

Review

Biodiesel production technologies: review

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Abstract: Biodiesel is a fuel with various benefits over the conventional diesel fuel. It is derived from renewable resources, it has less emission to environment, it is biodegradable so has very limited toxicity and above all its production can be decentralized so that it could have a potential in helping rural economies. However, there are also some worth mentioning challenges associated with production of biodiesel. Among them repeatedly mentioned are the cost of feedstock and the choice of convenient technology for efficient production of the fuel from diverse feedstock types. There are four main routes by which raw vegetable oil and/or animal fat can be made suitable for use as substituent fuel in diesel engines without modification. These are direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction. Due to the quality of the fuel produced, the transesterification method is the most preferred way to produce biodiesel from diverse feedstock types. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with reduced viscosity to near diesel fuel levels. There are different techniques to carry out transesterification reaction for biodiesel production. Each technique has its own advantages and disadvantages as well as its own specifically convenient feedstock character. There are also some very important reaction conditions to be given due attention in each of this techniques for efficient production of biodiesel, such as molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents, among others. This review is meant to investigate the main transesterification techniques for biodiesel production in terms of their choice of feedstock character as well as their determinately required reaction conditions for efficient biodiesel production, so that to give an overview on their advantages and disadvantages.

Keywords: Biodiesel; Transesterification; Acid catalyzed; Base catalyzed; Enzyme catalyzed; Supercritical

Abbreviations

ASTM	American Society for Testing and Materials
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GHG	Green House Gas
IEA	International Energy Agency
IUPAC	International Union of Pure and Applied Chemistry
OECD	Organization for Economic Co-operation and Development

1. Introduction

The U.S Energy Information Administration, in its International Energy Outlook 2016 report, indicated that the world total energy consumption is significantly increasing. In this report, the worldwide energy consumption is projected over the 28 year period from 2012 to 2040 as shown in Figure 1.

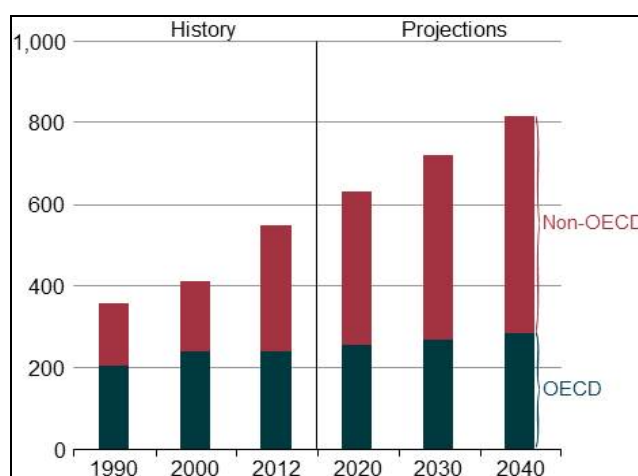


Figure 1. World energy consumption from 1990 up to 2040 in quadrillion Btu [1].

This projection specified that much of the growth in energy consumption is expected from non-OECD countries, where strong economic growth and expanding populations lead the increase in world energy use.

As countries develop and living standards improve, energy demand grows rapidly. For instance, in nations experiencing fast-paced economic growth, their life style changed and more economic activities emerge demanding more and more energy.

Crude oil, coal and gas are the main dominant resources for world energy supply [2]. However, most argue that demand for renewables would increase owing to limited reserve of the conventional

fuels, which jeopardize the energy security issue, as well as for the environmental benefit of using renewables as alternative energy supplies.

According to the IEA Medium Term Renewable Energy Report 2015, the renewable energy share in the total world energy consumption is expected to have at least 26% increment by 2020 [3]. And the International Energy Agency, world energy outlook 2013 [4], particularly showed that, for the next two decades, world fuel oil demand is concentrated in transport sector and in which, diesel fuel demand is expected to dominate by 5.5 million barrel per day as shown in Figure 2.

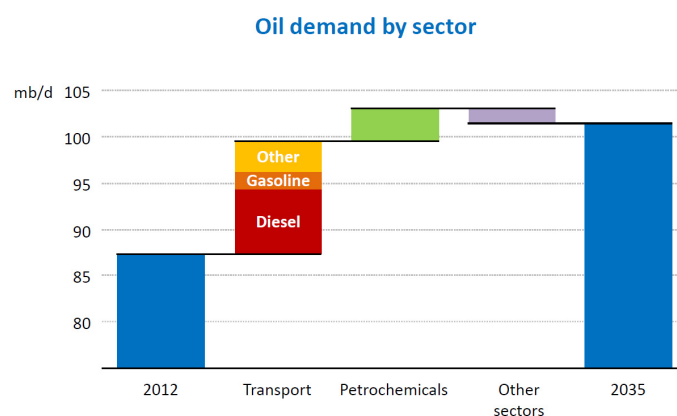


Figure 2. Oil demand by sector between 2013 and 2035 [4].

