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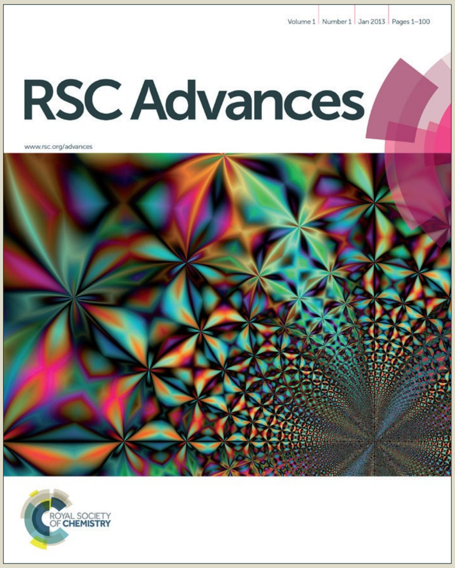

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State of the art of biodiesel production process: A review of the heterogeneous catalyst

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Abstract: Broadened focus on energy, the fast growing value of petroleum oil, and harmful atmospheric deviations because of evolution of greenhouse gases, natural contamination, and quick reduction approaches to obtain fossil fuels are critical parameters to search for alternative energy sources. The requirements for developing renewable energy sources with less environmental effects are increasing because of the problems caused by the extensive use of fossil fuels. Currently, creating energy from low-carbon origins and introducing eco-friendly modern technology are the main targets of researchers in the field. Biodiesel has been identified as an alternative renewable liquid fuel source that can be derived through thermal cracking, esterification and transesterification of different triglycerides. Among these processes, the most popular and convenient technique for biodiesel production is transesterification of triglyceride with the help of suitable alcohol and a catalyst. Many scientists have introduced different types of catalysts to optimize the reaction condition and the biodiesel production yield. Catalyst selection involves determination of the water content and free fatty acids in the oil. Base homogeneous catalyst provides faster reaction rates than homogeneous acid catalysts. Recent researcher has paid attention to heterogeneous catalysts because of their high activity, high

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selectivity, catalyst recovery, reusability, easy separation from the products, and water tolerance property. Biocatalysts present significant advantages in terms of environmental issues over conventional alkali-catalyzed processes. This article review focuses on various technologies used for biodiesel production, as well as the benefits and limitations of different types of catalysts in the relevant production technology. We also conduct a comparative study of homogeneous, heterogeneous, and biocatalysts in biodiesel production technology at the laboratory scale, as well as their industrial applications.

Keywords: *Biodiesel production, Homogeneous, Heterogeneous, Biocatalyst, Transesterification, Esterification,*

Nomenclature and Abbreviations

IC	Internal Combustion
CI	Compression Ignition
SI	Spark Ignition
HC	Hydrocarbon
ASTM	American Society for Testing and Materials
EN	European Standard
FAME	Fatty Acid Methyl Ester
FAEE	Fatty Acid Ethyl Ester
FFA	Free Fatty Acid
SC MeOH	Supercritical Condition in Presence of Methanol
PSI	Pound per Square Inch
HPAs	Heteropolyacids
MAT	Microwave-Assisted Transesterification
kHz	Kilo Hertz
MJ/kg	Mega Joule per Kilogram
°C	Degree Celsius
RSM	Response Surface Methodology
TGs	Triglycerieds
DGs	Diglycerides
MGs	Monoglycerides
IUPAC	International Union of Pure and Applied Chemistry
XRD	X-ray diffraction

SEM	Scanning Electron Microscope
HR-TEM	High Resolution Transmission Electron Microscopy
TEV	Tobacco Etch Virus
SMO	Sodium Methylate

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1. Introduction

The constantly growing expense of traditional fossil fuels and the related natural effects of their uses are significant concerns worldwide. The use of fuel increases daily given the high demand for energy. This demand is mostly met by fossil fuels such as coal, petroleum oils, and natural gas. Renewable sources are the most preferred alternative energy sources. Energy can be extracted from fossil fuels economically as well as in large quantities. Thus, scientists worldwide are working to enhance the development of fuel mileage and emission quality of internal combustion (IC) engines. Researchers have also concentrated on investigating alternative energy sources that can be utilized in IC engines without demonstrative changes in vehicle design. Thus, low carbon sources are preferred for producing energy and represent an eco-friendly green technology.

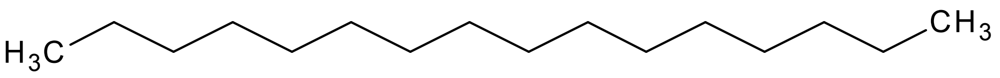
Considering the increase in global population, additional resources are needed to deliver energy for human consumption. To fulfill additional demands, researchers are considering renewable energy. The term biodiesel implies substitution of traditional energy sources with inexhaustible liquid fuel, which can be gained from triglycerides and supplement the additional requirements of conventional petroleum diesel [1]. Biodiesel research has recently become a popular field because of its renewability, biodegradability, nontoxicity, and carbon neutrality. The transesterification process is formed by adding triglyceride with methanol, ethanol, or any desirable alcohol, which is used to develop biodiesel [2-4]. Biodiesel can also be produced domestically from vegetable oils, animal fats, micro and macro algal oil [5] or used cooking oil. The biodiesel produced can be treated as a cleaner-burning substitute for conventional petroleum diesel. Biodiesel contains mono alkyl esters of long chain fatty acids [6] as well as methyl esters. These methyl esters include plant seed oils, animal fats, or even waste cooking oils and are produced by transesterification with methanol. Acids, bases, and enzymes catalyze transesterification reactions. Heterogeneous catalysts are promising materials for the synthesis of biodiesel from different feedstocks [7]. Biodiesel can fulfill requirements for additional energy. Biodiesel is an interesting product because of its natural advantages and production from renewable assets. Unfortunately, high costs and constrained accessibility of fat and oil resources limit the wider use of this alternative energy source. Biodiesel cost may be viewed from two aspects: the cost of raw materials (fats and oils) and the processing cost. The expense of crude materials represents 60%–75% of the cost of aggregate biodiesel fuel [8]. Utilization of waste cooking oil may significantly reduce the cost of raw materials but also reduces fuel quality [9]. Studies are expected to discover a less expensive approach to utilize used cooking oils to produce biodiesel fuel. A continuous transesterification procedure may allow reduction of the production cost associated with biodiesel. Feedstock obtainability, types, conversion technology, catalyst use, and process cost contribute to total biodiesel production expenses [5].

This review provides knowledge of the different biodiesel production technologies using different catalytic and non-catalytic processes. The use of biocatalysts to synthesize biodiesel is also discussed, and a comparative study of conventional biodiesel production processes is performed. In addition to catalyst preparation, their roles and the effects of different categories of heterogeneous and homogeneous catalysts on the esterification process of biodiesel production are described. This study also describes the advantages of non-catalytic biodiesel production processes over catalytic processes.

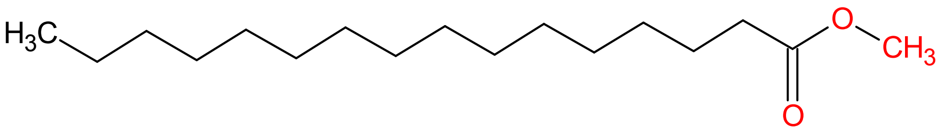
2. Biodiesel and its production process

Several techniques are available to obtain biodiesel from different feedstock. For example, transesterification through radio frequency, microwave, ultra-sonication, alcohol reflex temperature, and alcohol supercritical temperature are possible. All biodiesel production techniques can be classified as pyrolysis or thermal cracking, esterification, or transesterification processes.

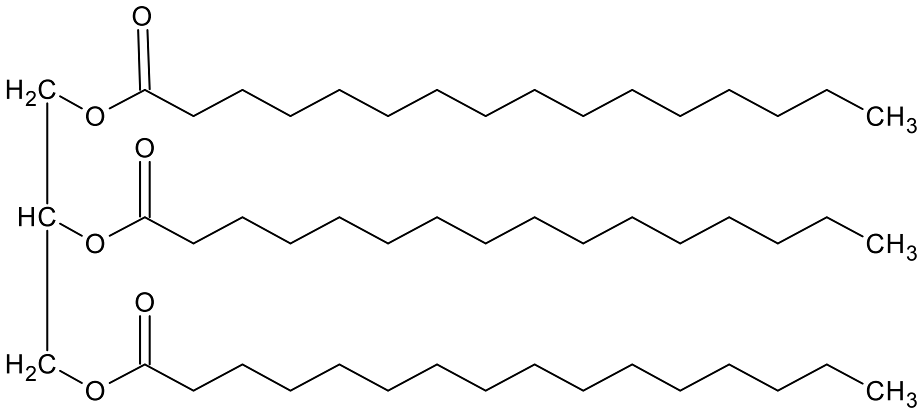
Petro diesel, widely known as diesel, is obtained through fractional distillation of crude oil. Petro diesel contains hydrocarbon molecules that range in size from 8 to 21 carbon atoms. An ordinary petro diesel containing 16 carbon atoms is presented in **Figure 1(a)**. A petro diesel molecule is composed of a pure hydrocarbon, that is, a molecule containing only hydrogen and carbon, with no oxygen molecule. Thus, for proper burning with atmospheric air, only CO_2 and H_2O are released from this molecule. Sometimes, hydrogen sulfide (H_2S) is also produced because of the presence of sulfur (S) content in diesel. Typically, biodiesel contains long chain carbon molecules with hydrogen atoms, similar to petro diesel with an additional ester functional group (–COOR). Biodiesel with 17 or 16 carbons with an ester group is illustrated in **Figure 1(b)**. Vegetable oil also typically contains long rows of carbon and hydrogen atoms with ester functional groups. Vegetable oil molecules are almost three times larger than normal diesel molecules. This large-sized structure is known as a triglyceride. The atomic size and structure of vegetable oil make it gel in cold weather, which means its direct use in engines is difficult. The ordinary atomic structure of vegetable oil is shown in **Figure 1(c).**



(a) Petroleum diesel



(b) Biodiesel



(c) Vegetable oil or Triglyceride

Figure 1: Molecular structure of (a) Petroleum Diesel (b) Biodiesel (c) Vegetable oil

Triglycerides are initially reduced to diglycerides, which are then reduced to monoglycerides. Monoglycerides are finally reduced to fatty acid esters. The gradual reaction mechanism producing the monoglycerides from triglycerides [10] or vegetable oils is briefly shown in **Figure 2**, where R represents an alkyl group; R^1, R^2, and R^3 the fatty acid chains; and k_1, k_2, k_3, k_4, k_5, and k_6 represent the catalyst.

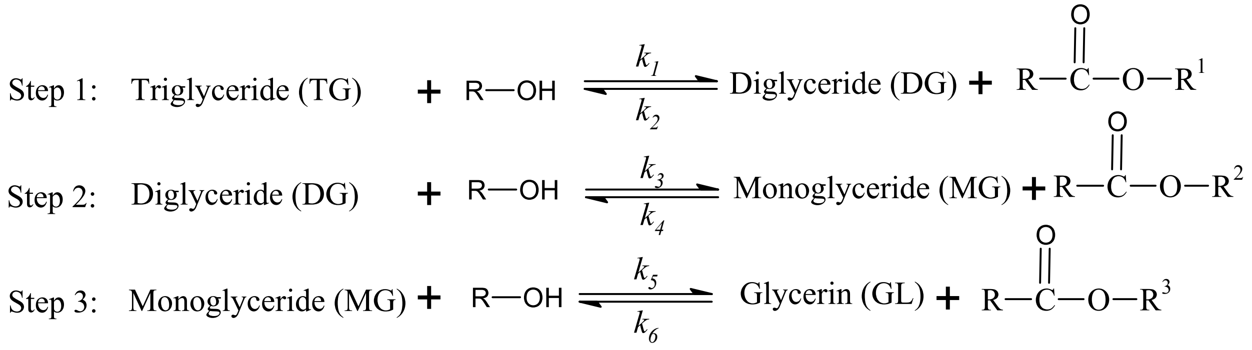


Figure 2: Step by step triglyceride to monoglycerieds production of vegetable oils

Biodiesel can be produced in single or two-step reactions depending on the feedstock quality, such as containing FFAs and water content. Higher FFA contents indicate a higher acid value of the feedstock. Crude oil with a high acid value is first esterified with acid catalyst and then transesterified with a suitable base catalyst. However, a large amount of wastewater is associated with this technique when a homogeneous catalyst used; thus, the process presents some harm to the environment. Laboratory-scale heterogeneous and bio-catalytic processes can minimize this problem. A flow diagram of laboratory-scale or fixed-bed or single-step transesterification biodiesel production process is presented in **Figure 3(a).** Researchers have attempted to utilize not only main oil sources (such as seeds) but also the dry waste shell of seeds. Other value-added products associated with biodiesel production have attracted research attention.

