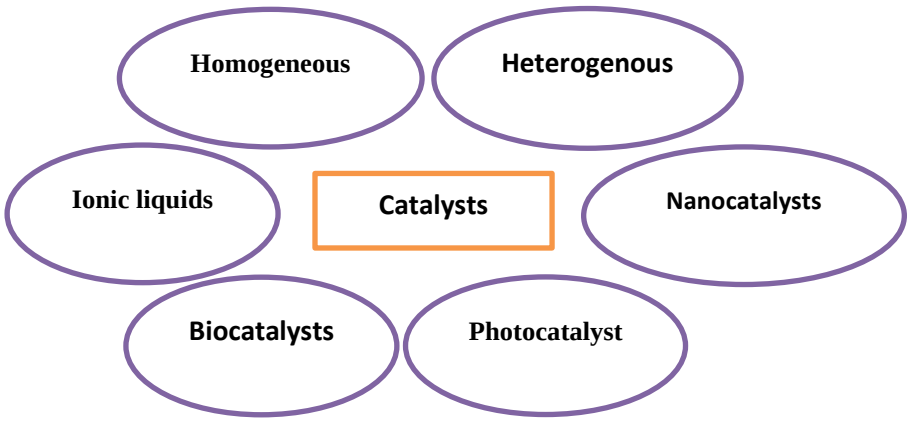


Figure 3. Different types of catalysts used for biodiesel production

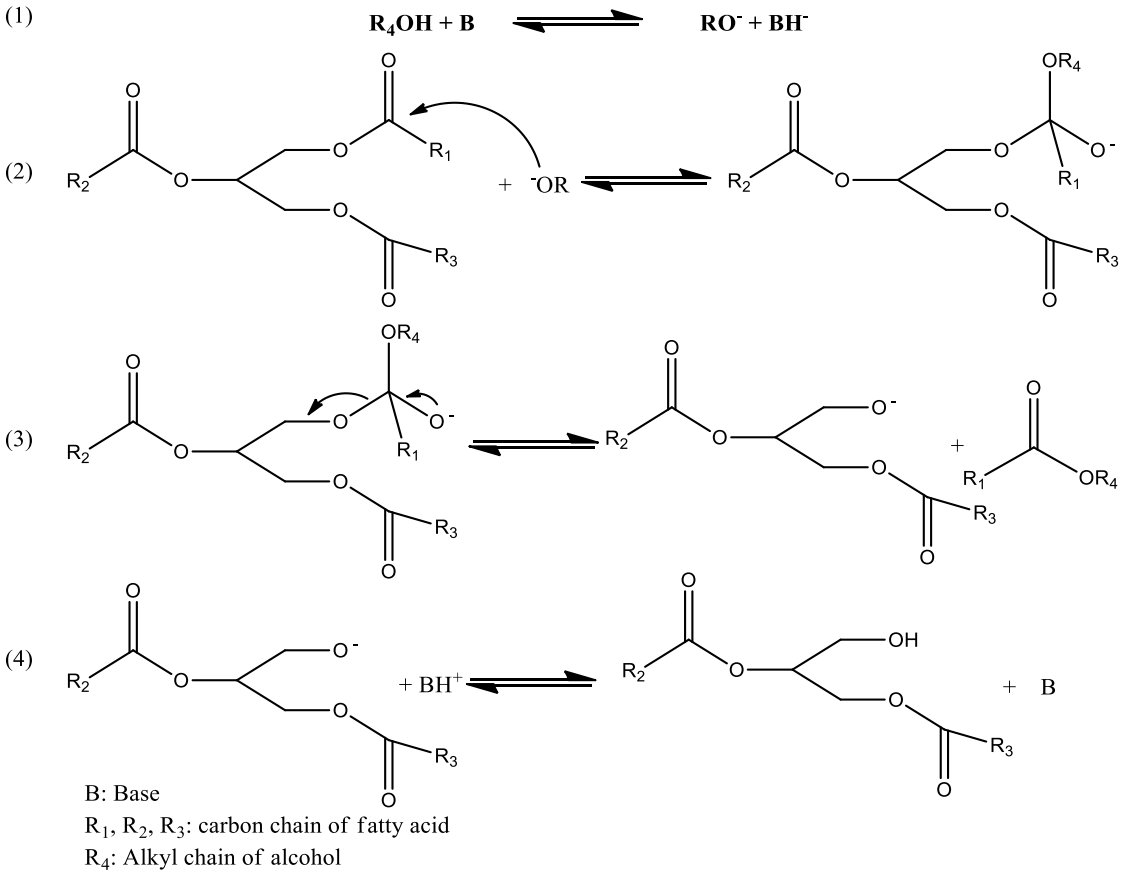


Figure 4. Homogeous based catalyzed transesterification reaction

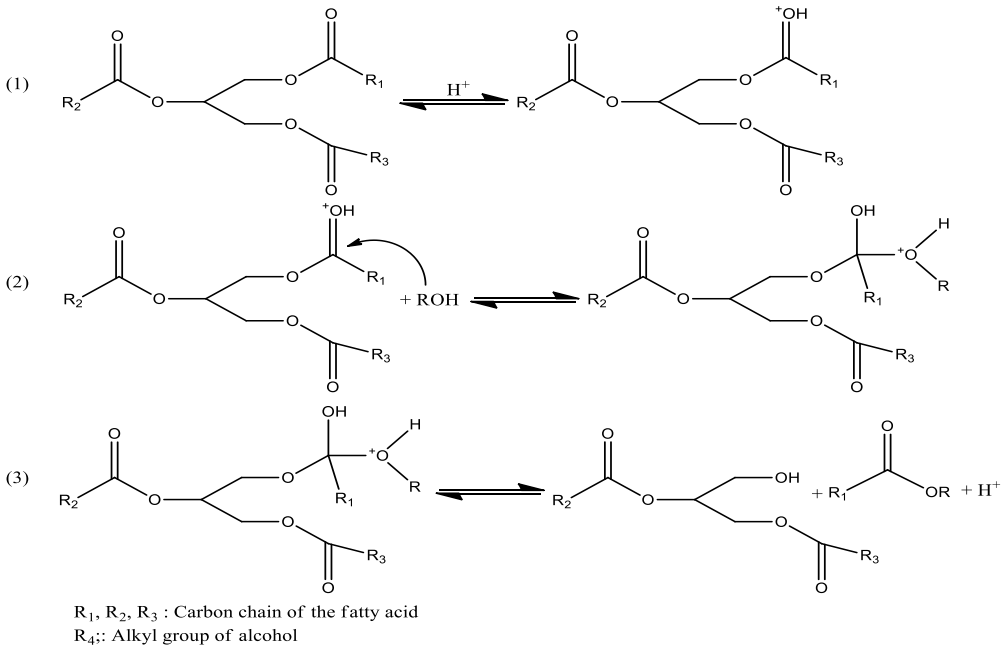


Figure 5. Homogenous acid catalyzed transesterification

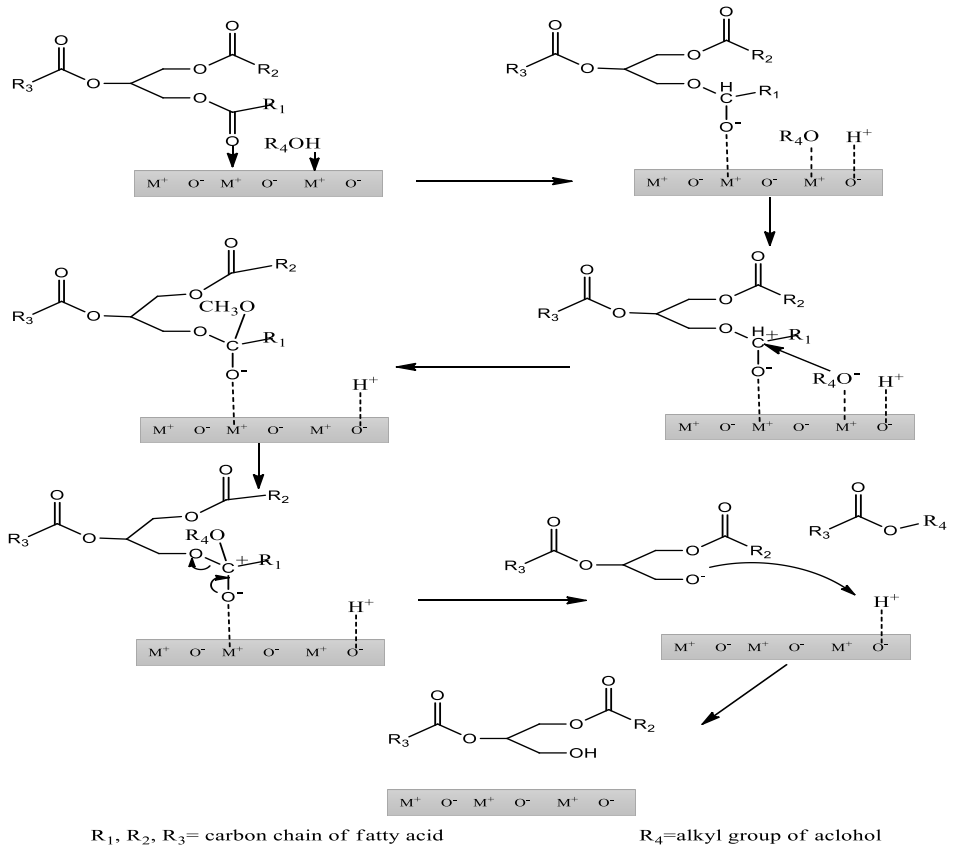


Figure 6. Heterogenous transesterification by metal oxides

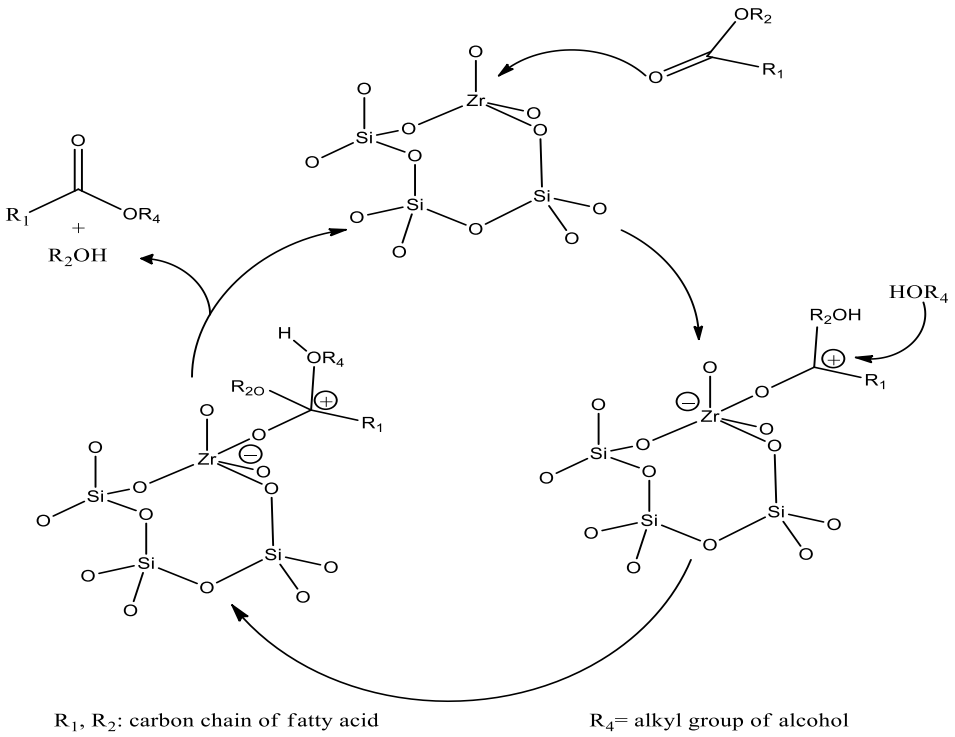


Figure 7. Transesterification by ZrO_2 nano-particles bases on SiO_2

Nano-catalysts exhibit significant surface activity, enabling the attachment of diverse organic groups. Moreover, their heightened surface activity promotes the amalgamation of nano-catalysts with minerals, resulting in the creation of composites. The performance of these catalysts can exhibit substantial variation due to their chemical modifiability, allowing for interaction with a range of groups. One of the main issues with solid catalysts is that they may need to be separated from the reaction mixture in order to be reused after being filtered through a membrane. Using magnetic nanocatalysts can solve these issues since, compared to filtering techniques, magnetic separation reduces catalyst loss and increases reusability [80].