As it can be seen from Figure 2, diesel fuel use is expected to be the main to get the highest score in increment in oil demand for the years to come. This indicates there is more practical opportunity in working towards substituting the conventional diesel fuel with biodiesel so that attaining the required demand without causing negative consequence to our environment.

In accordance with this, the awareness of energy issues and environmental problems associated with burning fossil fuels has globally encouraged many researchers to investigate the possibility of using alternative sources of energy instead of oil and its derivatives. Among them, biodiesel seems very interesting for several reasons.

The invention of the vegetable oil fueled engine by Sir Rudolf Diesel dated back in the 1900s, however, full exploration of biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and alcohol with or without a catalyst [5–9].

Biodiesel is highly biodegradable and has minimal toxicity. It has almost zero emissions of aromatic compounds and other chemical substances that are destructive to the environment. It has a small net contribution of carbon dioxide (CO₂) when the whole life-cycle is considered (including cultivation, production of oil and conversion of oil to biodiesel); and its production can be decentralized so that it could have significant potential for improvement of rural economy [5,10].

Compared to diesel fuel, biodiesel produces no sulfur, less carbon monoxide, less particulate matters, less smoke and hydrocarbons emission and more oxygen. More free oxygen leads to the complete combustion and reduced emission [11,12].

Vegetable oil and/or animal fat can be converted to fuel for diesel engine through four major possible ways: direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction. Among these methods, the most preferred one is transesterification reaction. Transesterification reactions enables the use of diverse feedstock types to produce a fuel highly resemble to conventional diesel in quality. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with viscosity similar to diesel fuel.

Transesterification reaction can be catalyzed or non-catalyzed. The catalysis of transesterification is usually either chemically like base catalyzed transesterification and acid catalyzed transesterification, or using enzyme catalysts like lipase-catalyzed transesterification. However, there are also some less investigated but efficient ways to produce biodiesel through esterification of oils and fats such as those using Nano catalysts and ionic liquid catalysts. The non-catalyzed transesterification is carried out without any catalyst only by using an alcohol at supercritical conditions where the alcohol, usually methanol, is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist [13,14,15]. In the supercritical state, the dielectric constant of alcohol is decreased so that two-phase formation of vegetable oil/alcohol mixture is not encountered and only a single phase is found favoring the reaction [16].

Each transesterification technique requires different feedstock character. For example, some can handle feedstock with high FFA content where as others are very sensitive to even small amount. Some esterification techniques are more advantages than the others at least with respect to cost of production, or minimum waste generation, or high productivity and the like. In addition, there are some very important reaction conditions, which should always be optimized for efficient production of biodiesel. Among them the very commonly studied are: molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents.

Accordingly, in this paper, more emphasis is given on reviewing the effect of the main reaction conditions for an efficient production of biodiesel from different feedstock types as well as on summarizing the advantages and disadvantages of these major transesterification techniques.

2. Oil and Fat as Fuel in Diesel Engines and Biodiesel Production Technologies

The dominant technologies, which enable us to use oil and fat feedstock types as fuel in diesel engines, are usually described as direct use or blending of oils, micro-emulsion, pyrolysis and transesterification. Transesterification being currently mentioned by various researchers as the most preferable due to better quality of fuel produced [17,18,19].

2.1. Pyrolysis

Pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or oxygen, or by the application of heat in the presence of a catalyst, which results in cleavage of bonds and formation of a variety of small molecules. Pyrolysis is conducted at temperature range of 400–600 °C. The process produces gases, bio-oil, and a char depending on the rate of pyrolysis. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis [20] as shown in Table 1. Fast pyrolysis is the one used for production of bio-oil.

This liquid fraction of the thermally decomposed vegetable oil, bio-oil, is likely to approach diesel fuel properties and characteristics. Ma et al. [21] mentioned that the chemical compositions (heavy hydrocarbons) of the diesel fractions produced by catalytic cracking of copra oil and palm oil stearin were similar to fossil fuels. The process was simple and effective compared with other cracking processes according to them.

According to Ma et al. [21] pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids.

In another study, Mahanta et al. [22] mentioned that pyrolyzate (product of pyrolysis) from any feedstock type has lower viscosity, flash point, and pour point than petroleum diesel fuel and equivalent calorific values. In addition, the cetane number of the pyrolyzate is lower. According to them, the pyrolyzed vegetable oils contain acceptable amounts of sulfur, water and sediments and give acceptable copper corrosion values but unacceptable quantities of ash, carbon residual and pour point.

Table 1. Classification of pyrolysis methods with differences in temperature, residence time, heating rate, and major products [20].

