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REVIEW

Technologies for Biodiesel Production from Waste Cooking Oil

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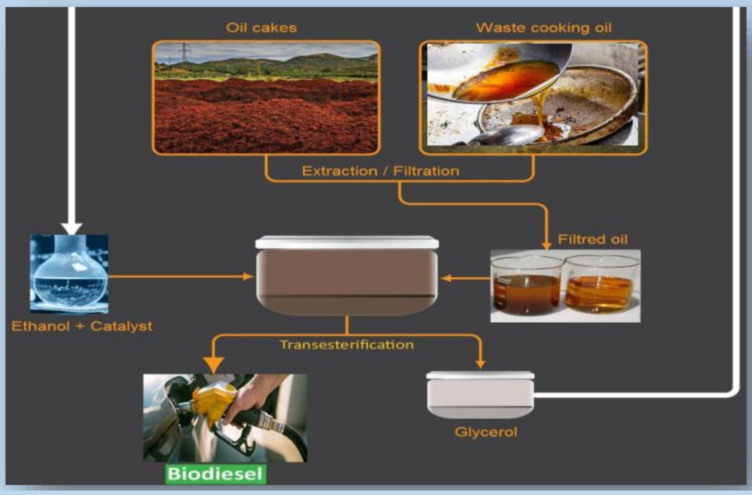
Abstract

For reasons that are now well known, bio-based alternative fuels like ethanol and biodiesel have received attention. They have the potential to reduce green-house gases, they can be produced from sustainable sources, and they can be combined with diesel fuel to increase its performance. The production and usage of biodiesel have seen a qualitative leap recently. Biodiesel can be produced from animal fats and vegetables oils. By transesterifying vegetable oils and fats on the basis of catalytic transesterification of oils, numerous commercial plants produce biodiesel. Typically, homogeneous, heterogeneous, and bio catalysts are used in this process. NaOH is used as alkaline catalyst, because of its low cost and higher reaction. In addition nanocatalysts and photocatalysts were used, they are well recognized for increasing reaction rates by providing a large number of active sites and having a high surface-to-volume ratio. This review paper focus on using waste cooking oil as a feed for biodiesel production, the various parameters influencing the process of biofuel production such as reaction rate, catalyst concentration, temperature, stirrer speed, catalyst type, alcohol used, alcohol to oil ratio, free fatty acid content, and water content.



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1. Introduction

In order to live in a developed society that is focused on modernity, we had to be aware of the pollution generated by the emissions from the burning of hydrocarbons, which endangers all living creatures (Latouche 2009). This forced our society to carefully consider reliable alternative sources to generate useful energy with the least amount of pollution and environmental harm, including global warming (Mathiyazhagan and Ganapath 2011; Bilgin et al. 2015) and to get beyond the fossil fuels' rising price and resource limitations (Musa et al. 2916; Munir et al. 2021; Akens and Ekeinde 2022). Herein lies the significance of biodiesel, which is referred to as a monoalkyl ester by the American Society for Testing and Materials (ASTM) (Ali et al. 2013), as a clean and sustainable energy source derived from biological matter, both animal and plant. The fact that biodiesel is biodegradable and has better combustion characteristics (higher flash point) and lower carbon dioxide emissions compared to conventional diesel fuels makes it a better alternative to fossil fuels (Falowo et al. 2021). The production of biodiesel has expanded dramatically over the past 20 years due to the rise in environmental awareness and the demand for reliable sustainable energy sources (Rashid et al. 2015), reaching roughly 14.11 million tons in 2018 compared to 6.129 million tons in 2007 (Van et al. 2022). Figure 1 displays the global output of biodiesel (Gnanaprakasam et al. 2013).

Biodiesel is mainly produced through a type of esterification reaction involving free triglyceride-es, alcohol, and a catalyst (Gnanaprakasam et al. 2013). The categorization of biodiesel is heavily influenced by the quality of triglycerides obtained from vegetable oils and animal fats, according to the definition of biodiesel and the fundamental process of its manufacture. The most common feed stocks used are shown in table 1 (Verma et al. 2016; Talebian et al. 2013). A recent trend sees an increasing use of waste cooking oil (WCO) as a feed stock because of the high cost of producing biodiesel from vegetable oils (Gashaw et al. 2014; Munir et al. 2021), mounting concern that using vegetable stock in biodiesel production could affect global food security, and the high cost of the raw material, which accounts for nearly 70–95 percent of the production total cost (Falowo et al. 2021). Figure 1 depicts the many sources of raw materials utilized to produce biodiesel (Kale et al. 2022). Because of the fact that (WCO) has a poor conversion and production rate due to the high quantity of saturated fat it contains, catalysts must be used to speed up the procedure and boost the reaction rate (Khodadadi et al. 2020). Studies on the generation of biodiesel from inexpensive, inedible, and biological sources are concentrated on non-order to assist the economically sustainable manufacturing process (Walker et al. 2010).