2.5.2 Magnetic Nano-Catalysts

These catalysts streamline the chemical reaction process without the need for ultra-filtration or centrifugation. They serve as efficient tools for swiftly extracting catalysts from reaction systems, providing an alternative to laborious, solvent- and energy-intensive extraction methods while preserving catalytic activity for subsequent cycles. Additionally, they present cost-effective options for raw materials [81]. Numerous magnetic catalysts have been discovered and used in the production of biodiesel recently, including Fe_3O_4, MgO / Mg Fe_2O_4, CaO/Fe_3O_4, $Ca(OH)_2/Fe_3O_4$, $Cs/Al/Fe_3O_4$, $KF/CaO\text{-}Fe_3O_4$, $Ca/Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2$ [82], for example, it has been established that the CaO- Fe_3O_4, magnetic catalyst is used in the synthesis of biodiesel from palm seed oil [83]. Furthermore, processes including soybean oil such as esterification, trans-esterification, and hydro-lysis have been made easier by magnetic nanocatalysts made of tin oxide and cadmium oxide [84]. Moreover, very efficient catalysts such as Fe_3O_4 and $Fe_3O_4@SiO_2$ magnetic nanoparticles have proven essential in generating 96% of the required biodiesel since they are recyclable catalysts [85]. $ZnO/BiFeO_3$ catalyst use has shown promise in producing biodiesel from canola oil, generating 95.43% and 95.02% in the first and second cycles, respectively [86]. In another example, SnO is used, and after an hour of reaction at 200°C, it obtains 84% esterification without any loss. Because of this, magnetic catalysts are very stable, efficient, and reusable, and they also follow environmentally benign processes [87].

2.6 Photocatalysts

Photocatalysis emerges as a promising method to reduce pollution, facilitate biodegradation, and contribute to biodiesel production. Recent research has explored different materials as photocatalysts for biodiesel synthesis, organic waste breakdown, and waste degradation. Metal-based nanoparticles exhibit efficient absorption of solar energy, initiating various chemical processes. Various metal-based

nanomaterials can absorb diverse types of light, including UV, visible, and solar light. The absorption of light at specific wavelengths leads to the production of the surface plasmon resonance effect by metal nanoparticles. Surface plasmon resonance refers to the release of electrons when light interacts with the thin metal surface of the semiconducting material [88].