Method	Temperature (°C)	Residence Time	Heating rate (°C/s)	Major products
Conventional/slow pyrolysis	Med-high (400–500)	Long 5–30 min	Low 10	Gases Char Bio-oil (tar)
Fast pyrolysis	Med-high (400–650)	Short 0.5–2 s	High 100	Bio-oil (thinner) Gases Char
Ultra-fast/flash pyrolysis	High (700–1000)	Very short < 0.5 s	Low 10	Gases Bio-oil

Abbaszaadeh et al. [23] also reported that biodiesel fuel produced through a pyrolysis process or known as bio-oil is suitable for diesel engines; however, low-value materials are produced due to the elimination of oxygen during the process. Undesirable properties that sometimes restrict the application of biodiesel produced through this process are low heating value, incomplete volatility, and instability [24]. But, in another view, Singh and Singh [25], mentioned that thermal pyrolysis of triglycerides has several advantages such as lower processing cost, simplicity, less waste, and no pollution.

Another disadvantage of pyrolysis is the need for distillation equipment for separation of the various fractions. Also the product obtained is similar to gasoline containing sulphur which makes it less ecofriendly [26].

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produces some low value materials and, sometimes, more gasoline than diesel fuel [21].

2.2. Micro-emulsification

Among the physical properties of raw vegetable oil, which makes it to be not directly used as fuel, is its viscosity. Ma et al. [21] pointed out that, the formation of micro-emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity.

According to IUPAC definition, micro-emulsion is dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm [27].

The components of a biodiesel micro-emulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol and ethanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers [28].

Mahanta et al. [22] reported that micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, and alcohol and a surfactant and a cetane improver, with or without diesel fuels. All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel. The 2-octanol is an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil [29].

Micro-emulsions can improve spray properties by explosive vaporization of the low boiling constituents in the micelles. Micro-emulsion results in reduction in viscosity, increase in cetane number and good spray characters in the biodiesel. According to Srivastava and Prasad [30], short term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of NO. 2 diesel fuel, in spite of the lower cetane number and energy content. NO. 2 diesel fuel is a fuel with distillation temperature of 640 degrees Fahrenheit at the 90% recovery point and meets the specifications defined in ASTM Specification D 975 [31].

However, as indicted by Parawira [32], continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, carbon deposit formation and incomplete combustion.

2.3. Dilution/Blending

Direct uses of vegetable oils have generally been considered not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. In another view, Ma et al. [21], pointed out that oil deterioration and incomplete combustion are the two severe problems associated with the direct use of vegetable oils as fuels.

In such cases, it is helpful to dilute vegetable oils with such materials as diesel fuels, solvent or ethanol. Dilution results in reduction of viscosity and density of vegetable oils. Bilgin et al. [33] indicated that the addition of 4% ethanol to diesel fuel increases the brake thermal efficiency, brake torque and brake power, while decreasing the brake specific fuel consumption. They also argued that since the boiling point of ethanol is less than that of diesel fuel, it could assist the development of the combustion process through an unburned blend spray.

In their review of biodiesel production methods, Ma et al. [21] mentioned that, the viscosities of 50/50 (winter rapeseed oil and diesel) and 70/30 (whole winter rapeseed oil and diesel) blends were much higher (6–18 times) than NO. 2 diesel. According to them, a blend of 70/30 winter rapeseed oil

and NO. 1 diesel fuel (A light distillate fuel oil that has distillation temperatures of 550 degrees Fahrenheit at the 90% recovery point and meets the specifications defined in ASTM Specification D 975 [31]) was used successfully to power a small single-cylinder diesel engine for 850 h. No adverse wear and no effects on lubricating oil or power output were noted.

2.4. Transesterification

Transesterification is the main convenient method to produce biodiesel from oil and fat feedstock types, which chemically resembles petroleum diesel. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with reduced viscosity to near diesel fuel levels. This product is thus a fuel with properties similar to petroleum based diesel fuel, which enable it be used in existing petroleum diesel engines without modifications. Generally, transesterification is a reversible reaction, which simply proceeds essentially by mixing the reactants usually under heat and/or pressure. However, if some kind of catalyst is added to the reaction, it will be accelerated. The simplest chemical reaction for transesterification of triglycerides is presented in Figure 3.

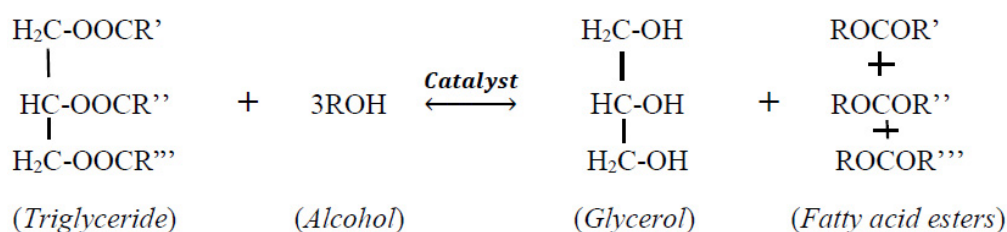


Figure 3. The general chemical reaction depicting transesterification of triglycerides [18].

There are a number of ways to produce biodiesel through transesterification. The general schematics diagram for these possible ways is shown in Figure 4.