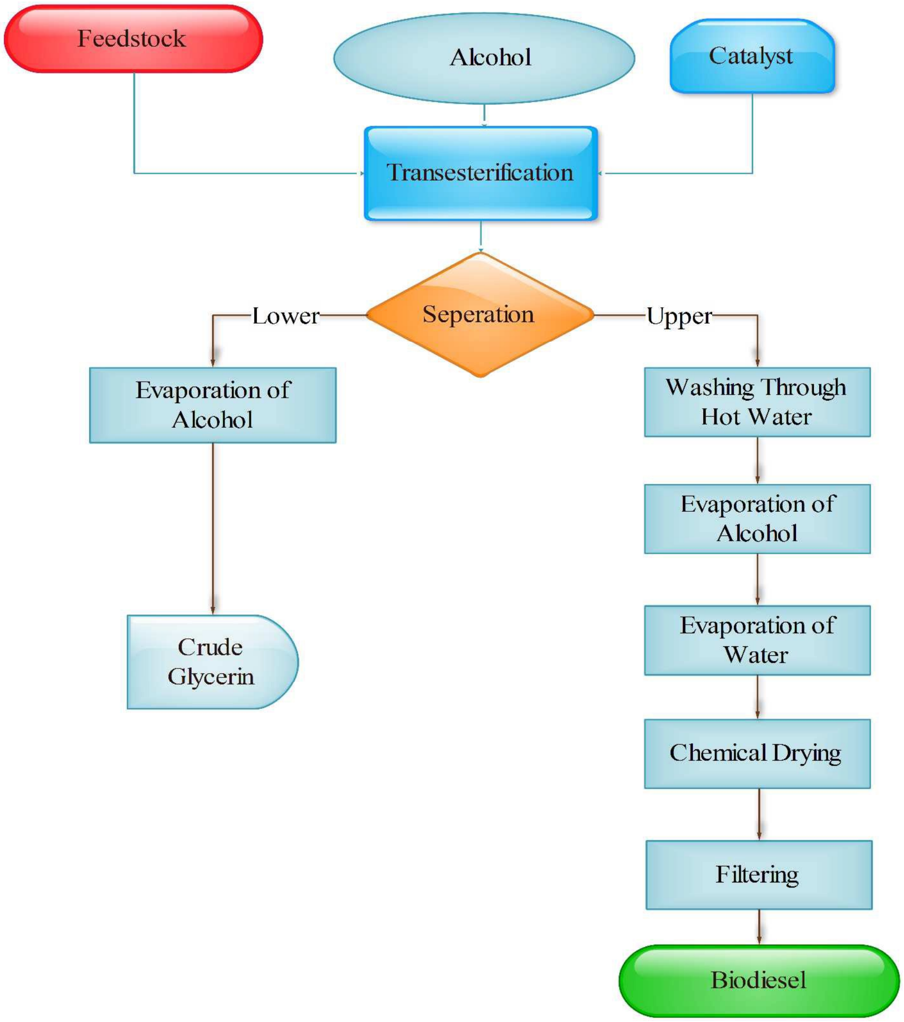


Figure 3 (a): Biodiesel production flow chart for laboratory scale (Single Step)

Maiti et al. [11] introduced an integrated system where power was generated from dry Jatropha seed shells through gasification. Then utilizing gasified producer gas, power was generated with the help of producer gas engine. This electric power partially utilized as energy sources in different steps of the integrated biodiesel production system from *Jatropha curcas* seeds. The relevant steps include screw pressing, oil refining, transesterification, glycerol purification, and soap making. The authors found that 8 h of continuous operation of gasification with 64.8% efficiency can generate 10 kW of captive power with 24.5% efficiency; here, the producer gas heating value was considered to be 5.2 MJm^{-3} and the calorific value of the empty shells was

17.2 $MJkg^{-1}$. Ghosh et al. [12] proposed an integrated process to produce oil-bearing Chlorella variabilis for lipid extrication utilizing a by-product of Jatropha methyl ester production. Later, Ghosh et al. [13] described an improved and integrated process to prepare fatty acid methyl ester (FAME) from whole seeds of *J. curcas* with the least energy use and zero effluent discharge; crude glycerol utilization was also integrated in this work. An integrated contentious *Jatropha curcas* biodiesel production process with its other value added products recovery techniques represented in **Figure 3(b).**

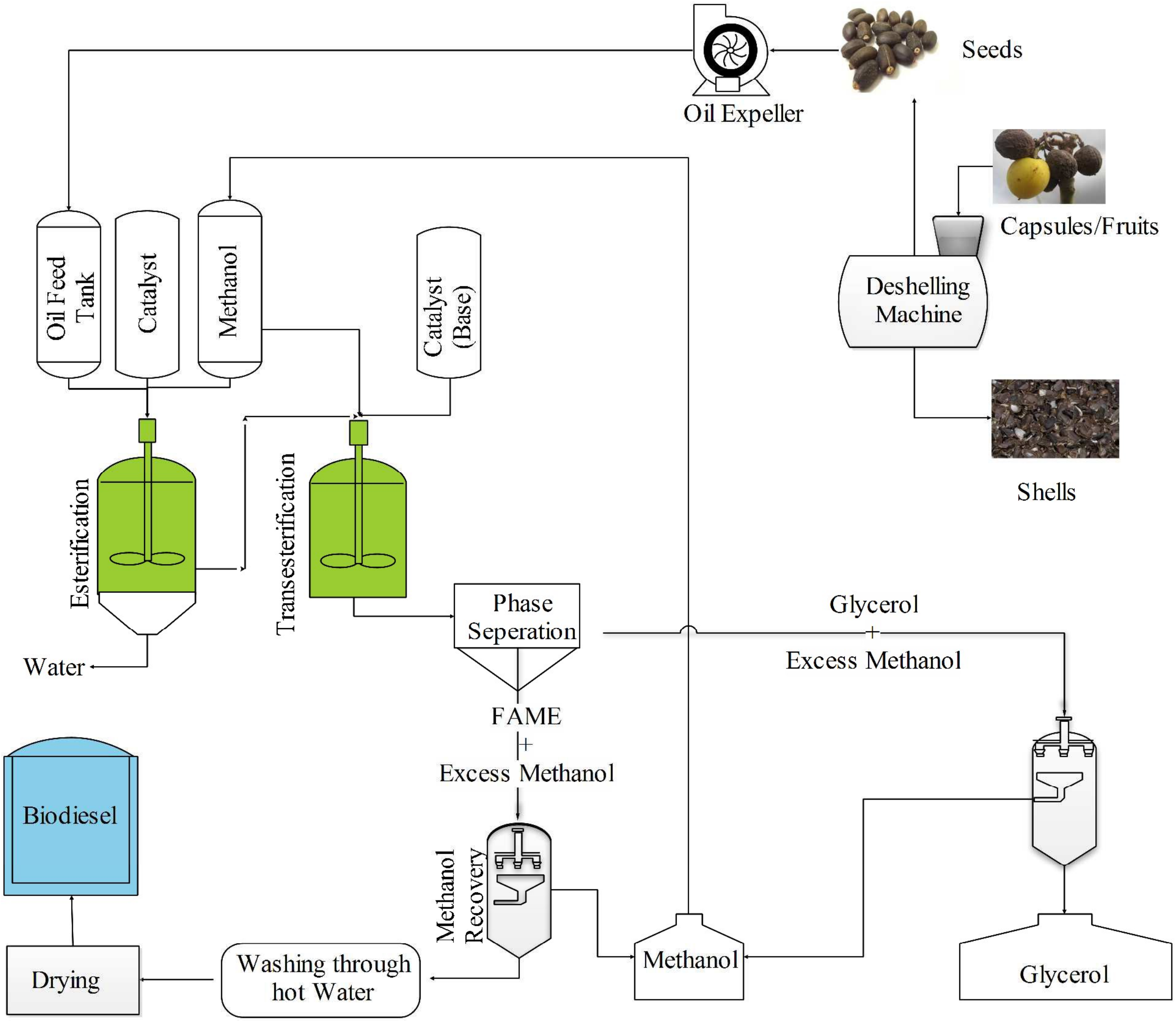


Figure 3 (b): Biodiesel production flow chart for industrial scale (Continuous)

The industrially produced pure biodiesel properties are not exactly similar to petroleum diesel, with a small variation in some properties. The properties of petroleum diesel and the produced biodiesel according to the American Society for Testing and Materials and European Standard are shown in **Table 1**.

Property	Unites	Diesel		Biodiesel (B100)	
		ASTM D975	EN 590	ASTM D6751	EN 14214
Density @ 15ºC (59ºF)	kg/m^3	850	835	800 -900	860-900
Kinematic Viscosity @ 40ºC	mm^2/s	1.3-4.1	3.5	1.9-6.0	3.5-5.0
Lower Heating Value	kJ/kg	-	43000	-	-
Cetane No.	-	40-55	53	48-65	Min. 51
Specific gravity @ 15ºC	g/cm^3	0.85	-	0.88	-
Carbon	% mass	87	-	77	-
Hydrogen	% mass	13	-	12	-
Oxygen, by dif.	% mass	0	0	11	-
Sulfur Content	ppm	500	Max.10(mg/kg)	Max. 0.05	Max. 0.0010

Table 1. Property comparison of biodiesel and petroleum diesel based on ASTM and European Standard (EN).

Boiling Point	ºC	180 to 340	-	315 to 350	-
Flash Point	ºC	60 to 80	Min. 55	100 to 170	Min. 120
Cloud Point	ºC	-15 to 5	-5	-3 to 12	-
Pour Point	ºC	-35 to -15	-	-15 to 16	-
Cold Flow Plugging Point	ºC	-	-	Max +5	-
Lubricity (HFRR)	µm	300-600	-	Max. 300	-
Water Content	mg/kg	-	-	-	Max. 500
Acid Value	mgKOH	-	-	Max. 0.80	Max. 0.50

2.1. Prior to biodiesel production

2.1.1. Pyrolysis (Thermal cracking) of oils

Pyrolysis indicates the shifting or transformation of one substance to another by employing heat. The catalyst is introduced to the process for minimizing conversion time. In other words, pyrolysis refers to the transformation of one organic material into another by thermal decomposition with the presence of desire catalyst and absence of air or oxygen [14]. Vegetable oil, animal fats, natural fatty acids, or methyl ester of fatty acids may be used as pyrolysis material. Transformation of vegetable oil and animal fat into biodiesel producible feedstock is a potential technology using thermal cracking reaction. This innovation is particularly encouraging in areas where the hydro preparing industry is entrenched because this innovation is fundamentally the same as that of traditional petroleum refining [15]. Dissimilar lower hydrocarbons are obtained by pyrolysis of vegetable oil, which could be used as fuel. The properties of treated pyrolytic synthesis fuel derived from vegetable oil are significantly near to that of diesel fuel. Thus, numerous scientists have stated that this fuel is a suitable alternative for diesel [15-18]. Based on its operating conditions, the pyrolysis process can be classified [19] as, conventional pyrolysis, fast pyrolysis, and flash pyrolysis. The mechanism of thermal decomposition of triglycerides is prone to complexity because of its various possible reaction and chemical structure, which depend upon the reaction condition or pathway. A simple systematic reaction mechanism of thermal decomposition of triglycerides is represented in **Figure 4** [18, 20]. Scientists have performed experiments on soybean, palm, and castor oils to determine the optimum distillation temperature, thereby obtaining fuel properties similar to those of petroleum-based fuel [19] . Comparing to the other conventional process with respect to the yield the equipment use for thermal cracking and pyrolysis is costly. By contrast, this process sometimes produces low-value materials and more gasoline than diesel fuel [21].

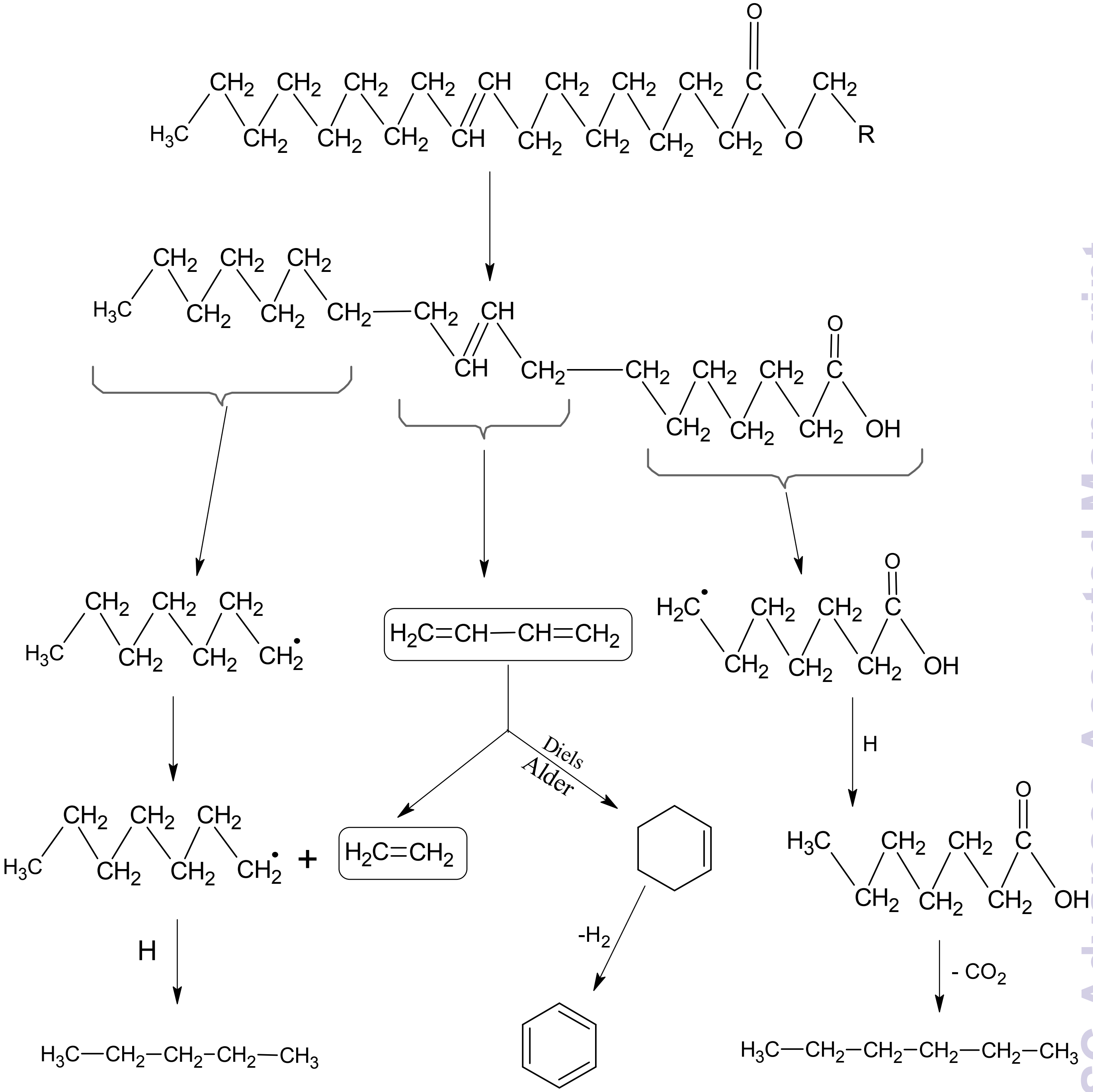


Figure 4: The mechanism of thermal decomposition of triglycerides

Nevertheless, pyrolysis process requires high temperatures ranging from approximately 300°C to 500°C and product characterization is difficult because of differences in the reaction pathway and products acquired from the reactants [14]. Lima et al. [18] employed zeolite as a catalyst during pyrolysis of soybean oil and found that the reaction temperature was approximately 400 °C in the N_2 flow. The obtained products were olefins, paraffin, carboxylic acids, and aldehydes. Ensöz et al. [22] inspected the effect of particle size on the pyrolysis of rapeseed. By changing the particle size of rapeseed in the scope of 0.224–1.8 mm, they observed that the yields of products are not dependent on particle size. More than 30 compounds were detected from the pyrolysis of Macauba fruit, and the amount of main products diminished by increasing the pyrolysis temperature [23].