Silver (Ag), copper (Cu), nickel (Ni), gold (Au), iron (Fe), nickel (Ni), and other metal nanoparticle compositions may all be used to create the Surface Plasmon Resonance (SPR) effect and effectively absorb visible light. A nanoparticle's ability to catalyze photosynthesis is dependent upon its size, composition, shape, and interactions with other nanoparticles. Therefore, by modifying these crucial variables, it may be possible to develop and manufacture metal-based nano-photocatalysts that efficiently capture solar energy. In the realm of biodiesel production, utilizing photo-driven metal nanoparticles proves to be a more environmentally friendly and energy-efficient approach compared to conventional thermal-driven methods. CuO/ZnO [89], Cr/SiO_2 [90],TiO_2, $CaO-TiO_2$ [91], TiO_2-Cu_2O[92], titania nanotubes [93], Graphene carbon nitride composite ($SrTiO_3$/g-C_3N_4) [94], CaO/TiO_2, TiO_2/g-C_3N_4nanocomposite are the recently developed photocatalytic nanomaterial that has been successfully used for the biodiesel production [95].

The remarkable photocatalytic properties of metal nanoparticles are hampered by issues including high prices, agglomeration problems, and toxicity concerns. These photocatalysts require both visible and ultraviolet light to activate, and are stable only in laboratory conditions. Enhancements in shape and properties combined with a lower band gap energy might make solar energy activation possible. The manufacture of biodiesel using photo-driven catalysis is confronted with several obstacles, such as the restricted investigation of esterification or transesterification techniques and the frequent utilization of costly noble metals [96].

3. Conclusions

Biodiesel contributes significantly to achieving net-zero emissions by providing a renewable and carbon-neutral alternative to traditional fossil fuels, reducing overall greenhouse gas emissions, enhancing energy security, and promoting sustainable and circular practices in the energy sector. Importance of catalysts in biodiesel production cannot be overstated. They are instrumental in accelerating reactions, increasing yields, ensuring product quality, supporting reusability, and promoting sustainability. The continuous improvement and innovation in catalytic systems contribute to the ongoing development of biodiesel. In conclusion, the recent surge in catalyst development has been fueled by the pursuit of superior catalytic effectiveness, especially in the context of biodiesel generation. A multitude of investigations has been undertaken to explore different catalysts, aiming to optimize the efficiency of biodiesel synthesis. The foundation of catalytic systems for this purpose encompasses both homogeneous and heterogeneous catalysts, representing the most advantageous choices among the diverse catalyst options available. Particularly noteworthy is the superior performance of heterogeneous catalysts over their homogeneous counterparts. These catalysts offer distinct advantages, including simplicity in operation, reusability, and ease of separation from reaction mixtures. Nano-catalysts stand out as pivotal contributors to the evolution of biodiesel synthesis methodologies. However, the pursuit of highly effective catalysts necessitates the development of innovative strategies to address challenges related to aggregation, durability, recyclability, and stability. Overcoming these issues is crucial for advancing the field and ensuring the practical applicability of catalysts in biodiesel production. The ongoing exploration and refinement of catalyst technologies hold the key to achieving enhanced efficiency, sustainability, and viability in meeting the rising global demand for biodiesel.

REFRENCES

[1] R. Shaheen, M.A. Hanif, S. Ali, R.W.K. Qadri. (2023). Screening of various hybrid composite materials for removal of extremely toxic acid yellow dye from wastewater. Desalination and Water Treatment. 312: 218-233.

[2] R. Shaheen, M.A. Hanif. (2024). Nanocomposite materials for decontamination of highly toxic acid dye from aqueous streams. International Journal of Environmental Analytical Chemistry. 1-15.

[3] R. Shaheen, M.A. Hanif. (2024). High speed removal of toxic acid red dye using photocatalytic-hybrid composite material. Desalination and Water Treatment. 100153.

[4] J. Kim, D. Jeong, D. Choi, E. Park. (2020). Exploring public perceptions of renewable energy: Evidence from a word network model in social network services. Energy Strategy Reviews. 32: 100552.

[5] A. Qazi, F. Hussain, N.A. Rahim, G. Hardaker, D. Alghazzawi, K. Shaban, K. Haruna. (2019). Towards sustainable energy: a systematic review of renewable energy sources, technologies, and public opinions. IEEE access. 7: 63837-63851.

[6] Y.C. Sharma, V. Singh. (2017). Microalgal biodiesel: a possible solution for India's energy security. Renewable and Sustainable Energy Reviews. 67: 72-88.

[7] M.K. Yesilyurt, Z. Yilbasi, M. Aydin. (2020). The performance, emissions, and combustion characteristics of an unmodified diesel engine running on the ternary blends of pentanol/safflower oil biodiesel/diesel fuel. Journal of Thermal Analysis and Calorimetry. 140: 2903-2942.

[8] A. Ghaly, D. Dave, M. Brooks, S. Budge. (2010). Production of biodiesel by enzymatic transesterification. Am J Biochem Biotechnol. 6(2): 54-76.

[9] J.-H. Ng, H.K. Ng, S. Gan. (2010). Recent trends in policies, socioeconomy and future directions of the biodiesel industry. Clean Technologies and Environmental Policy. 12: 213-238.

[10] B. Salvi, N. Panwar. (2012). Biodiesel resources and production technologies–A review. Renewable and Sustainable Energy Reviews. 16(6): 3680-3689.