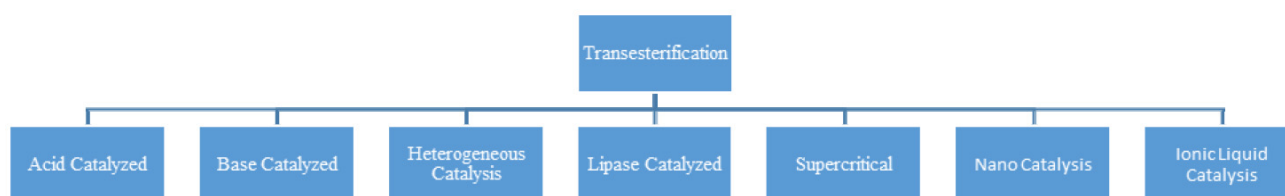


Figure 4. Schematic depicting major transesterification process types.

All of the catalytic transesterification processes involve the reaction of a triglyceride (fat or oil) with an alcohol in the presence of some catalyst to form esters and glycerol. A triglyceride has a glycerin molecule as its base with three long chain fatty acids attached. The characteristics of the oil/fat are determined by the nature of the fatty acids attached to the glycerin. The nature of the fatty acids can in turn affect the characteristics of the biodiesel [34].

A successful transesterification reaction for efficient biodiesel production is signified by easy and effective separation of the ester and glycerol layer after the reaction time. The heavier, co-product, glycerol can be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

2.4.1. Homogeneous acid catalyzed transesterification

Acid catalyzed transesterification was the first method ever in history to produce biodiesel (ethyl ester) from palm oil using ethanol and Sulfuric acid [35].

The acid catalyzed process is due to the reaction of a triglyceride (fat/oil) with an alcohol in the presence of acid catalyst to form esters (biodiesel) and glycerol. Specially, this method is convenient and economically viable in producing biodiesel from oil or fat resources with high free fatty acid content. However, the acid catalyzed reaction requires a longer reaction time and a higher temperature than the alkali catalyzed reaction [36].

Acid catalyzed transesterification starts by mixing the oil directly with the acidified alcohol, so that separation and transesterification occur in single step, with the alcohol acting both as a solvent and as esterification reagent [23].

The acid catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [22]. Park et al. [37] did an investigation of the effect of water on transesterification of oleic acid with methanol in the presence of sulfuric acid as a catalyst. In their work, the yield of fatty acid methyl ester (FAME) was studied at oil to methanol molar ratios of 1:3 and 1:6 and reaction temperatures of 60 °C and 80 °C. According to the result of their study, the rate of esterification of oleic acid significantly decreased as the initial water content increased to 20% of the oil [37].

Since transesterification is an equilibrium reaction, there should always be more alcohol than the oil to favor the forward reaction for complete conversion of the oil to alkyl ester. It is also known that the temperature and the amount of acid catalyst affect the transesterification rate and the yield of alkyl ester. However, more alcohol beyond the optimum will also cause some extra cost on separation of more produced glycerol from the alkyl ester and that is why there should always be an optimization of the ratio for efficient production. Different studies have been conducted to investigate how the molar ratio of oil to alcohol to acid as well as how temperature ranges affect the transesterification and thus the alkyl ester yield.

Zheng et al. [38] showed that, with convenient molar ratios and temperature ranges, methyl ester conversion of waste cooking oil in acid catalyzed transesterification can reach up to 99%. By their study, they concluded that, the oil: methanol: acid molar ratios and the temperature were the most significant factors affecting the yield of fatty acid methyl ester (FAME). According to their study result, at 70 °C with oil: methanol: acid molar ratios of 1:245:3.8, and at 80 °C with oil: methanol: acid molar ratios in the range 1:74:1.9–1:245:3.8, the transesterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion ($99 \pm 1\%$) at 4 hours. In the presence of the large excess of methanol, free fatty acids present in the waste oil were very rapidly converted to methyl esters in the first few minutes under the above conditions [38].

Sulphuric acid, sulfonic acid, and hydrochloric acid are the usual acid catalysts but the most commonly used is sulphuric acid. There are also various studies done to see the yield effect of using alternative acids.

Soriano et al. [39] demonstrated that AlCl_3 could be used to catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA. In their study, optimum conditions to afford 98% conversion of canola oil to FAME is with the use of methanol to oil molar ratio of 24:1 and reaction time of 18 h at 100 °C in the presence of 5% AlCl_3 as catalyst [39].

Marchetti et al. [40] mentioned that one of the drawbacks of producing biodiesel using acid catalyzed transesterification is having more amount of free glycerol in the biodiesel higher than the maximum value allowed to satisfy the international standard ASTM. However, they also mentioned in their study that this could be improved either by adding equipment for purification of the product stream or by modifying some of the process variable such as residence time in the reactor [40].