2.2. Esterification and Transesterification process

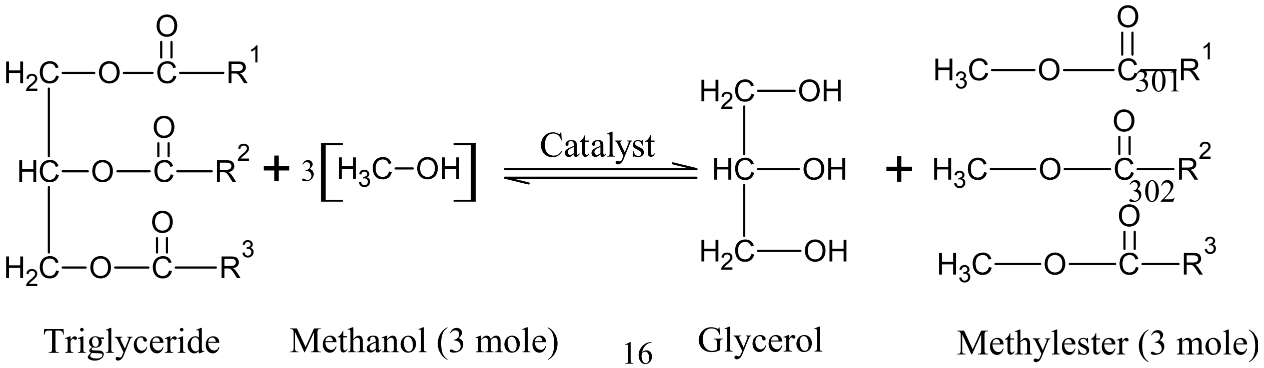
An esterification reaction is one where an ester is produced from one or two other organic substances. The most common method to produce ester is by chemically reacting an organic acid (carboxylic acid) and an alcohol (methanol) with the help of an acid catalyst. The general esterification reaction is shown in **Figure 5**, where R represents small alkyl groups and R^1 fatty acid chains.

$$R^1-\overset{O}{\overset{\|}{C}}-O-\boxed{H + H-O}-R \xrightleftharpoons{\text{Acid Catalyst}} R^1-\overset{O}{\overset{\|}{C}}-O-R + H_2O$$

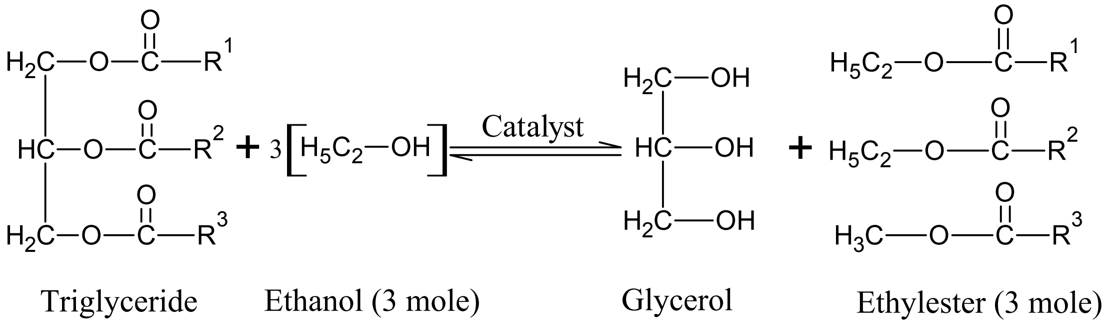
Figure 5: General esterification reaction

Esterification can be performed on vegetable oil or animal fat (triglyceride) with methanol or methanol (short chain alcohol) to produce biodiesel, especially where considerable quantities of free fatty acids (FFAs) are present. These include byproducts of waste oils, non-edible oils, animal oils, and refined vegetable oils. Such oils possess considerable quantities of saturated fatty acids, specifically stearic acid (IUPAC name: octadecanoic acid), which contains 18 carbon chains. In some cases, the homogenous acid-catalyzed reaction is not viable because it may produce corrosion and environmental problems. By contrast, heterogeneous reactions do not show corrosive behavior. In addition, heterogeneous reactions are easier to use for splitting products, diminishing wastewater quantity, and lowering process instrumentation, expenses, time, and environmental effects. Thus, the heterogeneous acid-catalyzed reaction is preferred for esterification reactions. Such catalysis plays a significant role for producing cleaner and more profitable biodiesel by esterification. Thus chemical process employing heterogeneous catalyst is the most acceptable to researchers for creating biodiesel by esterification [24].

Creating biodiesel from the transesterification reaction with the help of a catalyst is a highly favored method. The transesterification reaction for biodiesel production can be performed using various methods and is broadly described as the addition of alcohol (generally methanol or ethanol) with lipids (vegetable oil, algal oil or animals fat) in the presence of a catalyst (acid or base) [25]. Outlines of the transesterification reactions for fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE) are shown in **Figures 6(a)** and **6(b)**, respectively, where R^1, R^2, and R^3 represent mixture of long fatty acid chains [26].



(a) Fatty acid methyl ester (FAME)



(b) Fatty acid ethyl ester (FAEE)

Figure 6: Chemistry of transesterification reaction for glyceride to biodiesel production. (a) FAME (b) FAEE.

2.2.1. Microwave-assisted transesterification technology

Microwave irradiation or microwave-assisted transesterification is a technique where an electromagnetic microwave is used to heat up the system. Electromagnetic wave frequencies ranging from 0.3 GHz to 300 GHz, which are relatively low in the electromagnetic spectrum, are used to produce energy [27]. During microwave irradiation, the bonds are neither formed nor broken. However, the energy is rapidly transferred to the sample. A microwave is integrated with the process after the mixture (methanol, feedstock, and catalyst) chamber. Utilization of electromagnetic microwaves has drawn significant attention [28-31] because these waves present some advantages over conventional heating in transesterification. A simple schematic of the microwave-assisted transesterification process [29] shown in **Figure 7.** Faster and uniform heat distribution, higher yields of cleaner product, less energy consumption, and reduction of the catalyst to methanol ratio are among the attractive features of this technique.

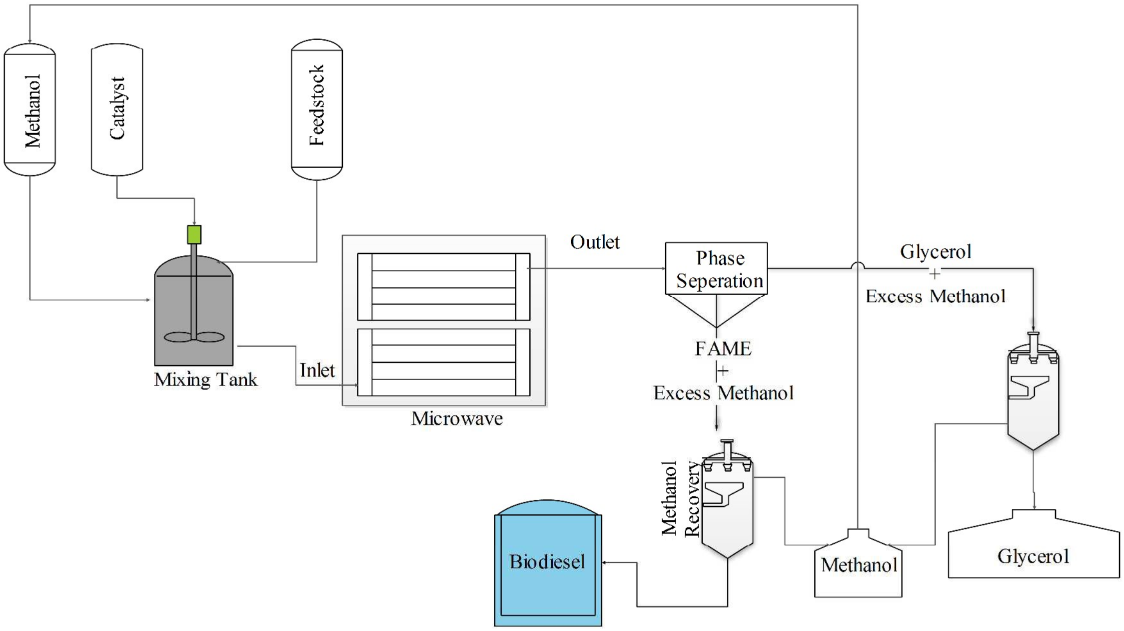


Fig.7 Microwave-assisted transesterification process

2.2.2. Ultrasonic technology

Ultrasonic technologies are typically used in a variety of biological and chemical reactions to enhance yield within a shorter reaction time. Ultrasonic technologies are an effective method to enhance the mass transfer rate between immiscible liquid–liquid phases within a heterogeneous catalyst [32]. Generally, the audible range of human beings lies between 16 and 18 kHz [33], whereas ultrasonic sound ranges lie between 20 kHz and 100 MHz. The principle of ultrasound action in biodiesel production is primarily based on the emulsification of immiscible liquid reactants by micro-turbulence generated by radial motion of cavitation bubbles. Molecules in the medium continuously vibrate and create cavities by compressing and stretching the molecular spacing of the medium, which is developed by a high-frequency sound wave. As a result, micro fine bubbles are formed by the sudden expansion and violent collapse, generating energy for chemical and mechanical effects [34]. This process allows a short reaction time and high yield because of the cavitation of the liquid–liquid immiscible system [32] Maneechakr et al. [35] stated that ultrasonic-assisted transesterification shortens the reaction time and minimizes the molar ratio of alcohol to oil, and reduces energy consumption compared with the conventional mechanical stirring method. According to Lee et al. [36] ultrasonic irradiation reduces reaction times by at least 30 min compared with the conventional method and produces the highest biodiesel yields.

3. Catalyst used for biodiesel production

At present, biodiesel is produced using soybean oil in the U.S.; rapeseed, sunflower, or soybean oils in the EU; and palm oil in Southeast Asia. Food versus fuel concerns have prompted the investigation of non-consumable oil feedstock. The top Asian countries in biodiesel generation, such as the Philippines and Malaysia, also exploit edible oil (coconut and palm oil, respectively). Other edible raw materials, such as sunflower, peanut, camelina, and linseed oil, are also utilized by some developing countries. The crude materials used for biodiesel generation worldwide are rapeseed oil at 84%, sunflower oil 13%, palm oil 1% and others 2%. The principal crude material utilized in India is jatropha, a non-edible oil [18]. Determination of oil for biodiesel generation depends on its availability, characteristics, and price[17] [18]. Some edible and non-edible feedstocks for biodiesel production and their properties are listed in **Table 2** and **Table 3**, respectively.

Table 2. Feedstock's and their oil yield for biodiesel production.