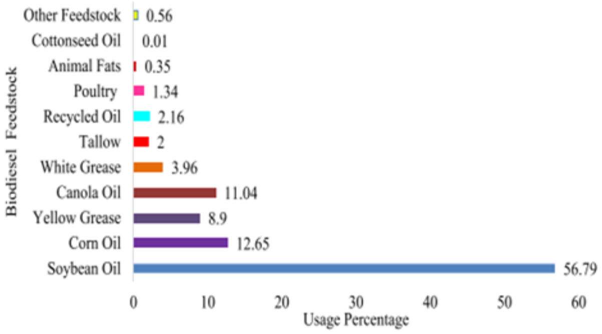

Figure 1. Production of biodiesel (Kale et al. 2022).

Table 1. Feedstock for biodiesel production (Walker et al. 2010).

Edible oils	Non-edible oils	Other sources
Cottonseed oil	Jatropha oil	Microalgae
Coconut oil	Karanja (pongamia oil)	Spirulina platensis algae
Sunflower oil	Mahua oil	Waste cooking oil
Canola oil	Neem	Animal fats
Soybean oil	Eucalyptus oil	Beef tallow
Castor oil	Linseed	Poultry fat
Mustard oil	Rubber seed	Fish oil
Peanut oil	Polanga	Chicken fat
Palm oil	Yellow oleander	Chlorella protothecoiders microalgae
Rapeseed oil		

Biodiesel is a liquid fuel obtained mainly from oils, whether vegetable or animal, and some types of short-chain alcohols by chemical processes (Romano et al. 2010) and the most important oils used are soybean, palm, rapeseed, sunflower, peanut and flaxseed oils, as well as the used oils that are not edible due to their economic important, as no expensive food is consumed to produce the fuel (Heterogenus 2018**.** As mentioned earlier, converting vegetables oils into diesel fuel is an expensive process due to the high price of these oils, so an alternative must be found and the use of cheap materials that are not suitable for use such as used waste cooking oils is a good example. All over the world edible oils are used for cooking. Because of the need to dispose of them after use, their use as alternatives to vegetable oils is considered an economical process. This is justified by the lower cost of the raw material, it reduces the generation of waste and residues from waste oil treatment before disposal, and its use will reduce the consumption of oils extracted from plants that are grown on large areas for this purpose (Nur et al. 2015). The most common method for converting cooking oil into fuel is transesterification, which is the process of converting fats into fatty acid methyl ester by alcohol and in the presence of a catalyst (Suzihaque et al. 2022).

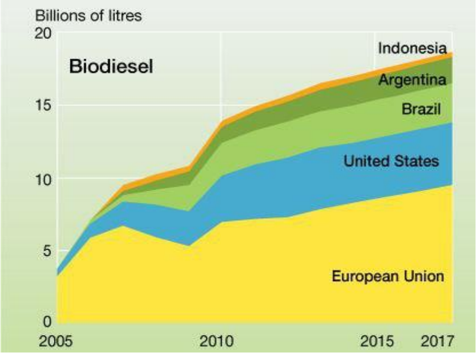

Figure 2. Usage of Biodiesel feedstock in year 2020 (Nur et al. 2015).