[11] P. Verma, M. Sharma. (2016). Review of process parameters for biodiesel production from different feedstocks. Renewable and Sustainable Energy Reviews. 62: 1063-1071.

[12] J. Mathushika, C. Gomes. (2022). Development of microalgae-based biofuels as a viable green energy source: challenges and future perspectives. Biointerface Res. Appl. Chem. 12: 3849-3882.

[13] F.O. Nitbani, P.J.P. Tjitda, B.A. Nurohmah, H.E. Wogo. (2020). Preparation of fatty acid and monoglyceride from vegetable oil. Journal of Oleo Science. 69(4): 277-295.

[14] V.D. Tsavatopoulou, A.F. Aravantinou, I.D. Manariotis. (2021). Biofuel conversion of Chlorococcum sp. and Scenedesmus sp. biomass by one-and two-step transesterification. Biomass Conversion and Biorefinery. 11: 1301-1309.

[15] H. Qian, G. Yu, Q. Hou, Y. Nie, C. Bai, X. Bai, H. Wang, M. Ju. (2021). Ingenious control of adsorbed oxygen species to construct dual reaction centers ZnO@ FePc photo-Fenton catalyst with high-speed electron transmission channel for PPCPs degradation. Applied Catalysis B: Environmental. 291: 120064.

[16] K.K. Shah, I. Tiwari, B. Modi, H.P. Pandey, S. Subedi, J. Shrestha. (2021). Shisham (Dalbergia sissoo) decline by dieback disease, root pathogens and their management: a review. Journal of Agriculture and Natural Resources. 4(2): 255-272.

[17] L. Andreani, J. Rocha. (2012). Use of ionic liquids in biodiesel production: a review. Brazilian Journal of Chemical Engineering. 29: 1-13.

[18] K. Ghandi. (2014). A review of ionic liquids, their limits and applications. Green and sustainable chemistry. 2014.

[19] R. Behling, S. Valange, G. Chatel. (2016). Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends? Green chemistry. 18(7): 1839-1854.

[20] S.A. Hosseini. (2022). Nanocatalysts for biodiesel production. Arabian Journal of Chemistry. 104152.

[21] M. Agarwal, G. Chauhan, S. Chaurasia, K. Singh. (2012). Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. Journal of the Taiwan Institute of Chemical Engineers. 43(1): 89-94.

[22] G. Vicente, M. Martınez, J. Aracil. (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresource technology. 92(3): 297-305.

[23] A. Bohlouli, L. Mahdavian. (2019). Catalysts used in biodiesel production: a review. Biofuels.

[24] A. Saydut, A. Kafadar, F. Aydin, S. Erdogan, C. Kaya, C. Hamamci. (2016). Effect of homogeneous alkaline catalyst type on biodiesel production from soybean [Glycine max (L.) Merrill] oil.

[25] B.M. Trost. (1995). Atom economy—a challenge for organic synthesis: homogeneous catalysis leads the way. Angewandte Chemie International Edition in English. 34(3): 259-281.

[26] I. Atadashi, M.K. Aroua, A.A. Aziz, N. Sulaiman. (2013). The effects of catalysts in biodiesel production: A review. Journal of industrial and engineering chemistry. 19(1): 14-26.

[27] S.S. Win, T.A. Trabold, Sustainable waste-to-energy technologies: Transesterification. In *Sustainable Food Waste-To-energy Systems*, Elsevier: 2018; pp 89-109.

[28] N.S. Talha, S. Sulaiman. (2016). Overview of catalysts in biodiesel production. ARPN Journal of Engineering and Applied Sciences. 11(1): 439-442.

[29] N.U. Soriano Jr, R. Venditti, D.S. Argyropoulos. (2009). Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. Fuel. 88(3): 560-565.

[30] H. Cao, Z. Zhang, X. Wu, X. Miao. (2013). Direct biodiesel production from wet microalgae biomass of Chlorella pyrenoidosa through in situ transesterification. BioMed research international. 2013.

[31] A. Abbaszaadeh, B. Ghobadian, M.R. Omidkhah, G. Najafi. (2012). Current biodiesel production technologies: A comparative review. Energy Conversion and Management. 63: 138-148.

[32] D.N. Thoai, C. Tongurai, K. Prasertsit, A. Kumar. (2017). A novel two-step transesterification process catalyzed by homogeneous base catalyst in the first step and heterogeneous acid catalyst in the second step. Fuel Processing Technology. 168: 97-104.

[33] A. Talebian-Kiakalaieh, N.A.S. Amin. (2015). Single and two-step homogeneous catalyzed transesterification of waste cooking oil: optimization by response surface methodology. International Journal of Green Energy. 12(9): 888-899.

[34] A.D.K. Wibowo. (2013). Study on production process of biodiesel from rubber seed (hevea brasiliensis) by in situ (trans) esterification method with acid catalyst. Energy Procedia. 32: 64-73.

[35] Y. Zhang, S. Sun. (2023). A review on biodiesel production using basic ionic liquids as catalysts. Industrial Crops and Products. 202: 117099.