Crops		Algae	
Name	**Oil yield (%)**	**Species**	**Oil yield (%)**
Babassu oil (*Attalea speciosa*)	60–70	*Botryococcus bruanii*	25–75
Borage oil (*Borago officinalis*)	20	*Chlorella* sp.	28–32
Camelina oil (*C. sativa*)	38–40	*Crypthecodinium cohni*	20
Castor oil (*Ricinus communis*)	45–50	*Cylindrotheca* sp.	16–37
Cuphea oil (*Cuphea viscosissima*)	25–43	*Nitzschia* sp.	45–47
Hemp oil (*Cannabis sativa*)	33	*Phaeodactylum tricornutu*	20–30

Jatropha oil (*J. curcas*)	45	*Schizochytrium* sp.	50–77
Jojoba oil (*Simmondsia chinensis*)	44	*Tetraselmis sueci*	15–23
Karanja oil (*P. pinnata*))	27–39	*Isochrysis galbana*	30–41
Linseed oil (*Linum usitatissimum*)	37–42	*Pavlova lutheri*	35.5
Neem oil (*Azadirachta indica*)	40–50	*Nannochloropsis* sp.	31–68

Table 3. Some edible and non-edible sources (feedstock) for biodiesel production and their properties

	Feedstock	**Density**	**Flash Point**	**Acid Value**	**Heating Value**	**Viscosity**	**Cloud Point**	**Peroxide value**	**Pour point**	**Cetane no.**	**References**
		g/cm^3	°C	mgKOH/g	MJ/Kg	mm^2/s at 40 °C	°C		°C		
Edible Oils	Soybean	0.910	254.0	0.20	39.60	32.60	2	44.5	-12.2	48.00	20, 37-39
	Rapeseed	0.910	246.0	2.92	39.70	37.00	—	30.2	—	—	35, 36, 40
	Sunflower	0.920	274.0	0.15	39.60	33.90	—	10.7	—	—	35, 36, 40
	Palm	0.920	267.0	0.10	39.90	36.00	12	—	13	61.15	35, 40, 41
	Peanut	0.900	271.0	3.00	39.80	39.60	—	82.7	—	—	35, 36, 40
	Corn	0.910	277.0	0.11	39.50	—	—	18.4	—	—	35, 36
	Cotton	0.910	234.0	—	39.50	—	—	64.8	—	—	35,
	Moringa	0.859	176.0	0.19	40.11	5.074	21	—	19	67.07	42, 43
	Calophyllum	0.877	162.5	0.30	39.51	5.538	12	—	13	57.30	42, 44, 45
	Coconut	0.860	118.5	0.11	38.30	3.144	1	—	-4	59.00	42, 46
	Aphanamixis polystachya	0.873	188.5	0.45	39.96	4.718	8	—	8	—	42, 45, 47,
	Rice bran	0.868	174.5	0.59	39.96	5.366	0	—	-3	73.60	42, 45, 48
	Neem	0.868	120	0.65	39.81	3.700	9	—	2 176	48-53	45, 48, 49
	Sesame	0.884	208.5	0.30	39.99	4.399	1	—	1	50.48	50, 51
Non Edible Oils	Jatropha curcas	0.920	225.0	28.0	38.50	—	—	—	10	57.10	35, 42, 42
	Pongamina pinnata	0.910	205.0	5.06	34.00	—	—	—	—	—	35
	Palanga	0.900	221.0	44.0	39.25	—	—	—	—	—	35
	Tallow	0.920	—	—	40.05	—	—	—	—	—	35

Poultry	0.900	—	—	39.40	—	—	—	—	—	[35]
Used cooking oil	0.900	—	2.50	—	—	—	—	—	—	[35]

Several catalysts are associated with biodiesel production technology. Based on a previous review [5, 52-55] catalysts can be classified as homogeneous catalysts, heterogeneous catalysts, and biocatalysts; these catalyst types, including their sub-orders are listed under **Figure 8**.

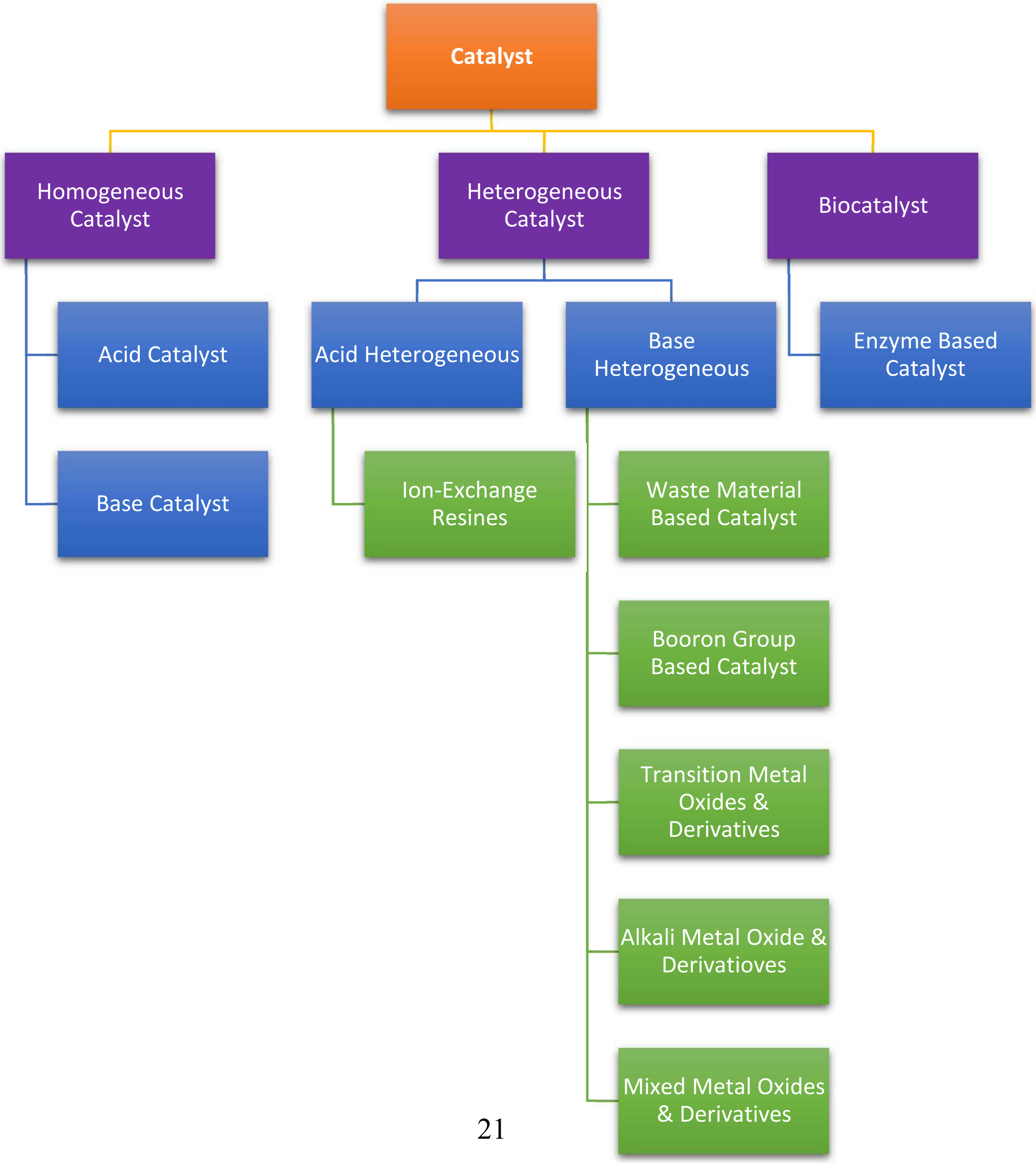


Figure 8: Catalyst used in biodiesel production technology

3.1. Homogeneous Catalyst

Homogeneous catalysis involves a sequence of reactions that includes a catalyst from the same phase as reactants. Phase in this article refers to solid, liquid, and gas. Most often, a homogeneous catalyst is dissolved or co-dissolved in the solvent with all reactants. Sodium hydroxide (NaOH) or potassium hydroxide (KOH) are currently the most popular homogeneous catalysts for biodiesel production [56]. However, some researchers suggest that these homogeneous base catalysts are only suitable for feedstocks with low FFA content. If the FFA content is larger than 6 wt.%, the base catalyst process is unsuitable for biodiesel synthesis [57]. Thus, some scientists recommend that the FFA content should be less than 2 wt.% [21, 58-60]. This homogeneous base catalyst is gradually gaining popularity in industrial biodiesel production for the following reasons:

(a) Low reaction temperature needed to synthesize biodiesel at atmospheric pressure
(b) High biodiesel yield could be possible at optimal condition
(c) Widely available and economical
(d) Handling reactants and catalyst is easier than one solid or a combination.

Although homogeneous catalysts present several advantages, they also feature some drawbacks. The limitations of using the homogeneous catalyst for biodiesel synthesis are listed below:

(a) Water generation throughout the acid esterification retards the process. Proper care should be taken to remove water via evaporation or chemical drying, which adds expenses to biodiesel production.

(b) Although instances of reusing catalysts have been reported, this method is almost never witnessed if ever completed over a production scale because of the associated expenditures.

(c) Corrosive nature of the catalysts concerned. The preferred acid (H_2SO_4) and base (SMO) catalysts presently employed in biodiesel synthesis are corrosive and must be handled conservatively.

3.2. Heterogeneous Catalyst

The catalysts with a phase or state different from that of the reactants are considered heterogeneous catalysts. A heterogeneous catalyst is often a practical material that regularly creates active sites with its reactants under the reaction atmosphere. The application of a heterogeneous catalyst will result in simpler and less costly separation processes, as well as additional capital and energy costs. The disadvantages of heterogeneous catalysts include elevated temperatures and higher oil to alcohol ratios than those required in the homogeneous catalytic procedure. Some of these catalysts have demonstrated good performance even under the reaction conditions employed for homogeneous catalysts [61, 62]. The separation, purification, and reusability of the catalyst are among the more attractive features of the heterogeneous catalytic process. Carbonates and hydrocarbonates of alkaline metals, alkaline metal oxides, alkaline metal hydroxides anionic resins, and base zeolite may be used as heterogeneous catalysts.

Dossin et al.[63] revealed heterogeneous catalyst transesterification process by employing MgO as a catalyst. About 1,00,000 tons biodiesel was generated in every year by this process from triolin feedstock. Right now, the remarkable heterogeneous procedure established the Esterfip-H technology, which grew by the Institute Français du Petrole (IFP). The plant beginning up in 2006 delivering production 160 000 ton every year [64]. The role and utilization of base and acid heterogeneous catalysts for biodiesel synthesis has been broadly described in this literature.

3.2.1. Acid heterogeneous catalyst for biodiesel production

Acid base catalysts have a corrosive but less toxic effect and create few environmental problems [65] . This type of catalyst is more popular for both esterification and transesterification reaction when producing biodiesel from low quality feedstock [66]. Transesterification is catalyzed by Bronsted acids. The most ordinarily employed acid catalyst is H_2SO_4. Broadly, heterogeneous acid catalysts can be divided into two types: the low temperature type and the high temperature type [67]; catalysts of these types show better activity at low and high temperatures, respectively. While these catalysts provide exceptional returns in alkyl esters, their rates of reaction are moderate, demanding reaction times longer than 3 h and temperatures higher than 100 °C to achieve complete transformation [68]. The basic mechanism of an acid catalyst is shown in **Figure 9**. Investigations using a heterogeneous acid catalyst to produce biodiesel are discussed in the next paragraph.

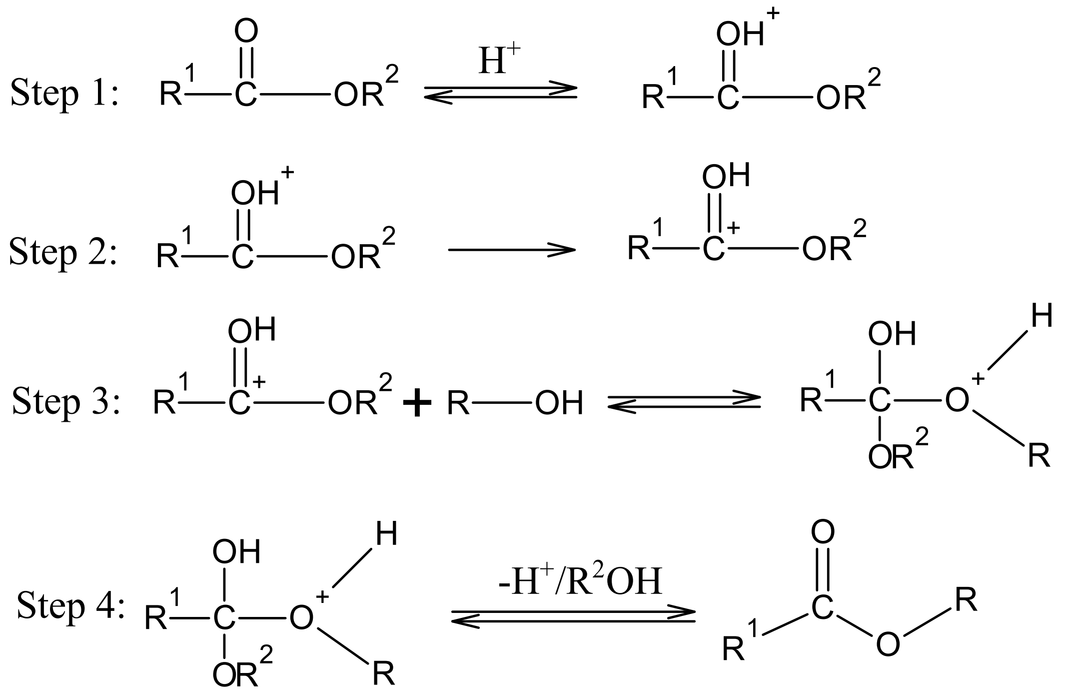


Figure 9: Basic reaction mechanism of an acid catalytic process

3.2.1.1. ZrO_2 as acid heterogeneous catalyst

Zirconium dioxide (ZrO_2), sometimes referred to as zirconia, is used as an acid heterogeneous by many researchers. This substance has strong surface acidity. Thus, many investigators often choose ZrO_2, sulfated ZrO_2 [69], and other modified metal oxides with sulfated ZrO_2 as acid heterogeneous catalysts [70].

According to Kiss et al. [71], sulfated zirconia (SO_4^{2-}/ZrO_2) shows the best performance as a heterogeneous catalyst for esterification among zeolites, ion exchange resins, and mixed metal oxides. Park et al. successfully performed transesterification of vegetable oil to convert FFA to FAME using sulfated zirconia (SO_4^{2-}/ZrO_2) and tungstated zirconia (WO_3/ZrO_2). However, tungstated zirconia (WO_3/ZrO_2) requires a longer reaction time. Approximately 140 h of reaction time and a 75°C reaction temperature are needed to achieve only 65% conversion.