2. The Steps of biodiesel production by Transesterification

Transesterification is a chemical reaction in which vegetable oil reacts with alcohols to produce esters and glycerol, and it is one of the most common ways to produce biodiesel. The reaction is carried out in the presence of the appropriate catalyst such as (NaOH, KOH), in order to improve the reaction rate and increase the productivity, It is also possible to avoid the usage of the catalyst, but in this case high temperature and pressure are required and the process yield will be lower (Gashaw et al. 2014). The reaction is reversible; as a result, to ensure equilibrium on the side of the product, an excess amount of alcohol could in theory be used at a molar ratio 3/1. In practice, however, a higher percentage of alcohol is used to push the equilibrium to the maximum productivity of the main product that is used as fuel in engines, which is ester (Gashaw et al. 2014). Recently, supercritical methods have attracted researchers due to several advantages over other methods, such as the absence of catalyst, low residence time, high rate of reaction, very low sensitivity towards FFAs, potential to treat a large range of feedstock's and no pre-treatment. Initially, this technology for biodiesel production was employed for methanol and ethanol. This method has gained attention due to production without glycerol using dimethyl carbonate and super-critical methyl acetate. A vast range of reactants with Triglyceride have been reported including methyl acetate, methanol, ethanol, and di methyl carbonate. Homogenous base catalyst forms soap that neutralizes FFAs and could be transformed back into FFAs by the inclusion of H_3PO_4 to decanted glycerol and soap mixture from the end product.

The main steps of the production of biodiesel are summarized in figure 3 and described in the following sections.

2.1. Mixing of Alcohol and Catalyst

This process is limited to the production of an alkoxide solution by dissolving alkali hydroxide (strong hydroxide, NaOH-KOH) in alcohol using a mixer (Romano et al. 2010).

2.2. Chemical Reaction

At this stage, a chemical reaction takes place between the alkoxide solution and the oil in the reaction vessel to obtain the ester. To speed up the reaction, the temperature is maintained close to the boiling point of the alcohol. Since alcohol is easy to evaporate the reactor must operate in a closed system. In order to obtain a maximum yield from the ester, an excess amount of alcohol is added (Gashaw et al. 2014).

2.3. Separation

In addition to the biofuel (ester) resulting from the reaction, we also get glycerol as a by-product. The purpose of this step is to separate the biofuel from the glycerol, which is usually done based on gravity using the sedimentation vessel, where the glycerol phase is denser than the biofuel phase, so the glycerol is withdrawn from the setting vessel and the biofuel as an upper product. A centrifugal system can be used to separate more quickly (Gashaw et al. 2014).

2.4. Alcohol Removal

Both reaction products (glycerol and biodiesel) are saturated with alcohol, so either excess alcohol is removed from both (after separation) through rapid evaporation or common distillation, or extraction distillation can be used for a more economical process. On the other hand, the excess alcohol can be removed and the mixture neutralized before the glycerol and esters have been separated to prevent the effect of basic media inside the reactor. In both cases, the extracted alcohol is returned to the process as a feed (Gashaw et al. 2014).

2.5. Biodiesel Washing

After biodiesel is obtained from the transesterification process, some traces of sodium hydroxide, methanol and glycerol may remain in small properties with biodiesel. These might become problematic at later stages even at low concentrations of methanol and sodium injector. All of these materials are soluble in water, so they can be removed by washing with water (6-4 times) where the fuel is sprayed with hot water (40-50 °C) tacking appropriate measures to prevent soap hydroxide can corrode the engine parts, glycerol can reduce fuel lubrication and cause coal deposits on the formation. After washing, traces of water may remain in the biodiesel, so it is dried to 110 °C. This last step is not always applied, and it depends on the quality of the biodiesel produced (Gashaw et al. 2014).

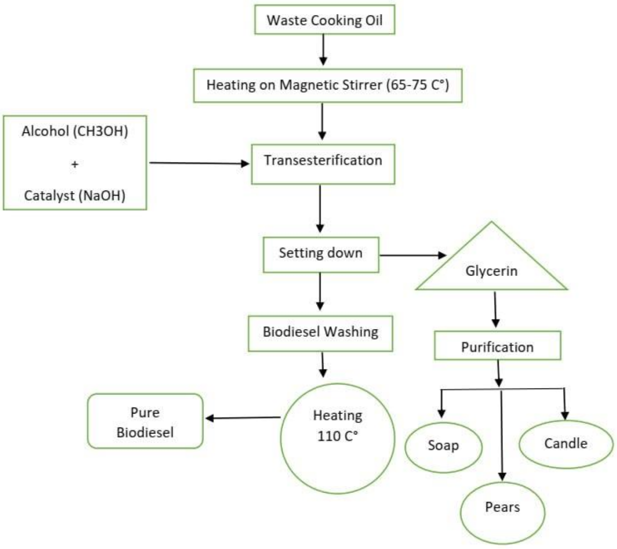

Figure 3. The Steps of biodiesel production.