The use of co-solvents to overcome the mass transfer resistance due to immiscibility of alcohol with oil as well as the use of different acids usually help to get different alternatives for efficient production of biodiesel from low value feedstock. In this regard, Miao et al. [41] studied the effectiveness of trifluoroacetic acid catalyzed transesterification of soybean oil to produce biodiesel. The results from their study showed that the oil could be converted to biodiesel directly by one-step trifluoroacetic acid catalyzed process without extreme temperature and pressure conditions. The optimum process combination was 2.0 M (M is for Molarity, which is defined as the number of moles of solute dissolved per liter of solution) catalyst concentration with 20:1 molar ratio of methanol to oil at temperature of 120 °C [41]. According to the authors this procedure represents a simple and mild method for biodiesel production with short reaction time and with high conversion rate, which would offer potential for an industrial process[41].

Table 2. Summary of the effect of process variables on acid catalyzed transesterification of different feedstocks.

Feedstock	Alcohol	Process variables						Yield % achieved	Ref.
		Alcohol to oil ratio	Temperature (°C)	Reaction time	Stirring speed	Acid Catalyst	Catalyst concentration		
Mixed oil ^b	Methanol	6:1	60	-	300 rpm	H_2SO_4	2.5%	96.6%	[43]
Soybean oil	Methanol	20:1	120	5 h	-	trifluoroacetic acid	2.0 M	98.4%	[41]
Canola oil	Methanol with terahydrofuran as Co-solvent	24:1	110	18 h	-	AlCl_3	5%	98%	[39]
Corn oil	Methanol with dimethyl ether as Co-solvent	6:1	80	2 h	-	p-toluenesulfonic acid	4 wt.%	100%	[44]
Canola oil up to 20% FFA	Methanol	9:1	200	-	-	12-Tungstophosphoric acid	3 wt.%	90 wt.%	[45]

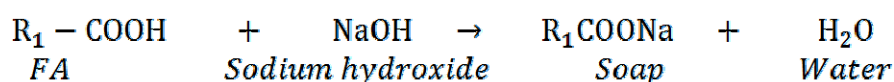
^b mixed oil- 50% sunflower and 50% soybean oil

Despite its relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pretreatment step. These advantages favor the use of the acid-catalyzed process when using feedstock types like waste cooking oil as well as most non-edible plant oil, which are usually associated with higher content of

fatty acid [42]. Table 2 indicates some selected research results about the effect of process variables on acid catalyzed transesterification of different feedstock types.

2.4.2. Homogeneous alkaline catalyzed transesterification

The alkaline catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of alkaline catalysts such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates to form esters (biodiesel) and glycerol. Alkali catalyzed transesterification is much faster than acid catalyzed transesterification and is less corrosive to industrial equipment and therefore is the most often used commercially [26,46]. However, presence of water and high amount of free fatty acid in a feedstock gives rise to saponification of oil and therefore, incomplete reaction during alkaline transesterification process with subsequent formation of emulsion and difficulty in separation of glycerol [32]. The saponification reaction is represented by the equation shown below:



The main disadvantage resulted due to saponification reaction is the consumption of catalyst and increased difficulty in separation process, which leads to high production cost. In addition to that, formation of water in the product will also inhibit the reaction. In this case, water generated either from vegetable oil (due to its high water content) or formed during saponification reaction will hydrolyze triglyceride to form more free fatty acid as shown in the equation below.

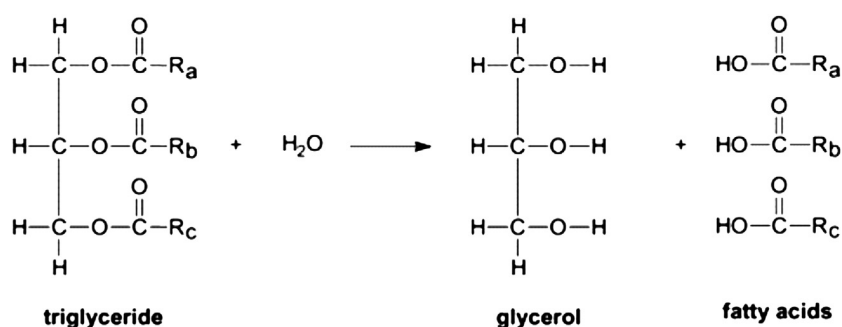


Figure 5. The chemical reaction depicting hydrolysis of triglycerides [47].

Generally, base catalyst manifest much higher catalytic activity than acid catalysts in the transesterification reaction, but are selectively suitable for deriving biodiesel only from refined oils having low content of free fatty acids (FFA) usually less than 0.5% [48]. This makes base catalyzed transesterification confined to use only best quality refined oil like vegetable cooking oil for input, which in turn makes it expensive way to produce biodiesel while creating food versus energy controversy. Here we can consider esterification as additional step to decrease the free fatty acid content of feedstock with greater than 0.5% FFA. This will enable us to choose among different feedstock types with higher FFA content. However, this additional process usually makes it more

complex in the instrumentation (because of the addition of esterification unit) than the sole alkaline-catalyzed process, thereby resulting in an increase in equipment and operating costs.