Implementation of tungstated zirconia-alumina (WZA) and sulfated zirconia-alumina (SZA) was assessed by Furuta et al.[72] during transesterification of soybean oil with methanol. The reaction was performed under atmospheric pressure and 200–300°C with the help of a fixed bed reactor. The investigators showed that WZA has higher activity than SZA but did not elaborate on the reason behind this phenomenon.

Jitputti et al.[73] utilized both sulfated zirconia (SO_4^{2-}/ZrO_2) and unsulfated zirconia (ZrO_2) for transesterification of palm kernel oil and crude coconut oil with the help of methanol. He reported 90.3% and 86.3% methyl ester yields from palm kernel oil and crude coconut oil, respectively, while using sulfated zirconia. Only 64.5% palm kernel yield and 49.3% crude coconut oil yield was possible in the case of unsulfated zirconia. These results clearly indicate that a slight change in metal oxide surface activity is a major parameter influencing the high yield of methyl ester.

3.2.1.2. Cation-exchange resin as a heterogeneous catalyst

Many researchers have extensively used cation-exchange resin for biodiesel production at the laboratory scale; this resin unsuitable for industrial application. Liang et al. [74] described an optimal operational condition to convert biodiesel from soybean oil with the help of choloroaluminate ($[Et_3NH]Cl-AlCl_3$). Soybean oil 5g, methanol 2.33g, reaction time 9h, and reaction temperature 70°C were recorded as optimal conditions for 98.5% biodiesel yield. The main advantages of the use of such a catalyst are low cost, high yield of biodiesel production, reusability of catalyst, no need for saponification, and simplicity of operation.

Some investigators have attempted to use poly (DVB) resin sulfated with H_2SO_4, Amberlyst-35 (Rohm & Haas) [75], Amberlyst-15 (Rohm & Haas) [75], Amberlyst 15 DRY [76] and Nafion SAC-13

[77] as sulfonic acid ionic exchange resins. Limited functionality with a significantly high ratio of oil to alcohol is one of the major shortcomings of this type of catalyst. By using an organically functionalized acid catalyst, the key shortcomings of the aforementioned catalyst, including leaching and low surface areas, could be solved [78].

3.2.1.3. Solid heteropoly acid as heterogeneous catalyst

Heteropoly acid (HPA) catalysts are another low temperature heterogeneous catalyst utilized by Chai et al. [79] for high-quality biodiesel production. Narasimharao et al. [80] studied insoluble HPA salts for solid acid esterification and transesterification processes; the general formula of these salts is y $Cs_xH_{3-x}PW_{12}O_{40}$, where x varies from 0.9 to 3. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst could be used in simultaneous esterification and transesterification reactions without losing activity and selectivity. Hamad et al. [81] introduced $H_3PW_{12}O_{40}/SiO_2$ and $Cs_2HPW_{12}O_{40}$ as heterogeneous HPAs for transesterification of rapeseed oil with the help of ethanol. The strengths of the acid sites are measured in terms of heating value.

Zhang et al. [65] studied the maximum yield of FAMEs using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a heterogeneous HPA for microwave-assisted transesterification to produce biodiesel from yellow horn (*Xanthoceras sorbifolia* Bunge) oil. The purpose of this study was to optimize the reaction temperature, reaction time, methanol to oil molar ratio, amount of catalyst, and catalyst reusability cycle. Approximately 96.22% FAME yield was achieved under optimal conditions. A reaction temperature of 70 °C, reaction time of 10 min, methanol to oil molar ratio of 12:1, catalyst loading of 1% wt., and minimum nine times of catalyst reusability were recorded as optimal conditions.

3.2.1.4. Zeolite as acid heterogeneous catalysts

Zeolites are crystalline solid structures made of silicon, aluminum, and oxygen that frame a structure with holes and channels inside where cations, water, and/or little atoms may dwell. Zeolites have unique properties as catalysts, including acidic strength and shape selectivity. The catalytic properties varies because of the porous structure. The inner electric fields from crystal and surface properties of zeolite can suit a wide assortment of cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+} that ascribe to its simple nature. Approximately 191 exceptional zeolite frameworks have been identified [82] About 40 naturally occurring zeolite frameworks are known. An improved (using La) zeolite called zeolite beta (La/zeolite beta) was studied by Shu et al. [83] as a heterogeneous acid catalyst for methanolysis of soybean oil. This catalyst was organized using an ion exchange process through suspension of zeolite beta in a lanthanum nitrate $La(NO_3)_3$ aqueous solution under high mixing at ambient temperature for 3 h and drying at 100 °C for 24 h. Then, the catalyst is calcined at 250 °C for 4 h. The author recorded only 48.9 wt.% triglyceride conversion by using this catalyst. Karmee et al. [84] studied Hβ-zeolite, montmorillonite K-10, and ZnO as heterogeneous catalysts for transesterification of non-edible *Pongammia pinnata* under reaction conditions of 1:10 oil to methanol ratio, 0.115 wt.% catalytic loading, 120 °C temperature, and 24 h reaction time. Yields of 59%, 47%, and 83%, respectively, were recorded. Suppes et al. [85] examined a biodiesel synthesis process where zeolites were used as the prospective acid heterogeneous catalyst. They used several types of zeolites and metals to examine the potential of zeolite during the transesterification of soybean oil possessing 2.6 wt.% FFA content. Xie et al. studied [4] NaX zeolites (Si/Al=1.23) as heterogeneous catalyst after improving the strength from <9.3 to 15.0–18.4. A yield of 85.6% was recorded under 10% catalytic loading, 125 °C reaction temperature, and 2 h of reaction time.

Ramos et al. [86] used zeolites (mordenite, beta, and X) to convert FAME from crude sunflower oil and recorded 93.5% –95.1% FAME yield at 60 °C. However, the time required to prepare the catalyst was relatively long because the process required heating at 500 °C for 10 h, drying at 120 °C for 12 h, and calcining at 550°C for 15 h.

Zeolite can sometimes be used as a base heterogeneous catalyst. Marchetti et al. [87] used basic nature NaY zeolites and VO_X over ultrastable acidic nature Y zeolites as heterogeneous catalysts for the conversion of FFA to FEME. At 300°C, the conversion times of FFA oil to biodiesel using these zeolites were only 10 min and 50 min, respectively. During reaction, the presence of H_2O initially accelerated the reaction. However, when the reaction proceeded further, the H_2O decelerated the reaction. Thus, overall biodiesel conversion rate was hampered.

Though acid heterogeneous catalyst are promising to the biodiesel production technology, it also have some drawbacks on the production process. Advantages and disadvantages of the acid heterogeneous catalyst are discussed in **Table 4.**

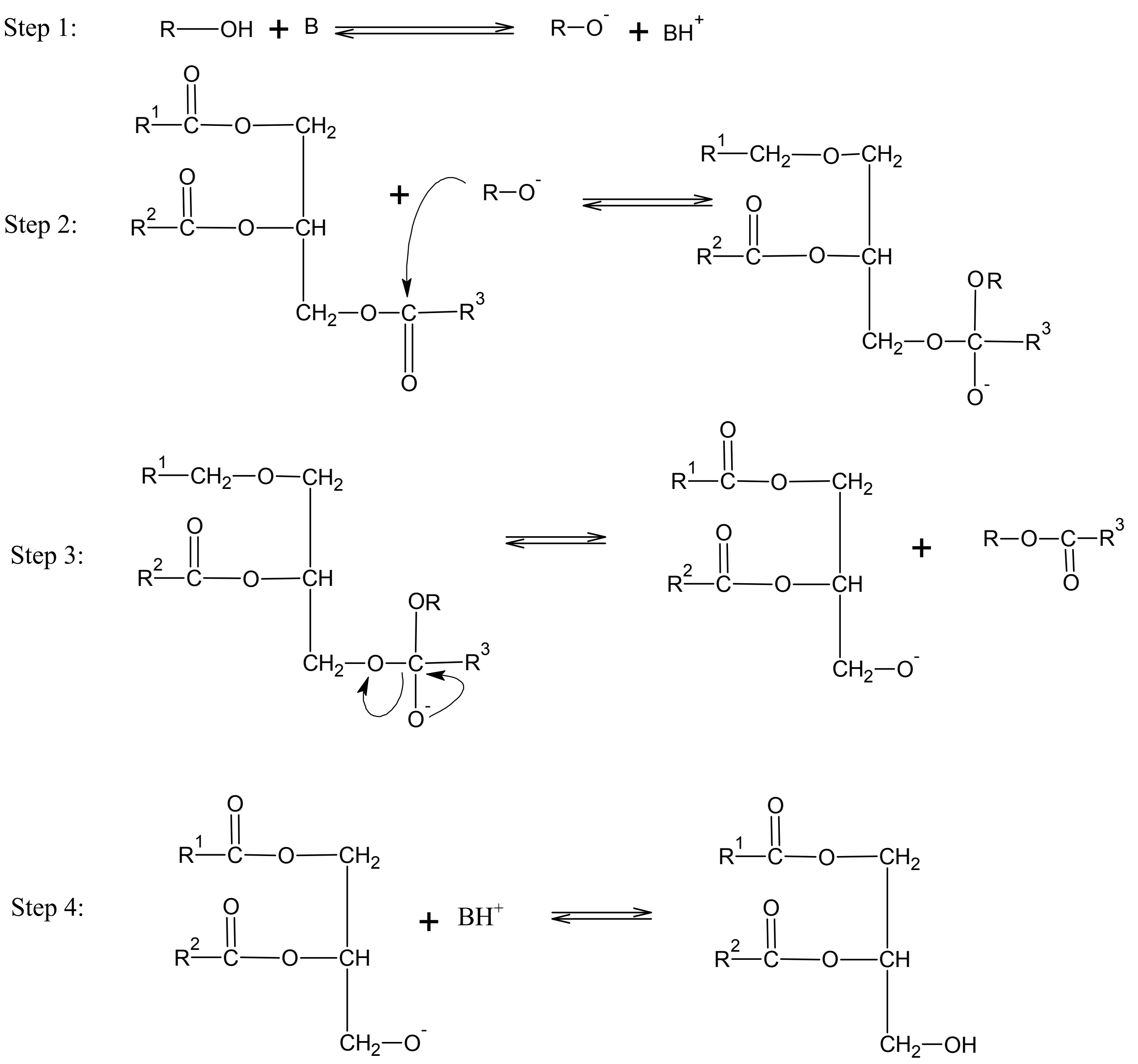
Table 4: Benefits and Limitations of acid heterogeneous catalyst for biodiesel production

Catalyst used	Reaction parameters	Benefits and Limitations	Ref.
Tungstated zirconia (WO_3/ZrO_2)	Reaction time 140h, reaction temperature 75°C and yield 65%	Long reaction times	66
Sulphated zirconia (SO_4^{2-}/ZrO_2)	Palm kernel oil yield 90.3% , Coconut oil yield 86.3% in optimal condition	Less reaction time then tungstated zirconia	66, 78
Unsulfated zirconia (ZrO_2)	palm kernel oil yield 64.5%, coconut oil yield 49.3% in optimal condition	Very poor biodiesel yield than others	78
Tungstated zircona-alumina (WZA)	Atmospheric pressure, Reaction temperature 200-300°C, with fixed bed reactor	Relatively higher activity than sulfated zirconia-alumina	67
Sulfated zirconia-alumina (SZA)	Atmospheric pressure, Reaction temperature 200-300°C, with fixed bed reactor	Relatively lower activity than tungstated zircona-alumina	67

Choloroaluminate ($[Et_3NH]Cl\text{-}AlCl_3$)	Soybean oil yield 98.5% , reaction time 9h, reaction temperature 70°C	Reaction time is quite high though yield is good	[69]
Heterogeneous HPA ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$)	Reaction temperature 70°C, reaction time 10 min, 12:1methanol to oil ratio, catalyst loading 1% wt. from yellow horn	Minimum time required with high oil to alcohol ratio and nine time reusability of catalyst.	[65]
Sulfonic acid ionic exchange resins	-	High oil to alcohol ratio is needed	[75-77]

3.2.2. Base heterogeneous catalyst for biodiesel production

Currently, several solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides, and hydrotalcites. The most general catalysts, which are used as base heterogeneous catalysts, are $K/\gamma\text{-}Al_2O_3$ catalyst [88], $HTiO_2$ hydrotalcite catalyst [89], Ca and Zn mixed oxide [90], calcium oxide (CaO) catalyst [91, 92], MgO catalyst , Al_2O_3 supported CaO & MgO catalysts [3], Li_4SiO_4 catalyst [93], Na_2SiO_3 catalyst [94, 95], alkaline earth metal oxides [96], KF/Ca–Al [97], basic zeolites, alkali metal loaded alumina [98]. In addition, alkaline earth steel oxides, particularly CaO, have attracted much notice owing to their relatively higher strength, significantly low solubility in methanol, and synthesis from affordable resources such as limestone and calcium hydroxide [99, 100]. Researchers recommend base heterogeneous-catalyzed transesterification for the following reasons: simplification of biodiesel production, simplification of the purification process, reductions in wastewater amount, lowering of the process and equipment costs, and reductions in environmental impact [67, 101]. In addition to ease of catalyst restoration, the action of the heterogeneous alkali catalyst may resemble that of its homogeneous counterpart under similar running conditions [102]. Transformation of the biodiesel from crude oil occurs in several steps. The systematic reaction mechanism of a simple base catalytic reaction is shown in **Figure 10.**



572

573 **Figure 10: The reaction mechanism of base catalysis process [103]**

574 3.2.2.1. CaO as a base heterogeneous catalyst

575 CaO is the most commonly exploited alkaline earth metal oxide for transesterification. FAME
576 yields of nearly were initially reported [104]. The ability to reutilize the catalyst is a major topic of
577 concern. The modification of CaO to organic metallic nature, for example, $Ca(OCH_3)_2$ and
578 $Ca(C_3H_7O_3)_2$, investigate the reutilization function. Collected works on biodiesel state that

approximately 93% biodiesel yield may be obtained from a 20-cycle reaction. 95% $Ca(C_3H_7O_3)_2/CaCO_3$ has also been determined to be a capable heterogeneous catalyst with a reusability of 5 cycles and good FAME yield [105].