3. Different Methods for production of biodiesel

3.1. Pyrolysis (thermal cracking)

It is the treatment process that takes place by heating in the absence of air or oxygen, or by heating with the presence of a catalyst, leading to the breaking of bonds and the formation of new smaller compounds. Thermal cracking is considered an expensive process, especially for developing countries, as it requires expensive equipment and techniques, in addition to the difficulties of the treatment process and preparation for treatment, such as heat deoxygenation removes useful environment products with it (Gashaw et al. 2014).

3.2. Dilution

To reduce the percentage of diesel fuel, a mixture of vegetable oil and diesel fuel is used, which acts as a diluent for vegetable oil to maintain the power provided by the engine without changing or modifying the engine. There are different proportions that were used previously, for example in 1980 a mixture of 10 wt% vegetable oil was added to 90 wt% of the diesel fuel in the engines by Caterpiller Brazil at that time, and a mixture ratio of up to 25 wt% was used from sunflower oil to 75 wt% of diesel. Short-term studies also use a mixing ratio of 50/50 wt%. This is in order to reduce the viscosity of the fuel mixture and thus improve the efficiency of the engine, in addition to reducing the amount of the diesel fuel (Nur et al. 2015).

3.3. Micro-Emulsion Process

Vegetables oil cannot be used directly due to their high viscosity, so it is necessary to reduce it. This can be achieved by using micro-emulsion with solvents such as ethanol, methanol and 1-butanol (Gashaw et al. 2014). Where light alcohols (methanol, ethanol) are responsible for reducing viscosity, heavier alcohols reduce the surface tension of the fuel, as well as additives that improve cetane number such as alkyl nitrate. These processes allow obtaining a biodiesel fuel with an appropriate viscosity, a high cetane number and good spray properties, but the continuous use of diesel micro-emulsion in engines causes problems such as injector needle sticking, carbon deposits and incomplete combustion (Gashaw et al. 2014). Micro-emulsion describes a dispersion of optically isotropic fluid microstructure as a colloidal equilibrium, with measurements typically 1–150 spontaneously produced by two ordinarily immiscible liquids as well as multiple ionic amphiphiles.

4. Factors affecting the biodiesel production

There are many factors that are strongly affected by this interaction, including; ratio of alcohol, catalyst, presence of water, free fatty acid in oil samples, reaction temperature, reaction time and agitation speed (Talebian et al. 2013; Sathya et al. 2023).

4.1. Water content

In this process, we can find a percentage of water in both the feed and the product as well, both of which are undesirable because of their negative impact on the process. The presence of water with the feed accelerate the water hydrolysis reaction and causes the formation of soapy materials and thus the consumption of the catalyst and reduce the reaction yield from ester for that its ratio must be less than 0.5% in the order to obtain a 90% yield of the ester, and the water resulting from the reaction has a negative impact on the performance of the engine. The water leaving the product can be removed using anhydrous sodium sulphate or anhydrous potassium sulphate or from the oil by heating the oil up to 120°C (Sathya et al. 2023; Talebian et al. 2013).

4.2. Type of alcohols

The most commonly used alcohols are methanol (because its commercial significance is smaller than that of other longer chain alcohols). The usage of methanol leads to a higher conversion rate, especially with cooking oil, and it causes a better decrease in viscosity compared to other alcohols. Furthermore, methanol is cheaper. However, its toxicity is higher than that of ethanol, and it also causes enzymes deactivation, denaturation or inhibition at higher concentration, so when we working with the enzyme system, ethanol is used. But ethanol and higher alcohols form an isotropic mixture with the water, which makes it difficult to separate the fuel from the alcohol in the distillation process (Romano et al. 2010).

4.3. Alcohol to oil ratio

Alcohol to oil ratio is one of the most important transesterification variables. Stoichiometrically 3 moles of alcohol and 1 mole of triglyceride are required for transesterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol (Gashaw et al. 2014). According to Le Chatelier's principle, the rate of product formation increases as reactant concentration is increased. Increasing the alcohol to oil ratio always has a positive impact on biofuel conversion. As a result, the rate of product creation will be sped up if the alcohol content is increased (Gnanaprakasam et al. 2013). The reaction won't result in the creation of a product if the ratio of oil to methanol is too low (Suzihaque et al. 2022; Peng et al. 2018). Since triglyceride transesterification is an irreversible process, an excess of alcohol is needed to tip the balance in favour of the production of alkyl esters (biodiesel) (Farooq et al. 2013). The catalyst type affects the oil to methanol ratio during transesterification. Higher oil to methanol ratio is required for an acid catalyst than a base catalyst. Compared to base catalyzed transesterification, which is likely preferable, acid catalyzed transesterification requires 1:15 oil to methanol ratio (Farooq et al. 2013). The capacity of triglycerides to convert into methyl esters will be affected by the alcohol to oil molar ratio, whereas the yield may be decreased by larger molar ratios (Verma and Sharma. 2016). The best biodiesel yield, according to the results, is at a ratio of 1:6 oil to methanol. In contrast, as the methanol molar ratio rises, the biodiesel yield using methanol consistently increases (Gashaw et al. 2014).