The efficient production of biodiesel using base catalyzed transesterification is not only dependent on the quality of the feedstock, it is also dependent on the crucial reaction operation variables such as alcohol to oil molar ratio, reaction temperature, rate of mixing, reaction time, type and concentration of catalyst and also on the type of alcohol used [19,25,49].

Even though in theory, the stoichiometric ratio of alcohol (usually methanol) to oil is 3:1, in order to assist the forward reaction so that to get more conversion, the concentration of the methanol has to be increased. This is because; lower amount of methanol means slower forward reaction and less percentage of yield. In contrary, high methanol amount beyond the optimum, interfere with the separation of glycerin because of an increase in solubility; the glycerin remaining in the solution drives the equilibrium back to the left side of reaction, resulting in the lower yield of esters. This is due to the fact that methanol, with one polar hydroxyl group, can act as an emulsifier that enhances emulsions [19].

Sodium hydroxide, potassium hydroxide and sodium methoxide are catalysts usually used in base catalyzed transesterification. Sodium hydroxide is mostly preferable owing to its intermediate catalytic activity and a much lower cost [50]. Lueng et al. [51] evaluated the effect of catalyst on transesterification by comparing the maximum ester content and yield percentage attained using three base catalysts while other determinant variables were kept the same for all conditions during the base catalyzed transesterification processes. The result of their study is shown in Table 3.

Table 3. Comparison of different types of catalysts used in the transesterification of used frying oil (temperature at 70 °C, reaction time 30 min, and methanol/oil molar ratio of 7.5:1) [51].

Catalyst	Concentration of the catalyst (wt.%, by weight of crude oil)	Ester content (wt.%)	Product yield (wt.%)
NaOH	1.1	94.0	85.3
KOH	1.5	92.5	86.0
CH ₃ ONa	1.3	92.8	89.0

This study revealed that sodium hydroxide is better in attaining purity percentage (ester content) than the others whereas sodium methoxide is good in providing higher yield percentage.

The relative concentration of catalysts required for maximum production is dependent on the type of feedstock used. Dias et al. [52] compared the performance of three alkali catalysts for transesterification of virgin and waste soybean and sunflower oil and they reported that, the optimum conditions which ensured that the attainment of the final product being in agreement with the European biodiesel standard were: 0.6 (wt.%) CH₃ONa for both virgin oils; 0.6 (wt.%) NaOH for sunflower oil and 0.8 (wt.%) for soybean oil and; 0.8 (wt.%) using both sodium based catalysts for waste frying oils. They also reported that under these optimum conditions, a purity of 99.4 (wt.%) could be obtained.

In the study carried out by Hossain and Boyce [53] in spite of higher yield, using NaOH as catalyst during biodiesel synthesis from waste sunflower cooking oil, causes more emulsion than KOH and makes separation of biodiesel from glycerin complicated, as they reported. The solution of alkaline catalyst in methanol is recommended to be prepared freshly in order to avoid the moisture absorbance and to maintain the catalytic activity [54].

Leung et al. [51] reported that the conversion of waste cooking oil using sodium hydroxide catalysts was approximately 86%. As presented in Table 4, Ojolo et al. [55], explained that the increase of the catalyst concentration influences the ester yield in a positive manner up to 0.80% NaOH for *Jatropha* oil and then after that it decreases.

Table 4. The influence of catalyst content on ester yield [55].

Catalyst (gm)	Oil (gm)	Methanol (gm)	Reaction Time (hr)	Reaction Temp. (°C)	Biodiesel (%)	Glycerin (%)
1.2	100	20	1	65	87.20	30.80
1.0	100	20	1	65	92.40	27.35
0.8	100	20	1	65	95.33	24.22
0.6	100	20	1	65	74.45	45.37

Parawira [32] reported that, the alkaline catalyst concentration in the range of 0.5–1% by weight yield 94–99% conversion of most vegetable oils into esters. There are several disadvantages in using an alkaline catalysis process although it gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times. According to Parawira [32], the process is energy intensive, recovery of glycerol is difficult, the alkaline catalyst has to be removed from the product, alkaline wastewater generated requires treatment and the level of free fatty acids and water greatly interfere with the reaction. The risk of free fatty acid or water contamination results in soap formation that makes the separation process difficult [56].

Table 5. Summary on effect of process variables on base catalyzed transesterification of different feedstock types.