The mechanics of transesterification introduced by Lam et al. [56] used CaO as a heterogeneous base catalyst. CaO was reacted with FFAs, and a certain amount of the catalyst was transformed into Ca soap by rejoining with the FFAs, causing limited catalyst recovery. As a basic standard of biodiesel, the concentration of mineral matter should be less than 200 ppm. Kouzu et al. [106] determined a Ca concentration of 3065 ppm in the reaction products, thus exceeding this standard.

Some investigators noted that soluble matter can be removed by CaO throughout transesterification. CaO slightly dissolves in methanol, thus transforming into soluble calcium diglyceroxide, where CaO reacts with glycerin during the transesterification of soybean oil with methanol [106-108]. Stimulated CaO is used to study the function of H_2O and CO_2 in the loss of catalytic performance in the presence of O_2 during the transesterification of sunflower oils [109]. In the above studies, CaO quickly hydrated and carbonated in the air. Stimulated CaO was affected because of surface activity, as well as absorption of CO_2 and H_2O on surface area. If CaO is exposed to deal at 700 °C to eliminate carbonate groups from the surface, then the catalytic action of CaO might be restored. However, filtering or removing the catalyst from the product was noticeable in the transesterification reaction, whereas temperature dealing was occupied. Considering its low solubility in methanol, CaO results in high basic strength and fewer ecological effects. Furthermore, CaO can be produced from economical resources such as limestone and $Ca(OH)_2$.

KOH can use altered CaO, however advantages of CaO over KOH include lower price, lower solubility, higher basicity, and easier handling. In actual practice, reaction rate is unsatisfactory during transesterification for relatively low activity [108, 110]. However, reusable activity can be enhanced by washing [108] and improving thermal activation treatment [104]. Being nano sized, CaO provides effective catalyst activity because of high surface area. A surface structure of a metal oxide is presented in **Figure 11**.

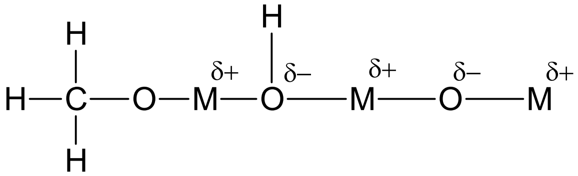


Figure 11: Surface structure of metal oxides compare with its acidic & basic sites.

The biodiesel production from sunflower oil using a heterogeneous base catalyst (CaO) was conducted by Vujicic et al. [111]. Experiments were accomplished using a commercial bench stirred tank reactor. The experiment was conducted using changeless factors such as $2dm^3$ of reactor volume, 200 rpm of stirring speed, a 6:1 methanol to oil ratio, and 1 wt.% of CaO catalyst loading. Temperature (60–120°C), pressure (1–15bar), and reaction time (1.5–5.5h) operated the ester yields. Optimal transformation to methyl ester (almost 91%) was observed at 100°C, although a positive effect of pressure (up to 10 bar) was observed at 80°C. The founding of basic sites depends on catalyst activation in air, which occurs at 900°C. Catalyst corpuscle coalescence occurred during the reaction, which provided gum-like construction and meaningful catalyst deactivation.

CaO was produced using a simple and flexible technique [112] to raise activity and to improve the properties of calcined nature calcites through the hydration-dehydration method. This process prepares CaO to be extremely fit for biodiesel production. Newly prepared CaO has a relatively higher surface area and more basic sites than CaO obtained from the decomposition of calcite. With calcined calcite, methyl ester content was enhanced to 93.9 wt.% from 75.5 wt.%. This study, developed through new hydration, delivers different important information on the influence of water on the properties and activities of CaO, and ensures thermal disintegration technique of calcined calcite.

Hai-xin et al.[113] established a novel morphology for producing CaO simply and at low cost. This morphology possesses high catalytic activity in catalyzing transesterification reaction for biodiesel. A CaO microsphere with tiny holes was obtained by calcining spherical $CaCO_3$ precursor prepared simply through the involvement of $CaCl_2$ and Na_2CO_3. During the canalization of the transesterification of soybean oil, the CaO microsphere was employed, which possesses outstanding catalytic capability. Approximately 98.72% FAME yield was obtained.

3.2.2.2. BaO as heterogeneous catalyst

Mootabadi et al.[96] conducted a palm oil transesterification experiment with the aid of alkaline earth metal oxide catalysts such as CaO, SrO, and BaO. The experiment was performed to observe the result of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), and catalyst loading (0.5–3%) by creating 20 kHz ultrasonic cavitation and fluctuating ultrasonic amplitudes (25–100%). The natures of catalysts were mostly dependent on their basic strengths. The activity ranking of the catalysts was CaO < SrO < BaO. In ideal circumstances, 95% yield was reached with respect to 2–4 h formal stirring within 60 minutes. Moreover, yields accomplished within 60 min for CaO, SrO, and BaO were 5.5–77.3%, 48.2–95.2% and 67.3–95.2%, respectively. Ultrasonic irradiation at 50% amplitude was estimated as optimal, and the physical variations of catalysts can be effectively explained after ultrasonic-assisted reaction.

The major reason for this activity drop of recycled catalyst, dissolution, was investigated, especially for BaO catalyst.

3.2.2.3. MgO as base heterogeneous catalyst

Among the alkali earth materials, MgO is one of the widely used materials for transesterification [70]. Lopez et al. [114] studied MgO used as a base heterogeneous catalyst where 18% yield of feedstock was achieved through a calcination temperature of 600 °C. The low surface area of the catalyst takes almost 8 h for reaction. MgO is used to analyze catalytic activity to produce biodiesel. An experiment by Di Serio et al. [115, 116] that used a 12:1 methanol to oil molar ratio and 5.0 wt.% of the catalyst (MgO) gave 92% biodiesel yield within 1 h. Another experiment stated [117]] that in a batch reactor, MgO worked efficiently and 500 tones of biodiesel production was achieved by transesterification at ambient temperature. In batch reactor biodiesel production, cost is minimal because of temperature. Some researchers [115, 118] stated that in supercritical conditions (300°C) and high methanol to oil molar ratio (39.6:1), a MgO catalyst gives a 91% FAME yield.

3.2.2.4. SrO as base heterogeneous catalyst

In solid base catalysis, although Ca and Mg are the more extensively used alkaline Earth materials, strontium oxide (SrO) has also seen used in biodiesel production. Using CO_2 temperature programmed desorption, pure SrO was confirmed the the maximum basic strength [119], which is comparable to that of BaO (26.5<H). In addition, SrO deposits the inferior surface area with respect to MgO and CaO [120]. Only few experiments have been conducted using SrO as a heterogeneous catalyst for the transesterification of biodiesel production.

Zabeti et al. [121] discussed the appropriateness of using SrO as catalyst for transesterification reaction. Liu et al. [122] found that in the reaction medium, SrO acts as an extremely active and soluble metal oxide. However, vegetable oil, methyl esters and SrO remains insurable in methanol, thus becoming a suitable heterogeneous catalyst for transesterification. In 30 min at 65°C with an alcohol to oil molar ratio of 12 wt.% and a 3 wt.% catalyst loading, 90% yields of methyl esters were accomplished during the transesterification of soybean oil. However, the specific surface area of the catalyst was as low as $1.05 m^2/g$.

Salamatinia et al. [123] investigated the heterogeneous transesterification of palm oil for biodiesel production using an ultrasonic process. Briefly, response surface methodology was applied to optimize the biodiesel production process with the help of two (BaO and SrO) alkaline earth metal oxide catalysts. To optimize production, four variable factors were considered. Reaction time (10–60 min), alcohol to oil molar ratio (3:1–15:1), catalyst loading (0.5–3.0 wt.%), and ultrasonic amplitude (25–100%) were included as the optimized factors. The mathematical frameworks and the steps of the process were established. The frameworks were able to correctly predict the biodiesel yield with less than 5% error for SrO and BaO catalysts. The high activity of a catalyst mostly depends on its basic strength. Ultrasound was found to significantly enhance the process by decreasing reaction time by almost 50 min, and 2.8 wt.% catalyst loading for creating biodiesel yields more than 95%. The best results were determined by a 9:1 alcohol to oil ratio and ~70% and ~80% ultrasonic amplitude for both BaO and SrO catalysts, respectively.

3.2.2.5. Boron group supported (Al_2O_3) upon CaO and MgO

Boron bunch components, especially aluminum and Al_2O_3, are widely utilized stacked with different other metal oxides, halides, nitrates, and alloys [3, 88, 122, 124]. Boron and aluminum oxides are the most commonly used catalysts for mixed metal oxide production among the boron group elements. To achieve a decent yield of biodiesel production, different forms of oxides such as Al_2O_3, γ-Al_2O_3, and Al_2O_3 supported upon CaO and MgO are used as heterogeneous base catalysts. Xu et al. [125] used a mesoporous polyoxometalate–tantalum pentoxide composite catalyst, $H_3PW_{12}O_{40}/Ta_2O_5$, which was prepared using a one-step sol–gelhydrothermal method in the presence of a triblock copolymer surfactant.

3.2.2.6. Biodiesel production with carbon group catalyst

Formulating a carbon-based heterogeneous catalyst is simple, and is profitable for biodiesel production when used as a catalyst. Shu et al. [126] used the sulfonation of carbonized vegetable oil asphalt as a solid catalyst to produce biodiesel via the transesterification of vegetable oil. This catalyst can be used in both the esterification and the transesterification process, while waste vegetable oil with large amounts of FFAs is present in feedstock. The maximum conversion of triglyceride and FFA reached 80.5% to 94.8% after 4.5 h at 220 °C when using a methanol to oil ratio of 16.8:1 and 0.2 wt.% of catalyst to oil.

Dehkhoda et al.[127] studied the transesterification reaction of palm oil for biodiesel production, where KOH/AC was used as a heterogeneous catalyst. In their study, operating conditions were 70 °C, the molar ratio of alcohol to oil was 15:1, catalyst loading was 5 wt.%, and reaction time was 15 h. Approximately 94% biodiesel yield was achieved, and the catalyst could be reused up to three times. Through the incineration of commercial grade sugar, a carbon catalyst was prepared and studied by Toda et al. [128]. Only 50% of oil to ester conversion could be achieved from these carbon structures at the end of its first cycle, although catalytic activity remained unchanged.

Lou et al.[129] reported the arrangements of carbohydrate-deduced catalysts from different d-glucose, sucrose, cellulose, and starch sort starches. The synergist and textural properties of the arranged impetuses were examined in points of interest, and the starch-inferred impetus was found to have the best reactant execution. The carbohydrate-deduced catalysts displayed considerably higher synergist exercises for both esterification and transesterification contrasted with the two ordinary strong solid acid catalysts, sulfated zirconia (S-ZrO_2) and niobic acid (Nb_2O_5 nH_2O). The carbohydrate-deduced catalysts also gave a significantly upgraded yield of methyl esters in changing over waste cooking oils containing 27.8 wt.% high FFAs to biodiesel. In addition, under the maximum response stipulation, the starch-inferred catalyst held a significantly high extent (approximately 93%) of its unique synergist action after 50 cycles of progressive re-use and showed exceptional operational dependability. The carbohydrate-inferred catalysts, particularly the starch-determined catalyst, were exceptionally compelling, recyclable, eco-accommodating, and apposite for the creation of biodiesel from waste oils containing high FFAs.

Faria et al.[130]] utilized tetramethyl guanidine on a silica gel surface area [131] as a base catalyst. ^{13}C and ^{29}Si atomic attractive reverberation points of interest are in concurrence with the proposed structure. The investigator stated that biodiesel yield was approximately 86.73% and the reaction time was approximately 3h. In addition, catalyst recovery was complete; almost 62% after the 9th cycle of catalysis reuse.

3.2.2.7. Waste materials based heterogeneous catalyst

Mainly calcium-enriched waste materials are used as catalysts synthesis sources, with mollusk shell, eggshell, and bones being the more common. Researchers examined a number of systems to remove misused atoms and change useable catalysis with high cost viability. CaO force obtained from these waste materials could be a potential probability for biodiesel era. Boey et al.[132] reported that waste shells can be utilized for the transesterification of palm olein into methyl esters as a catalyst, which is an issue of CaO. Categorization consequences showed that the fundamental segment of the shell was $CaCO_3$, which changed into CaO when enacted over 700 °C for 2 h. The economically produced catalyst affected transesterification for biodiesel production, similar to laboratory CaO. Ideal conditions were found at a 0.5:1 methanol to oil mass ratio, 5 wt.% catalyst loading, stirring speed 500 rpm, and a reaction temperature 65 °C. Reusability consequences established that the arranged catalyst could be recycled for up to 11 cycles. Factual examination was performed utilizing a central composite design to assess the commitment and execution of the parameters on biodiesel quality. Chakraborty et al. [133] obtained CaO from waste eggshells, which was considered as a viable catalyst for transesterification at 65 °C, with an oil/alcohol proportion of 1:9, and catalyst stacking at 10 wt.%. Approximately 97% to 98%. FAME yield was achieved, and the catalyst could be reused up to 17 reaction cycles. Viriya–empicul et al. [134] studied the transesterification reaction of palm olein oil for biodiesel production, where waste eggshell, golden apple, and *Meretrix venus* were used as a waste base for solid heterogeneous catalyst. In their study, operating conditions were 60 °C, molecular ratio of alcohol to oil was 18:1, catalyst loading was 10 wt.%, and reaction time was 1 h. The study produced 97%, 83%, and 78% biodiesel yields, respectively. Effective waste administration and waste to vitality transformation can facilitate biodiesel generation utilizing eggshells.