4.4. Catalyst concentration

One of the most crucial aspects determining biodiesel yield is catalyst concentration. Typically, less biodiesel is produced at lower catalyst concentrations. Yields frequently peak and then decrease as catalyst concentration rose. Increased catalyst concentration decreased biodiesel yield by creating sludge and raising viscosity (Suzihaque et al. 2022). Additionally, the conversion of triglycerides into biodiesel is increased when the catalyst concentration in oil samples rises. On the other hand, a lack of catalyst causes triglycerides to only partially convert into fatty acid esters, and further increasing the catalyst concentration has been shown to have a negative effect on the yield of the final product. Due to the fact that adding too much alkali catalyst causes triglycerides to react, more soap is produced (Moser. 2009).

4.5. Catalyst type

Transesterification depends on the type of catalyst used and its concentration. For feedstocks with a high amount of FFA, an acid catalyst is preferable, whereas a base catalyst is preferable for feedstocks with a low level of FFA (Suzihaque et al. 2022). The table 2 shows the types of catalysts, their advantages and disadvantages, with the most important examples of each type.

4.5.1. Homogeneous catalysis

Sodium hydroxide (NaOH) or potassium hydroxide (KOH) as homogeneous base catalysts are the most often used catalysts for the manufacture of biodiesel due to their rapid reaction, higher yield, mild reaction conditions, and low cost (Gashaw et al. 2014). However, the homogeneous acid-catalyzed reaction has a significant advantage over the base catalysed technique in that the presence of FFA has no negative impact on the performance of acid catalysts. In fact, acids can catalyse both esterification and transesterification at the same time (Moser. 2009).

4.5.2. Heterogeneous catalysis

Due to their high activity and selectivity, improved reusability, decreased processing steps, and waste generation, heterogeneous catalysts are used in the industry to produce biodiesel (Sahu et al. 2018). Heterogeneous acid catalysis, solid acid catalysts like zeolites, mixed oxides, sulfated zirconia, and ion exchange resins might be very interesting for the production of biodiesel from feedstocks with high FFA contents, but their activity is still low as it depends on the reaction conditions and consumes a greater amount of catalyst in comparison to homogeneous catalysts (Raqeeb et al. 2015). Both acid-functionalized MNPs in magnetic heterogeneous catalysis showed outstanding catalytic activity in the process of oleic acid esterification. However, in the transesterification of glyceryl trioleate, the sulfamic acid functionalized MNPs displayed superior reactivity. By using magneto-precipitation, both acid-functionalized MNPs may be recovered (Wang et al. 2015).

4.5.3. Bio catalysis

Heterogeneous lipases are typically not tolerant of methanol, hence enzymatic techniques are more frequently used to produce ethyl or higher esters (Moser. 2009). Numerous microbes have been identified in the literature as effective producers of lipase, which is frequently employed in the production of biodiesel. According to reports, Candida antarctica is the most significant yeast for producing lipase B, however some other Candida species are also known to be effective lipase makers. On the other side, there are several strategies for inhibiting enzymes, including whole-cell stabilization, adsorption, covalent bonding, and entrapment.

4.5.4. Carbon based catalysis

The production of biodiesel from a variety of feedstocks, including waste, crude, and pre-treated oils, has found applications for carbon-based materials such as activated carbon (AC) and carbon nanotubes (CNTs). AC is primarily synthesized from high carbon feedstocks like coal, wood, and coconut shell. Pyrolysis and carbohydrate products can both be used to make carbon-based solid acid (CBAS) catalysts. A number of CBASs with different sources, including D-glucose, sucrose, starch, cellulose, and vegetable oil asphalt, have been investigated as catalysts (Clohessy and Witold. 2020).