[36] Z. Ullah, A.S. Khan, N. Muhammad, R. Ullah, A.S. Alqahtani, S.N. Shah, O.B. Ghanem, M.A. Bustam, Z. Man. (2018). A review on ionic liquids as perspective catalysts in transesterification of different feedstock oil into biodiesel. Journal of Molecular Liquids. 266: 673-686.

[37] L.-L. Wang, Y. Zhang, F. Zhang, R. Feng. (2016). A bronsted basic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from soybean oil and methanol. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 38(18): 2770-2776.

[38] B.Y. Han, T. Li, R.Q. Deng, X.F. Xiong, C.Y. Chen. (2013). A review on Brønsted acid ionic liquids catalysts for biodiesel synthesis through transesterification. Applied Mechanics and Materials. 389: 46-52.

[39] A. Robles-Medina, P. González-Moreno, L. Esteban-Cerdán, E. Molina-Grima. (2009). Biocatalysis: towards ever greener biodiesel production. Biotechnology advances. 27(4): 398-408.

[40] P. Verma, M. Sharma, G. Dwivedi. (2016). Impact of alcohol on biodiesel production and properties. Renewable and Sustainable Energy Reviews. 56: 319-333.

[41] Z.C. Litman, Y. Wang, H. Zhao, J.F. Hartwig. (2018). Cooperative asymmetric reactions combining photocatalysis and enzymatic catalysis. Nature. 560(7718): 355-359.

[42] B. Norjannah, H.C. Ong, H. Masjuki, J. Juan, W. Chong. (2016). Enzymatic transesterification for biodiesel production: a comprehensive review. RSC advances. 6(65): 60034-60055.

[43] G. Sandoval, L. Casas-Godoy, K. Bonet-Ragel, J. Rodrigues, S. Ferreira-Dias, F. Valero. (2017). Enzyme-catalyzed production of biodiesel as alternative to chemical-catalyzed processes: advantages and constraints. Current Biochemical Engineering. 4(2): 109-141.

[44] F.T.T. Cavalcante, F.S. Neto, I.R. de Aguiar Falcão, J.E. da Silva Souza, L.S. de Moura Junior, P. da Silva Sousa, T.G. Rocha, I.G. de Sousa, P.H. de Lima Gomes, M.C.M. de Souza. (2021). Opportunities for improving biodiesel production via lipase catalysis. Fuel. 288: 119577.

[45] I. Fechete, Y. Wang, J.C. Védrine. (2012). The past, present and future of heterogeneous catalysis. Catalysis Today. 189(1): 2-27.

[46] S. Maroa, F. Inambao. (2021). A review of sustainable biodiesel production using biomass derived heterogeneous catalysts. Engineering in Life Sciences. 21(12): 790-824.

[47] J. Li, Y.-J. Fu, X.-J. Qu, W. Wang, M. Luo, C.-J. Zhao, Y.-G. Zu. (2012). Biodiesel production from yellow horn (Xanthoceras sorbifolia Bunge.) seed oil using ion exchange resin as heterogeneous catalyst. Bioresource technology. 108: 112-118.

[48] J.C. Védrine. (2017). Heterogeneous catalysis on metal oxides. Catalysts. 7(11): 341.

[49] Ž. Kesić, I. Lukić, M. Zdujić, Č. Jovalekić, V. Veljković, D. Skala. (2016). Assessment of CaTiO3, CaMnO3, CaZrO3 and Ca2Fe2O5 perovskites as heterogeneous base catalysts for biodiesel synthesis. Fuel Processing Technology. 143: 162-168.

[50] E. Yalman. Biodiesel production from safflower using heterogeneous CaO based catalysts. İzmir Institute of Technology, 2012.

[51] S. Nasreen, M. Nafees, L.A. Qureshi, M.S. Asad, A. Sadiq, S.D. Ali. (2018). Review of catalytic transesterification methods for biodiesel production. Biofuels: State of Development. 6: 93-119.

[52] T. Alemu, A.G. Alemu. (2023). Recent Developments in Catalysts for Biodiesel Production Applications.

[53] X. Rong, J. Parolin, A.M. Kolpak. (2016). A fundamental relationship between reaction mechanism and stability in metal oxide catalysts for oxygen evolution. Acs Catalysis. 6(2): 1153-1158.

[54] M. Jayakumar, N. Karmegam, M.P. Gundupalli, K.B. Gebeyehu, B.T. Asfaw, S.W. Chang, B. Ravindran, M.K. Awasthi. (2021). Heterogeneous base catalysts: Synthesis and application for biodiesel production–A review. Bioresource Technology. 331: 125054.

[55] I.V. Kozhevnikov. (2007). Sustainable heterogeneous acid catalysis by heteropoly acids. Journal of Molecular Catalysis A: Chemical. 262(1-2): 86-92.

[56] J.A. Melero, R. van Grieken, G. Morales. (2006). Advances in the synthesis and catalytic applications of organosulfonic-functionalized mesostructured materials. Chemical reviews. 106(9): 3790-3812.