Du et al.[135] studied the biodiesel production from soybean oil where waste eggshells were used as a heterogeneous catalyst. Operating conditions were as follows: temperature was 70 °C, molar ratio of alcohol to oil was 6.9:1, catalyst loading was 5 wt.%, and reaction time was 5 h. Approximately 97.73% biodiesel yield was achieved, and the catalyst could be reused up to 6 times. An alternate specialist, Nakatani et al.[136] inspected the transesterification of soybean oil catalyzed by calcination shellfish shells.

3.2.2.8. Alkali metal inserted complexes as heterogeneous catalyst

Xie et al.[4] studied the transesterification reaction of soybean oil for biodiesel production using NaX zeolites loaded with 10% KOH as a heterogeneous catalyst. In their study, operating condition were 65 °C, a molar ratio of alcohol to oil of 10:1, a catalyst loading of 3 wt.%, and a reaction time of 8 h. Approximately 85.6% biodiesel yield was achieved. Fabbri et al.[137] studied the transesterification reaction of soybean oil for biodiesel production using Na_2PEG (300), a dimethyl carbonate, as solid heterogeneous catalyst. In their study, operating conditions were 70 °C, a molar ratio of alcohol to oil of 30:1, a catalyst loading of 6 wt.%, and a reaction time of 5 h. Approximately 99% biodiesel yield was achieved.

Kondamudi et al.[138] incorporated extraordinary bifunctional catalysts Quntinite-3T (Q-3T) for biodiesel generation from waste vegetable oils, restaurant oil, and poultry fat. These oils picked up mechanical vitality compared with costly sustenance-based vegetable oils. This bifunctional heterogeneous catalyst simultaneously changes FFAs and triglycerides (TGs) into biodiesel. This Q-3T is obtained from sodium source (Na-Q-3T) and ammonium (NH_4-Q-3T) sources using the sol–gel process and is characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), and high resolution transmission electron microscopy (HRTEM). The catalyst was tried for soy, canola, espresso, and waste vegetable oils with variable measures of FFAs (0–30 wt.%). The catalyst effectively changed both FFAs and TGs in a solitary step bunch reactor.

3.2.2.9. Transition metal oxides and derivatives as heterogeneous catalyst

Many transitional materials of the periodic table exist. Some transitional materials and their oxides are chosen as base heterogeneous catalysts by researchers for biodiesel production. ZnO, TiO_2 [139], TiO_2/SO_4^{2-} and ZrO_2/SO_4^{2-} [118], ZnO, and ZrO_2 [73, 140, 141] are most commonly used heterogeneous catalysts. The action of ZrO functionalized with TiO was likewise investigated by Lopez et al. [142]. Nakagaki et al.[143] orchestrated sodium molybdate (Na_2MoO_4) and utilized it as a heterogeneous catalyst for the methanolysis of soybean oil. Transesterification responses occurred under moderately gentle weather, obliging low temperatures, short reaction times, and normal pressure. In their study, the produced methyl ester was characterized by reverse-phase and size-exclusion chromatography and hydrogen-nuclear magnetic response spectroscopy. Transesterification responses occurred under moderately gentle meteorological conditions, calling for low temperatures, short response times, and typical energy every unit territory. The methyl esters combined were described by opposite stage and size-exclusion chromatography and hydrogen-nuclear magnetic resonance spectroscopy. The transesterification response of triglycerides with methanol was exceptionally effective with yields higher than 95% methyl esters. The molybdenum (VI) complex appeared for have high Lewis acidity and definitely follow up on liquor O–H bonds, prompting transient types with high nucleophilic characteristics. The impetus was effortlessly recouped and in the wake of being washed, demonstrated recyclability for an alternate synergist response with comparative movement.

Yoo et al.[139] recommended ZnO as the best catalyst during the transesterification of rapeseed oil using transition metal oxides (ZnO, TiO_2, and ZrO_2) as heterogeneous catalysts because of their high activity. Operating conditions include a molar ratio of methanol to oil 40:1, a catalyst loading of 1 wt.%, and a reaction time of 10 min. Brito et al.[144] studied transesterification and esterification reactions to obtain methyl ester using two series of complexes with the general formula M(n-butoxide)$_{4-x}$(maltolate)$_x$, where M = Ti or Zr and $x = 0–4$, as catalysts. Mixes containing different ratios of maltolate and *n*-butoxide ligands were produced from the response of maltol (3-hydroxy-2-methyl-4-pyrone) and n-butoxide metal forerunners. All structures, containing maltolate as ligand, were exceptionally productive as catalysts in esterification, mostly those situated in zirconium. By contrast, these catalysts showed exceptionally poor activity for transesterification.

Da Silva et al.[145] studied the transesterification reaction of soybean and babassu oils for biodiesel production where Cu (II) and Co (II) used as catalysts. The catalysts were characterized by infrared, atomic absorption, and TG, and the biodiesels were characterized by infrared, NMR, CG, TG, and physic chemistry analysis. In their study, the maximum adsorption values reported for Cu(II) and Co(II) cations were 1.584 mg/g and 1.260 mg/g, respectively, in 180 minutes. However, the conversion of oil to biodiesel was better when Co (II) was adsorbed on chitosan. Krohn et al.[146] considered the generation of algal biodiesel from *Dunaliella tertiolecta*, *Nannochloropsis oculata*, wild freshwater microalga, and macroalga lipids utilizing a highly effective continuous catalytic Mcgyan® process. The heterogeneous catalytic procedure utilizes supercritical methanol and permeable titania microspheres in a settled bunk reactor to catalyze the synchronous transesterification and esterification of triacylglycerides and FFAs, separately, into biodiesel. Up to 85% alky esters were obtained from triglycerides and FFAs, as measured by a 300 MHz HNMR spectroscopy.

3.2.2.10. Some mixed metal oxides and derivatives as heterogeneous catalyst

Xu et al.[125] studied the transesterification reaction using KF/Zn(Al)O as a catalyst. The prepared KF/Zn(Al)O catalyst had the highest activity compared with that of Zn–Al hydrotalcite, such as Zn(Al)O, KF, KF/γ-Al_2O_3, and KF/ZnO compounds. This catalyst was especially viable when operating conditions were 65 °C, a molar ratio of methanol to oil of 6:1, KF/Zn(Al)O catalyst loading of 3 wt.%, and a reaction time of 3 h. Approximately 95% biodiesel yield was achieved. The high action was credited to the establishment of new stages KF and KOH, and the effect of Zn(Al)O.

Wang et al.[147] produced MgO-$MgAl_2O_4$ by utilizing γ-Al_2O_3, this $MgAl_2O_4$ composite used as heterogeneous catalyst. That indicated a more noteworthy biodiesel yield identified with MgO/$MgAl_2O_4$/γ-Al_2O_3 material with the comparable stacking of magnesium arranged by an ordinary impregnation process. The improved catalytic action of the prior material could be attributed to its higher basicity, specific surface area, pore volume, and size. Wen et al.[148] studied the transesterification of soybean oil with methanol for biodiesel production. Kalsilite ($KAlSiO_4$) was used as a heterogeneous catalyst. A method called co-precipitation was introduced to produce kalsilite and add lithium because of property improvement as well as catalytic performance improvement for the transesterification of soybean oil. Comparatively low catalytic activity was shown by kalsilite. However, a small amount of lithium nitrate added using the impregnation method significantly boosted catalytic activity. With operating conditions of a reaction temperature of 120 °C, a 3.84 cSt kinematic viscosity, and a 2.3 wt.% of lithium modified kalsilite, almost 100% biodiesel yield achieved.

3.2.2.11. Hydrotalcite metal oxides as heterogeneous catalyst

Georgogianni et al.[149] studied the transesterification of rapeseed oil for biodiesel production where alkaline catalysts were used as either a homogeneous or heterogeneous catalyst. In his study, NaOH was used as a homogeneous catalyst, Mg MCM-41, Mg–Al Hydrotalcite, and K+ impregnated zirconia were used as heterogeneous catalysts, and a 24 kHz ultrasonication frequency 600 rpm stirring speed was maintained. Heterogeneous catalyst criteria depend on porosity and surface basicity of the catalyst, and catalytic activity depends on basic the strength of the catalyst. Approximately 97% biodiesel yield can be achieved when Mg-Al shows the heights activity. Increasing amounts of potassium cations with catalyst increases the activity of ZrO_2 in transesterification. The involvement of ultrasonication frequency enhanced the transesterification reaction rather than the involvement of mechanical stirring. By performing filtration, the heterogeneous catalyst can be easily separated from the reaction mixture after reaction.

Glisic et al.[150] studied various systems for developing FAME production at higher temperatures and pressures with or without catalysts. His aim was to find the optimum way to produce biodiesel with minimum energy consumption and improve life cycle energy efficiency. Energy consumption (MJ/kg FAME) relies on degree of conversion of triglycerides. Degree of conversion of triglycerides will be less than 25% if conversion increased from 97 wt.% to complete conversion. Others meaningful decrease of energy consumption might be gained at subcritical condition by using appropriate catalyst. This study exposed that if heterogeneous process of biodiesel synthesis is acknowledged at subcritical conditions, then further decrease of energy consumption is possible.

The comparative assessment, in terms of yield, reaction condition and reusability of different promising heterogeneous catalyst utilized by several researcher have been listed in the **table 5.**

Table 5: Comparative assessment of promising heterogeneous catalyst with different feedstock for biodiesel production

Catalyst name	Feedstock	Reaction condition				Yield (v/v %)	Ref.
		Temp. (°C)	Time	Loading in wt.%	Alcohol to Oil ratio by molar		
Tungstated zirconia WO_3/ZrO_2	Vegetable oil	75	140 h	-	-	65	Kiss et al. [71]
Sulphated zirconia (SO_4^{2-}/ZrO_2)	Palm kernel	-	-	-	-	90.3	Jitputti et al. [73]
Unsulfated zirconia (ZrO_2)	Coconut oil	-	-	-	-	86.3	Jitputti et al. [73]
Choloroaluminate ([Et3NH]Cl-AlCl3)	Soybean oil	70	9h	-	0.5:1	98.5	Liang et al. [74]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Yellow horn oil	70	10 min	1%	12:1	96.22	Zhang et al. [65]
La/zeolite beta	Soybean oil	100	3 h			48.9	Shu et al. [83]
Hβ-zeolite	Pongamia pinnata	120	24h	0.12%	10:1	59	Karmee et al. [84]
Montmorillonite K-10	Pongamia pinnata	120	24h	0.12%	11:1	47	Karmee et al. [84]
ZnO	Pongamia pinnata	120	24h	0.12%	12:1	83	Karmee et al. [84]
NaX zeolites (Si/Al=1.23)	Pongamia pinnata	125	2h	10%	-	85.6	Xie et al. [4]
Zeolites	Sunflower oil	60	-	-	-	93.5-95.1	Ramos et al. [86]
CaO	Sunflower oil	100	1.5-5.5 h	1%	6:1	91	Vujicic et al. [111]
CaO	Palm oil	-	1 h	0.5% - 5%	3:1-15:1	48.2-95.2	Mootabadi et al. [96]
SrO	Palm oil	-	1 h	-	-	67.3-95.2	Mootabadi et al. [96]
BaO	Palm oil	-	1 h	-	-	55-77.3	Mootabadi et al. [96]
MgO	Vegetable oil	600	8h	-	-	18	Lopez et al. [114]
MgO	Vegetable oil	-		5%	12:1	92	Di Serio et al. [115]
BaO & SrO	Vegetable oil	-	10-60 min	0.5-3%	3:1-15:1	95%	Salamatinia et al. [123]
SrO	Vegetable oil	65	30 min	3%	12:1	90	Liu et al. [122]
KOH/AC	Palm oil	70	15 h	5%	15:1	94	Dehkhoda et al.[127]
Silica gel	Vegetable oil	-	3h	-	-	-	Faria et al. [130]
CaO from eggshell	Palm olein	65		10%	9:1	97.98	Chakraborty et al. [133]
CaO from eggshell	Palm olein	60	1 h	10%	18:1	97	Viriya-empicul et al. [134]
Golden apple	Palm olein	60	1 h	10%	18:1	83	Viriya-empicul et al. [134]
Meretrix venus	Palm olein	60	1 h	10%	18:1	78	Viriya-empicul et al. [134]
CaO from eggshell	Soybean oil	70	5h	5%	6.9:1	97.73	Du et al. [135]
NaX zeolites loaded with 10% KOH		65	8h	3%	10:1	85.6	Xie et al. [4]
Dimethyl carbonate	Soybean oil	70	5h	6%	30:1	99	Fabbri et al. [137]
KF/Zn(Al)O	Vegetable oil	65	3h	3%	6:1	95	Wang et al. [147]
Kalsilite ($KAlSiO_4$)	Soybean oil	120	-	2.30%	-	100	Wen et al. [148]

3.3. Biocatalyst

Biocatalysts are catalysts obtained from a living organism and to promote chemical reactions without being affected itself. Biocatalysts are also called enzymes or enzyme catalysts. These catalysts initiate or modify nearly all biochemical reactions in the living cells. Each enzyme possesses individual three-dimensional patterns that suit the shape of the reactants. Biocatalysts have recently become progressively critical in the examination of biodiesel generation. These catalysts are hypothesized to beat synthetic catalysts [151]. The search for an environmentally friendly methodology for biodiesel synthesis was explored under the utilization of proteins as catalysts. Typically, difficulties confronted with conventional catalysts such as employed-feedstock pretreatment, catalyst elimination, wastewater treatment, and high-energy necessity are addressed in enzyme-catalyzed transesterification reactions. Biocatalysis is interceded utilizing a accumulating of enzymes known as lipases generated through microorganisms, animals, and plants [152, 153]. Lipases could be separated from different sources of bacterial species, such as *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Rhizomucor miehei*, *Rhizopus oryzae*, *Candida rugosa*, *Thermomyces lanuginosus*, and *Candida antarctica* [154].