Table 2. Various methods used for production of biodiesel from waste cooking oil PVC transesterification.

Catalyst	**examples**	**advantages**	**disadvantages**	**Ref.**
Heterogeneous base catalyst	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$	high availability and low cost, Separation of catalyst from product is easy, Formation of soap is avoided,	sensitive to FFA content and soap is formed when FFA content in WCO is higher than 2 wt%	(Raqeeb et al. 2015)
Heterogeneous acid catalysis	ZnO/I2, ZrO_2=SO_2, Sr/ZrO2TiO_2=SO_2, carbon-based solid acid catalyst, carbohydrate-derived catalyst,	Less corrosive, Less toxicity Less environmental problem Low cost	Sever parameters preparation of the catalyst is difficult and consequently expensive;	(Suzihaque et al. 2022)
Homogeneous base catalysis	NaOH KOH) , CH_3OK, Sodium methoxide	Fastest reaction ،Higher yield ،Mild reaction condition ،Low cost	Formation of soap ،Difficult to separate it from the final product, water interferes with reaction	(Farooq et al. 2013)
Homogeneous acid catalysis	Concentrated H_2SO_4, HNO_3, sulfonic acid	Suitable for high free fatty acid feed stock, Yield is high	Slow reaction, Need extreme pressure and temperature conditions, Difficult to separate	(Degfie et al. 2019)
Bio-catalysis	Candida antarctica fraction B lipase, Rhizomucor mieher lipase, E. aerogenes lipase, lipase immobilized on hydrotalcite and zeolites	being cost effective catalysts shorter reaction time and lower reaction temperature ,	they need more amount of catalyst and production yield is less compared to homogeneous and heterogeneous, the high production cost of enzyme and longer enzymatic reaction time	(Borah et al. 2019)
Magnetic heterogeneous catalysis	Magnetic nanoparticles $ZnFe_2O_4$	The high catalytic activities, high stability, simple preparation, and magnetism, inexpensive, easy handling		(Borah et al. 2019)
Carbon based catalysis	AC, CNTs, CBCs	They do not require extensive washing steps, have a simplified overall process, reduce biodiesel production costs while maintaining quality, and they can also be reused in several cycles		(Erchamo et al. 2021)

4.5.5. Nanocatalyst

Nanocatalyst applications have grown more beneficial for enhancing catalytic processes. They are well recognized for increasing reaction rates by providing a large number of active sites and having a high surface-to-volume ratio.

4.5.5.1. CaO nanocatalyst

The highest conversion to biodiesel is estimated to be 96% when WCO and methanol are recycled in the presence of calcium oxide (CaO) nanocatalyst. These ideal experimental conditions include 50°C, a 1:8 WCO oil to methanol molar ratio, 1% by weight of catalyst loading rate, and a 90-minute reaction time

(Degfie et al. 2019). The ideal biodiesel production of 94% was reached at 1:12 oil to methanol molar ratio, 2.5 wt% catalyst loading, 60 °C, and 120-min reaction time. CaO nanocatalyst can be produced from chicken egg shell. Different types of nanocatalysts that can be used for biodiesel production are presented in table 3.

Table 3. Types of Nano catalysis

	Type	Optimum Conditions	Yield %	Ref.
CaO nanocatalyst	CaO	50°C, 1:8 WCO oil to methanol molar ratio, 1% W of catalyst loading rate and 90minutes	96%	(Degfie et al. 2019)
	CaO from Chicken eggshell waste	1:12 oil to methanol molar ratio, 2.5 wt% catalyst loading, 60 °C, and 120-min reaction time	94%	(Erchamo et al. 2021)
	Zn substituted waste egg shell derived CaO nanocatalys	20:1 methanol to oil molar ratio, 5 wt% catalyst loading, 65 °C reaction temperature and 4 h of reaction time	96.74%	(Borah et al. 2019)
MgO nanocatalyst	MgO nanocatalyst synthesized by sol-gel method	10:1methanol to oil molar ratio, 2wt% catalyst loading , for 2 hr at 60ºC , stirring rate of 250 rpm	80%	(Amirthavalli et al. 2018)
	MgO nanocatalyst synthesized by the coprecipitation method	24:1 methanol/oil molar ratio , 2wt% catalyst loading , at 65 °C and reaction time 1 h	93.3%	(Ashok et al. 2018)
	CaO@MgO nanocatalyst	16.7:1 methanol-to-oil ratio , catalyst concentration of 4.571 wt% ,at 69.37 C , reaction time of 7.08 h,	98.37%	(Foroutan et al. 2020)
CZO nanocatalyst	CZO nanocatalyst	1:8) O/M ratio, 12% (w/w) nanocatalyst concentration, at , 55°C , 50 min of reaction time	97.71%	(Gurunathan et al. 2015)
$LaPO_4$ foam nanocatalyst	$LaPO_4$ foam nanocatalyst	5:1 methanol to oil molar ratio, with 2.5 wt % of LaPO4, at 90 C, 120 min	91%	(Rezania et al. 2021)
ZnCuO/N-doped graphene nanocomposite catalyst	ZnCuO/N-doped graphene (NDG)	15:1 methanol:oil molar ratio, 10 wt.% catalyst loading , , 8 h reaction time and 180 °C reaction temperature	97.1%	(Kuniyil et al. 2021)
CNTs nanocatalyst	Na_2O supported CNTs nanocatalyst	20:1 of methanol-to-oil molar ratio, 3 wt% of catalyst amount, at 65 °C , 3 h of reaction time	97%	(Rezania et al. 2020)