[57] J.A. Melero, J. Iglesias, G. Morales. (2009). Heterogeneous acid catalysts for biodiesel production: current status and future challenges. Green Chemistry. 11(9): 1285-1308.

[58] A.P. Ingle, A.K. Chandel, R. Philippini, S.E. Martiniano, S.S. da Silva. (2020). Advances in nanocatalysts mediated biodiesel production: a critical appraisal. Symmetry. 12(2): 256.

[59] Y. Zhang, L. Duan, H. Esmaeili. (2022). A review on biodiesel production using various heterogeneous nanocatalysts: Operation mechanisms and performances. Biomass and Bioenergy. 158: 106356.

[60] H.N. Pandya, S.P. Parikh, M. Shah. (2022). Comprehensive review on application of various nanoparticles for the production of biodiesel. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 44(1): 1945-1958.

[61] I. Fatimah, I. Yanti, T.E. Suharto, S. Sagadevan. (2022). ZrO2-based catalysts for biodiesel production: A review. Inorganic Chemistry Communications. 109808.

[62] A. Nambo, C.M. Miralda, J.B. Jasinski, M.A. Carreon. (2015). Methanolysis of olive oil for biodiesel synthesis over ZnO nanorods. Reaction Kinetics, Mechanisms and Catalysis. 114: 583-595.

[63] A. Wang, W. Quan, H. Zhang, H. Li, S. Yang. (2021). Heterogeneous ZnO-containing catalysts for efficient biodiesel production. RSC advances. 11(33): 20465-20478.

[64] P.H. NARENDRAKUMAR. ROLE OF NANOPARTICLES FOR PRODUCTION OF BIODIESEL.

[65] G. Sahu, S. Datta, S. Saha, P.D. Chavan, D. Yadav, V. Chauhan. (2023). Efficiency of Catalysts During Biofuel Extraction. Biofuel Extraction Techniques. 441-493.

[66] L.L. Mguni, R. Meijboom, K. Jalama. (2012). Biodiesel production over nano-MgO supported on titania.

[67] E. Dahdah, J. Estephane, Y. Taleb, B. El Khoury, J. El Nakat, S. Aouad. (2021). The role of rehydration in enhancing the basic properties of Mg–Al hydrotalcites for biodiesel production. Sustainable Chemistry and Pharmacy. 22: 100487.

[68] N. Oueda, Y.L. Bonzi-Coulibaly, I.W. Ouédraogo. (2016). Deactivation processes, regeneration conditions and reusability performance of CaO or MgO based catalysts used for biodiesel production—a review. Materials Sciences and Applications. 8(1): 94-122.

[69] U. Jamil, A.H. Khoja, R. Liaquat, S.R. Naqvi, W.N.N.W. Omar, N.A.S. Amin. (2020). Copper and calcium-based metal organic framework (MOF) catalyst for biodiesel production from waste cooking oil: A process optimization study. Energy Conversion and Management. 215: 112934.

[70] C. Liu, P. Lv, Z. Yuan, F. Yan, W. Luo. (2010). The nanometer magnetic solid base catalyst for production of biodiesel. Renewable Energy. 35(7): 1531-1536.

[71] R.P. Patil, V.A. Kalantre, K.N. Alasundkar. (2023). Recent trends of nanocatalyst for organic transformations via sustainable environmental benign route. Research on Chemical Intermediates. 49(12): 5163-5203.

[72] V.D. Dasireddy, B. Likozar. (2017). Selective catalytic reduction of NOx by CO over bimetallic transition metals supported by multi-walled carbon nanotubes (MWCNT). Chemical Engineering Journal. 326: 886-900.

[73] C. Queirós, X. Paredes, T. Avelino, D. Bastos, M. Ferreira, F. Santos, A. Santos, M. Lopes, M. Lourenço, H. Pereira. (2020). The influence of water on the thermophysical properties of 1-ethyl-3-methylimidazolium acetate. Journal of Molecular Liquids. 297: 111925.

[74] J.-Q. Lai, Z.-L. Hu, P.-W. Wang, Z. Yang. (2012). Enzymatic production of microalgal biodiesel in ionic liquid [BMIm][PF6]. Fuel. 95: 329-333.

[75] Z. Huang, Y. ChenYang, X. Wang, R. Cai, B. Han. (2024). Biodiesel synthesis through soybean oil transesterification using choline-based amino acid ionic liquids as catalysts. Industrial Crops and Products. 208: 117869.

[76] M. Khanian-Najaf-Abadi, B. Ghobadian, M. Dehghani-Soufi, A. Heydari. (2023). Experimental evaluation of simultaneous variations in biodiesel yield and color using choline hydroxide catalyst in an ultrasonic reactor. Journal of Cleaner Production. 382: 134767.

[77] S. O'Connor, S.C. Pillai, E. Ehimen, J. Bartlett. (2020). Production of biodiesel using ionic liquids. Nanotechnology-Based Industrial Applications of Ionic Liquids. 245-269.

[78] D. Tomida, S. Kenmochi, T. Tsukada, K. Qiao, Q. Bao, C. Yokoyama. (2012). Viscosity and thermal conductivity of 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-octyl-3-methylimidazolium tetrafluoroborate at pressures up to 20 MPa. International Journal of Thermophysics. 33: 959-969.