Biocatalysts could be classified in major parts as follows. (a) **Microbes:** A microscopic organism such as, yeast and other anaerobic bacteria, Archaea, bacteria, fungi, viruses, and microbial Mergers. (b) **Lipases:** The most widely used class of enzymes in organic synthesis, lipases are preferred widely because of their better stability compared with other biocatalyst. Lipase can be classified into extracellular and intracellular lipase [153]. Extracellular lipases are mainly obtained from live-producing microorganism broth through purification. Major extracellular microorganisms are *Mucor miehei, R. oryzae, C. antarctica,* and *P. cepacia.* Intracellular lipases are present inside or in the cell-producing wall. In most of cases, intracellular lipases are found in immobilized form. (c) **Proteases:** Enzymes that break down proteins. This type of proteases can be found in animals, plants, bacteria, Archaea, and viruses. For example, TEV protease and Trypsinogen. (d) **Cellulases:** Enzymes that break down cellulose. (e) **Amylases:** Enzymes that break down starch into simple sugars.

Researchers choose enzyme transesterification because of some advantages over the chemical catalyzed transesterification process. Easy product removal, moderate process temperature (35–45 °C), zero by-product, and reusability of catalysts are main features of using this type of catalyst. However, enzymatic reactions are insensitive to FFAs and the water content of the feedstock. Some investigations conducted by researchers using lipase-catalyzed transesterification of different feedstock to biodiesel are presented in **Table 6.** Different types of catalysts assessment in biodiesel production process are listed in **Table 7.**

Table 6: Transesterification of different feedstocks using biocatalyst

Enzyme	Feedstock	Alcohol	Temperature (°C)	Time (h)	Yield (%)	Refs.
IM *B. cepacia* lipase	Palm oil	Methanol	30	72	100	155
Lipozyme IM60	Tallow oil	Primary alcohols	45	5	94.8-98.5	156
Lipozyme IM-20	Mowrah oil	Alcohols (C4-C18)	60	6	86.8-99.2	157
E. aerogenes lipase	Jatropha oil	Methanol	55	48	94	158
Novozym®435	Soybean oil	Methyl acetate	40	14	92	159
Lipozyme IM-77	Soybean oil	Methanol	-	-	92.2	160
R. oryzae lipase	Plant oil	Methanol	-	-	90	161
P. expansum lipase	Corn oil	Methanol	40	24	86	162
Cryptococcus spp. S-2	Rice bran oil	Methanol	30	96	80	163
Pseudomonas lipase	Sunflower oil	Methanol	45	5	79	164
PS 30 lipase	Palm oil	Ethanol	40	8	72	165

Table 7: Relative advantages and disadvantages of different catalyst involving in biodiesel production technology

Catalyst Type	Advantages	Disadvantages	Refs.
Homogeneous	• Effectively active on metal atoms • Very fast reaction rate • Reaction can occur at mild condition thus relatively less energy required for esterification and transesterification • Relatively cheap and available (NaOH and KOH) • Preferred method for low-grade feedstock • Sometimes esterification and transesterification occur instantaneously	• Hazardous for the environment compared to heterogeneous • Hydroscopic nature (NaOH, KOH) • Low quality glycerol produce thus requires lengthy distillation process for purification • Homogeneous base catalyst sensitive to FFA content present in the oil. • Soap forms in case of higher (2 wt.%) FFA content in the oil, thus reduces biodiesel conversion rate. • Purification of biodiesel from product is relatively difficult and required huge amount of water. • Poisoning occurs when the catalyst exposed to ambient air. • Acid homogeneous catalyst are very harmful, very corrosive to reactor, pipeline and required careful handling.	56, 166
Heterogeneous	• Glycerol and catalyst separation from biodiesel is much easier • Not mixed with ethanol or methanol thus • Because of large pour size, minimize diffusion problem • High catalytic stability against leaching and poisoning • Easy separation of catalyst from product • Economic because of its reusability nature	• Converts triglycerides relatively slower rate • Complicated catalyst synthesis procedures leads to higher cost • Effectively active only surface atoms	56
Biocatalyst	• Tolerate free fatty acid and water content • Easy purification of biodiesel and glycol • Environmental friendly and does not produces volatile organic compound • High possibility to reuse and regeneration the catalyst • Only simple purification step is required. • Transesterification can be carried out at low reaction temperature, even lower than homogeneous base catalyst.	• Could not be able to commercialized for production of biodiesel due to long residence time and high cost • High cost • Long process time due to very slow reaction rate. • Sensitive to alcohol, normally methanol that can deactivated the enzyme.	19, 56

4. Non-catalytic biodiesel production

Several techniques are involved in biodiesel synthesis inside a catalytic response, such as purification of esters, supercritical transesterification, BIOX co-solvent transesterification, and separation catalyst. Considering some advantages over catalytic biodiesel synthesis, as well as the environmental impact, supercritical transesterification, and BIOX co-solvent transesterification process getting popularity [167].

4.1. Supercritical alcohol transesterification

Biodiesel can be produced by the transesterification reaction during the supercritical condition in methanol (SC MeOH) without using any catalyst [103, 168]. Forward reaction rates are as high as 50–95%, and forward reactions occur within the initial 10 minutes [169, 170]. However, this reaction needs higher temperature and pressure, approximately 250–400 °C and 1200 psi [171, 172] respectively. For this reason, this reaction consumes more energy and increases production cost. Supercritical methanol, ethanol, propanol, and butanol have been demonstrated to be probably the optimistic procedure for the transesterification of triglycerides without the involvement of a catalyst. Supercritical alcohol techniques are a non-catalytic method for biodiesel synthesis, where high pressure and high temperature sustain the transesterification reaction [173]. Initially, conversion is significantly fast because of the reaction conditions, which are high temperature, high pressure, and high ratio of alcohol to oil. Approximately 50–95% of conversion occurs within the first 10 minutes but temperature ranges are quite high (250–400 °C). During the transesterification of vegetable oil, approximately 1:6 to 1:40 oil/alcohol molar ratio is used in supercritical alcohol conditions [108].

The major difficulties or shortcomings of supercritical alcohol are high temperature (350–400 °C), high pressure (200–400 bar), and [64] high alcohol to oil ratio [174], usually at 41:1, which increases the biodiesel production cost. In the supercritical alcohol transesterification process, the presence of little water does not hamper the oil to biodiesel conversion [103, 175, 176]. Moreover, the presence of water accelerates the formation of methyl ester and esterification of FFA in one stage. The reaction took 4 min at 250–400 °C and 35–60 MPa. Iijima et al.[177] suggested a supercritical condition where reaction conditions were 643–773 K reaction temperature, 20–60 MPa reaction pressure, and reaction time of only 4–12 min for making biodiesel without producing glycerin (by-product).

Supercritical transesterification procedure involves high temperature and pressure conditions that enhance phase solubility, reduce mass transfer impediments, provide higher conversion rates, and provide easier steps for separation and purification. **Table 8** represents the supercritical transesterification of vegetable oil with corresponding reaction conditions [178].

Table 8: Reaction parameter and corresponding yield of supercritical alcohol process

Reaction Parameter	Unit	Methanol	Ethanol	1-Propanol	1-Butanol	1-Octanol
Temperature	°C	239.2	243.2	264.2	287.2	385
Pressure	MPa	8.09	6.38	5.06	4.9	2.86
Yield in 10 min.	Mass %	98	79	81	80	-
Yield in 30 min.	Mass %	98	88	85	75	-

4.2. BIOX co-solvent transesterification

BIOX (co-solvent) is a new method proposed by Canadian professor David Boocock from the University of Toronto. Owing to the lower solubility of methanol in oil, the rate of transformation of oil directly onto ester is quite slow. This problem could be minimized by introducing a co-solvent, which can mix with methanol and oil. Tetrahydrofuran (THF) is a type of co-solvent with a boiling point significantly close to methanol; thus, it requires a significantly low operating temperature of 30 °C. The continuous BIOX co-solvent process takes less than 90 min near ambient temperature and at atmospheric pressure. FFA and triglycerides both converted in a single phase in two steps [179]. By improving the solubility of alcohol in triglyceride using the co-solvent, the slow reaction rate could be improved. Reaction becomes 5–10 min aside from catalyst residues minimized to only one phase (ester or the glycerol phase).

Demirbas [180] studied THF as a co-solvent with methanol to form single phase. After finishing the reaction, biodiesel glycerol phase was clean. Overabundance of alcohol and the THF co-solvent were both recovered in a single step. Nevertheless, because of the probable hazard and toxicity with the co-solvents, the solvent needs to be entirely removed within the glycerol phase and the biodiesel phase; in addition, the end products must be water-free [181]. Using a co-solvent such as tetrahydrofuran as well as methyl tertiary butyl significantly accelerates methanolysis. In spite of this, similar to one-phase butanolysis, one-phase methanolysis originally displays a rapid development of ester, but then drastically slows [181].

The restoration of excessive alcohol is challenging in the case of the BIOX co-solvent approach because the boiling point for the THF co-solvent is quite close to that of methanol [182]. The particular remarkable benefit of the BIOX co-solvent technique is that it employs inert, recoverable co-solvents in a single pass reaction that normally requires only seconds at ambient temperature and pressure, and no catalyst residues appear in both the biodiesel stage and the glycerol stage [182]. This technique can be used with crude vegetable oils, waste cooking oils, and animal fats. **Table 9** presents a comparative study between catalytic and non-catalytic transesterification biodiesel production processes.

Table 9: Advantages & disadvantages of using non-catalytic transesterification over conventional transesterification

	Advantages	Disadvantages
Non-catalytic method	• Less water is produced as by product and sometimes presence of water accelerate the conversion rate. • Simpler purification of step involves • Simpler separation steps involves • High quality of glycerin is generated as by products • Environmental friendly as less amount of chemical used • Less time required • Low quality feedstock could be transformable easily into biodiesel	• Higher energy is required by the reaction step especially in heating step high power consumption involves • High temperature and pressure required • High alcohol to oil ratio 0is needed • Relatively lower production yield than conventional. • Need more care of production process as it involves with higher pressure and temperature
Conventional method	• Lower power consumption regarding heating. • Higher amount of yield is possible • Relatively lower temperature and pressure required	• Higher process cost • Greater time is required than non-conventional method • Cost involves with catalyzing loading • Preparation of catalyst is quite complex
References [179], [180], [181], [182].		

5. Conclusion

Among the several biodiesel synthesis processes from natural oils and fats, transesterification is currently the most attractive approach because transesterification is essentially a successive response. The motivation behind the methodology is to reduce the viscosity of the oil or fat. Although mixing oils and different solvents and microemulsions of vegetable oils reduces the viscosity, problems of engine performance (i.e., lubricating oil contamination, carbon decomposition) still exist. Involving specialized focal points in both materials science and reactor design is crucial if biodiesel is to remain a vital participant in the renewable energy sector in the 21st century.

The targets of this study were to review distinctive biodiesel generation techniques (both catalytic and non-catalytic) and the utilization of heterogeneous catalyst in biodiesel to date. The accompanying conclusions are in view of the audit:

- A base homogeneous catalyst process has a rapid reaction rate, high yield, needs mild reaction conditions, and has less energy consumption; it is insensitive to water content, easy to obtain, and has low cost. However, this process is sensitive to FFA content (>2 wt.%) in the oil and forms soap and glycerol as byproducts, thereby needing excess water during purification.
- Acid homogeneous catalyst is insensitive to both FFAs and water content in oil and is suitable for low-grade oil, which has a high acid value. However, some problems are associated with this catalyst compared with the heterogeneous catalyst, including relatively slow reaction rate, corrosive nature, catalyst separation from product, reusability of catalyst, and soap formation.
- A heterogeneous catalyst has some advantages over a homogeneous catalyst, including easy separation, simple recovery techniques, and reusability of catalyst from the product. In addition, this catalyst has faster reaction rate (base) and less reaction conditions required than the homogeneous process. Sometimes, catalyst preparation is expensive and unavailable. This catalyst is still a long way from industrial applications because its assessment has only been completed in stirred batch reactors. Only a few studies have been conducted on persistent procedures utilizing pressed bed stream reactors.

- A relatively lower reaction temperature is needed for biocatalytic processes, compared with that of both homogeneous acid and base catalytic processes. The major limitation is preparation cost of enzymes and reaction rate, which is the slowest among the processes. Furthermore, its catalyst cost is relatively more expensive than that of both homogeneous acid and base catalytic processes. In addition, the low solubility of glycerin in biodiesel reduces enzyme activity. Further development of the existing process, enzyme flexibility, and adaptability must be studied, which can lower the cost and improve conversion rate.
- Non-catalytic supercritical alcohol needs high reaction conditions (temperature, pressure, and methanol to oil ratio). However, non-catalytic supercritical alcohol takes less time, and FFAs completely convert into ester. In addition, the BIOX co-solvent process is a more acceptable process to minimize the low solubility of methanol in oils.

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