4.5.6. Photoctalyst for biodiesel production

Semiconductor-based photocatalysts are of great interest due to their environmental friendliness and high stability. Waste cooking oil can be converted into biodiesel through a photocatalyzed transesterification reaction (Khan et al. 2021). Upon exposure to light, photogenerated electrons (e^-) move from the valence band (VB) to the conduction band. At the same time, the same number of photogenerated holes (h^+) are generated in VB. Photocatalytic (Trans) esterification for biodiesel production follows the Langmuir-Hinshelwood reaction pathway (Huang et al. 2022). Figure 4 presents thermal- and photo-driven biodiesel production from FFA using acid/base catalysts and photocatalytic materials.

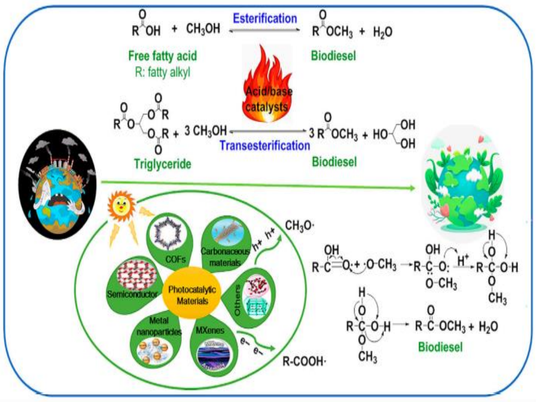

Figure 4. Schematic illustration of thermal- and photo-driven biodiesel production from FFA using acid/base catalysts and photocatalytic materials (Huang et al. 2022).

4.5.6.1. Cr/SiO_2 photocatalyst

A heterogeneous photocatalytic process at room temperature under solar radiation is used for the esterification of free fatty acids in vegetable oils for the efficient production of biodiesel. Cr/SiO_2 as a heterogeneous photocatalyst showed very high activity for the esterification of free fatty acids present in used frying oil with methanol. Solar-irradiation driven biodiesel production using Cr/SiO_2 photocatalyst exploits cooperative interaction between Cr^{6+} and Cr^{3+} moieties. This process has led to the production of high quality biodiesel (Corro et al. 2017).

4.5.6.2. $La^{3+}/ZnO\text{-}TiO_2$ photocatalyst

In a study a highly active and recyclable $La^{3+}/ZnO\text{-}TiO_2$ photocatalyst was prepared by a sol-gel method. In the first step, the photocatalytic $La^{3+}/ZnO\text{-}TiO_2$ esterification of ethanol with free fatty acids (FFA) in used edible oil (WCO) was investigated under UV irradiation. In the second step, NaOH catalyzed transesterification of triglycerides with ethanol. Optimum conditions were identified by an orthogonal design. At 35 °C, the ethanol/oil molar ratio was 12:1, the catalyst dosage 4 wt%, the UV irradiation time 3 hours, the reaction time 3 hours, and the conversion rate of FFA reaches 96.14%. After 5 test cycles, the FFA conversion rate was over 87%. This indicates that the catalyst has stable activity and easy recovery (Guo et al. 2021).