Feedstock	Alcohol	Process variables					Yield % achieved	Ref.	
		Alcohol to oil ratio	Temperature (°C)	Reaction time	Stirring speed	Catalyst type			Cat. Concentration
Rice bran oil	methanol	1:09	55	60 minute	-	NaOH	0.75% (w/w)	Optimum	[57]
Sunflower cooking oil	methanol	6:01	40	-	320 rpm	KOH	1%	99.50%	[53]
refined cooking vegetable oils	methanol	6:01	65	60 minute	-	KOH	1.2 wt.%	97.50%	[58]
Waste cooking vegetable oils	methanol	6:01	65	60 minute	-	KOH	1.2 wt.%	93.20%	[58]
<i>Jatropha</i> oil	methanol	5:01	65	60 minute	-	NaOH	0.80%	95.5%	[59]
Soybean oil	methanol	6:01	60 ± 1	60 minute	-	NaOH	1%	90%	[60]
Cottonseed oils	methanol	6:01	60 ± 1	60 minute	-	NaOH	1%	98.50%	[60]
Waste frying oils	methanol	7.5:1	50	30 minute	-	NaOH	0.50%	96%	[61]
Karanja oil	methanol	6:01	65	15 minute	360 rpm	KOH	1%	> 85%	[54]
Karanja oil	methanol	12:01	65	60 minute	360 rpm	KOH	1%	98%	[54]
Duck tallow	methanol	6:01	65	180 minute	-	KOH	1 wt.%	97%	[62]
Silurus triostegus Heckel fish oil (STFO)	methanol	6:01	32	60 minute	-	KOH	0.50% w/w	96%	[49]
Waste cooking oil	methanol	6:01	microwave power of 750 W	3 minute	-	CH ₃ ONa	0.75 wt.%	97.90%	[63]
soybean oil -assisted by low-frequency ultrasound (20 kHz)	Ethanol	6:01	60	6 minute	600 rpm	KOH	1% (m/m)	98%	[64]
Waste frying oils	methanol	12:01	65	150 minute	-	Tetramethylguanidine	3 wt.%	> 90%	[65]

Table 5 summarizes the results of some researches done to study the effect of different process variables on base catalyzed transesterification of different feedstock types.

2.4.3. Heterogeneous catalyzed transesterification

The use of homogeneous catalysts, especially base catalysts, are associated with some amount of difficulty in purification of by-product glycerol as well as in the requirement of wastewater treatment. To alleviate these problems, the use of heterogeneous catalysts usually solid base catalyst is recommended. Solid base catalysts have many advantages, such as having mild reaction condition, easy separation, and high activity and less contaminant [66].

Many researchers argued that the use of heterogeneous catalysts both in acid and base form brought about the advantage of having easy and less costly separation as well as possibility of reusing the catalyst. Parawira [32] mentioned that, the heterogeneous catalyst eliminates the additional cost associated with the homogeneous sodium hydroxide to remove the catalyst after transesterification. In addition, the heterogeneous catalyst offers a wide option for the catalytic selection because of its high selectivity and reusability characteristics [67]. Dell'Anna et al. [68] investigated transesterification of polyunsaturated compounds catalyzed by a recyclable polymer supported palladium catalyst. They found out that the heterogeneous solid catalyst, palladium exhibited a remarkable activity and was reusable for eight consecutive cycles.

Heterogeneous solid catalysts are usually categorized as acid solids capable to catalyze free fatty acids esterification reaction; base solids, which are able to catalyze triglycerides transesterification reaction; and bifunctional solids (acid-base character) which show ability to simultaneously catalyze esterification and transesterification reaction [69].

There are various efforts made to find effective solid catalysts in both acid and basic form for heterogeneous catalyzed process. Bournay and Casanave [70] investigated the use of new solid catalyst for continuous transesterification process. They mentioned that this new solid catalyst consists of a mixed oxide of zinc and aluminum, which promotes the transesterification reaction without catalyst loss. Actually using this new catalyst, the reaction has to be performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol, which can finally be removed by vaporization and recycled to the process [70]. In contrary, however, there are some solid metal oxides, such as oxides of tin, magnesium, and zinc, which are well known as catalysts, and perform like homogeneous catalysis and end up as metal soaps or metal glycerates [70].

Bournay and Casanave [70] claimed also that, while using this new solid catalyst, neither catalyst recovery nor aqueous treatment steps are required. The purification steps of products could then be much more simplified so that very high yields of methyl esters, close to the theoretical value, could be obtained. In addition, the glycerin can directly be produced with high purity levels (at least 98%) without any salt contaminants.

Heterogeneous catalysts such as amorphous zirconia, titanium and potassium zirconias have also been used for catalyzing the transesterification of vegetable oils. Furuta et al. [71] evaluated amorphous zirconia catalysts, titanium-, aluminum-, and potassium-doped zirconias, in the transesterification of soybean oil with methanol at 250 °C, and the esterification of n-octanoic acid with methanol at 175–200 °C. They reported that, titanium- and aluminum-doped zirconias are promising solid catalysts for the production of biodiesel fuels from soybean oil because of their high performance, with over 95% conversion in both of the reactions.

In another study, Huaping et al. [72] demonstrated the potential of preparing biodiesel from *Jatropha curcas* oil catalyzed by solid super base of calcium oxide. When treated with ammonium carbonate solution and calcinated at high temperature, calcium oxide becomes a solid super base, which shows high catalytic activity in transesterification. They reported that, under the optimum conditions, the conversion of *Jatropha curcas* oil can reach 93%.