[79] M. Khraisheh, F. AlMomani, M. Inamdar, M.K. Hassan, M.A. Al-Ghouti. (2021). Ionic liquids application for wastewater treatment and biofuel production: A mini review. Journal of Molecular Liquids. 337: 116421.

[80] M. Mofijur, S.Y.A. Siddiki, M.B.A. Shuvho, F. Djavanroodi, I.R. Fattah, H.C. Ong, M. Chowdhury, T. Mahlia. (2021). Effect of nanocatalysts on the transesterification reaction of first, second and third generation biodiesel sources-A mini-review. Chemosphere. 270: 128642.

[81] H. Veisi, M. Pirhayati, P. Mohammadi, T. Tamoradi, S. Hemmati, B. Karmakar. (2023). Recent advances in the application of magnetic nanocatalysts in multicomponent reactions. RSC advances. 13(30): 20530-20556.

[82] A.P. Ingle, R. Bhagat, M.P. Moharil, S.L. Rokhum, S. Saxena, S. Kalbande. (2022). Nanocatalysts in biodiesel production. Biodiesel Production: Feedstocks, Catalysts, and Technologies. 167-192.

[83] M.A. Ali, I.A. Al-Hydary, T.A. Al-Hattab. (2017). Nano-magnetic catalyst CaO-Fe3O4 for biodiesel production from date palm seed oil. Bulletin of Chemical Reaction Engineering & Catalysis. 12(3): 460-468.

[84] N. Ghosh, G. Halder. (2022). Current progress and perspective of heterogeneous nanocatalytic transesterification towards biodiesel production from edible and inedible feedstock: A review. Energy Conversion and Management. 270: 116292.

[85] W. Xie, H. Wang. (2020). Immobilized polymeric sulfonated ionic liquid on core-shell structured Fe3O4/SiO2 composites: A magnetically recyclable catalyst for simultaneous transesterification and esterifications of low-cost oils to biodiesel. Renewable Energy. 145: 1709-1719.

[86] D. Bousba, C. Sobhi, E. Zouaoui, K. Rouibah, A. Boublia, H. Ferkous, A. Haddad, A. Gouasmia, I. Avramova, Z. Mohammed. (2024). Efficient biodiesel production from recycled cooking oil using a NaOH/CoFe2O4 magnetic nano-catalyst: synthesis, characterization, and process enhancement for sustainability. Energy Conversion and Management. 300: 118021.

[87] M. José da Silva, A. Lemos Cardoso. (2013). Heterogeneous tin catalysts applied to the esterification and transesterification reactions. Journal of Catalysts. 2013.

[88] R. Ameta, M.S. Solanki, S. Benjamin, S.C. Ameta, Photocatalysis. In *Advanced oxidation processes for waste water treatment*, Elsevier: 2018; pp 135-175.

[89] M. Guo, W. Jiang, J. Ding, J. Lu. (2022). Highly active and recyclable CuO/ZnO as photocatalyst for transesterification of waste cooking oil to biodiesel and the kinetics. Fuel. 315: 123254.

[90] G. Corro, N. Sánchez, U. Pal, S. Cebada, J.L.G. Fierro. (2017). Solar-irradiation driven biodiesel production using Cr/SiO2 photocatalyst exploiting cooperative interaction between Cr6+ and Cr3+ moieties. Applied Catalysis B: Environmental. 203: 43-52.

[91] M. Aghilinategh, M. Barati, M. Hamadanian. (2019). Supercritical methanol for one put biodiesel production from chlorella vulgaris microalgae in the presence of CaO/TiO2 nano-photocatalyst and subcritical water. Biomass and Bioenergy. 123: 34-40.

[92] Y.K. Venkatesh, M.P. Ravikumar, S. Ramu, C.H. Ravikumar, S. Mohan, R. Geetha Balakrishna. (2023). Developments in Titanium-Based Alkali and Alkaline Earth Metal Oxide Catalysts for Sustainable Biodiesel Production: A Review. The Chemical Record. 23(12): e202300277.

[93] M.C. Manique. (2019). TiO 2 Nanotubes as Photocatalyst for Biodiesel Production. Nanomaterials for Eco-friendly Applications. 49-66.

[94] N. Ghani, J. Iqbal, S. Sadaf, H.N. Bhatti, M. Asgher. (2021). A Facile Approach for the Synthesis of SrTiO3/g-C3N4 Photo-catalyst and its Efficacy in Biodiesel Production. ChemistrySelect. 6(43): 12082-12093.

[95] A.B. Naveed, A. Javaid, A. Zia, M.T. Ishaq, M. Amin, Z.U.R. Farooqi, A. Mahmood. (2023). TiO2/g-C3N4 Binary Composite as an Efficient Photocatalyst for Biodiesel Production from Jatropha Oil and Dye Degradation. ACS omega. 8(2): 2173-2182.

[96] V. Gadore, S.R. Mishra, M. Ahmaruzzaman. (2024). Advances in photocatalytic biodiesel production: Preparation methods, modifications and mechanisms. Fuel. 362: 130749.