4.5.6.3. TiO_2 composite with graphitic carbon nitride as a photocatalyst

In a study by Khan et al. (2021) the WCO was recovered and esterified with acid to reduce the FFA concentration (less than 3%). The trans- esterification reaction was carried out using the esterified WCO under solar irradiation at 60 °C with different $TiO_2/g\text{-}C_3N_4$ catalysts (10, 20 and 30%) with different catalyst concentrations of 1%, 2% and 3%. Results showed that a concentration of two catalyst of $TiO_2/20\%\ g\text{-}C_3N_4$ provided the highest yield (89.5%) in biodiesel production compared to other catalyst concentrations used (Khan et al. 2021).

4.5.6.4. CuO/ZnO

In a study by Guo et al. (2022) CuO/ZnO photocatalysts were prepared using a precipitation method. The optimal reaction conditions for biodiesel production were 9:1 molar of ethanol to waste cooking oil at 64 °C for 2 hours at a dose of 5 wt% using 1 mole of ethanol in spent cooking oil, yielding 93.5% biodiesel (Guo et al. 2022).

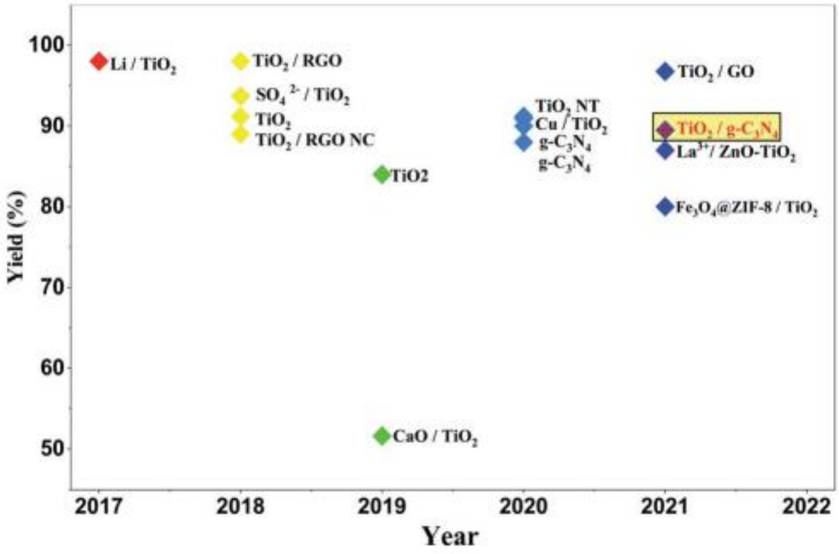

Figure 5. Represent the recent catalyst yields of similar catalysts used for biodiesel production for transesterification (Khan et al. 2021).

Table 4. Comparison of similar catalysts used for transesterification.

Feed stock oil	**Catalyst**	**Oil TO methanol ratio**	**T (C)**	**Time (min)**	**Yield %**	**Ref**
Waste olive oil	TiO_2	1:12	120	240	91.2	(Mihankhah et al. 2018)
Kemiri sunan oil	TiO_2	1:15	60	90	84	(Redjeki et al. 2019)
Waste cooking olive oil	TiO_2 NT	1:08	65	180	91.2	(Khaligh et al. 2021)
WCO	TiO_2/RGO	1:12	65	180	98	(Borah et al. 2018)
Plam oil	TiO_2-GO	1:09	70	40	96.7	(Alsharifi et al. 2017)
Microalgae biomass	CaO/TiO_2	1:08	55	120	51.6	(Chen et al. 2018)
WCO	LaZnO-TiO_2	1:12	65	180	87	(Guo et al. 2021)
WFO	Fe_2O_4@ZIF-8TiO_2	1:30	50	65	80	(Sabzevar et al. 2021)

5. Conclusion

Biodiesel is an alternative and renewable fuel for diesel engines and has become more attractive in recent times. Biodiesel is commonly produced from different types of oils and fats, but biodiesel production from waste cooking oil is an interesting alternative because of its economic and sustainable nature. A number of researchers have successfully produced biodiesel using homogeneous and heterogeneous catalysts.

Different studies also showed that employing transesterification method and using nanocatalyst or photocatalyst instead of NaOH can reduce the viscosity of oil or fat that is used as well as the side reactions in the presence of methanol or ethanol. However, the biodiesel production by transesterification is strongly affected by molar ratio of alcohol, reaction temperature, reaction time and catalyst concentration.

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