Sánchez et al. [73] studied the influence of the reaction temperature, the alcohol:oil ratio and the catalyst percent on the methanolysis of Jojoba oil using CaO as a catalyst, which was particularly derived from mussel shells. According to their study, the variables which had the higher positive effect on the methanolysis of Jojoba oil, in a pressurized environment (with approximate 10 bars in Parr reactor), are the methanol:oil ratio and the temperature, whereas the catalyst percent had a slight negative impact on the process. They reported that, using this catalyst, the reaction time could be reduced by half, from 10 to 5 hours and the Jojoba oil conversion reached a maximum of 96.3% with a pressurized environment in the reactor.

Avhad et al. [74] investigated the catalytic activity of glycerol-enriched calcium oxide for ethanolysis of avocado oil. The calcium oxide catalyst was derived from *Mytilus Galloprovincialis* shells through thermal and glycerol (with glycerol dosage of 10% with respect to catalyst weight) treatment before using for the ethanolysis reaction. This shell is simply a waste generated from the fish industry. In this study, they examined the influence of temperature, ethanol-to-oil molar ratio, and the catalyst amount on the variation in the concentration of triacylglycerols and biodiesel with reaction time. They also determined the interaction between the reaction variables (ethanol-to-oil molar ratio and catalyst amount), their influence on the ethanolysis process, and the optimum variables affecting the process through the response surface methodology. According to their conclusion, both catalyst amount and ethanol-to-oil molar ratio significantly affected the described ethanolysis process. They also reported that, temperature of 75 °C, ethanol-to-oil molar ratio of 9:1, and 7 wt.% catalyst amount was taken to be suitable for the studied glycerol-enriched CaO assisted avocado oil ethanolysis process.

The sensitivity of the base catalyzed transesterification to the FFA and water content of the feedstock still persist as the main problem in case of heterogeneous base catalyzed transesterification reaction too. Again, to solve such feedstock quality problem, solid acid catalyst for simultaneous esterification of FFAs and transesterification of triglycerides can be good alternative for biodiesel production from feedstock with higher FFA and water content. Moreover, Melero et al. [75] mentioned that a heterogeneous acid catalyst if incorporated into a packed bed continuous flow reactor, can simplify product separation and purification and reducing waste generation. Solid acid catalyst can be recycled, easily removed and can simultaneously catalyze esterification and transesterification [76].

Peng et al. [76] characterized and studied the activity of a solid acid catalyst comprising $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$ for the production of biodiesel from several low cost feedstocks with high FFAs. They studied the influence of reaction parameters and found out that optimum yield could be attained at reaction temperature of 200 °C, molar ratio of methanol to oil 9:1 and catalyst concentration of 3wt.%. They finally concluded that, the solid acid catalyst $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$ is inexpensive and environment friendly, has high catalytic activity, and is stable for biodiesel production from cheap raw feedstocks with high FFAs.

In another study, Juan et al. [77] carried out transesterification of refined and crude vegetable oils with a sulfonic acid-modified mesostructured catalyst. According to them the catalyst could

enable to yield fatty acid methyl ester (FAME) with purity over 95 wt.% and oil conversion close to 100% under best reaction conditions of temperature 180 °C, methanol/oil molar ratio 10, and catalyst loading 6 wt. %. They reported that, regardless of the presence of free fatty acids, the sulfonic acid-modified mesostructured catalyst showed high activity towards simultaneous esterification and transesterification.

2.4.4. Lipase catalyzed transesterification

The other way of transesterification of oils and fats for biodiesel production is using enzymes in which there is no problem of saponification, purification, washing and neutralization so that it is always a preferred method from these perspectives. Enzymatic catalysts can also be applied on a feedstock with high FFA and can convert more of the oil into biodiesel. However, the problems associated with enzyme catalysts are their higher cost and longer reaction time [19]. Usually because of these two drawbacks, enzyme catalyzed transesterification method is not very frequently used.

In another view, it is more frequently pointed out that enzymatic transesterification has currently attracted much attention for biodiesel production as it produces high purity product (esters) and enables easy separation from the by-product, glycerol [26,78]. The enzymes that are usually found to be capable of catalyzing transesterification are the lipases.

The lipase catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of lipase enzyme as a catalyst to form esters (biodiesel) and glycerol. Mahanta et al. [22] mentioned that, in a lipase catalyzed process no complex operations are needed not only for the recovery of glycerol but also in the elimination of catalyst and soap. This is an environmentally more attractive option to the conventional process. However, Mahanta et al. [22] again argued that the reaction yields as well as the reaction times are still unfavorable compared to the alkaline catalyzed reaction systems.

Lipases for their transesterification activity on different oils can be found from different sources. Ability to utilize all mono, di, and triglycerides as well as the free fatty acids, low product inhibition, high activity and yield in non-aqueous media, low reaction time, reusability of immobilized enzyme, temperature and alcohol resistance are the most desirable characteristics of lipases for transesterification of oils for biodiesel production [79].

Some also argue that, biocompatibility, biodegradability and environmental acceptability of the biotechnological procedure when using lipase as a catalyst are the desired properties in this alternative biodiesel production method [46,78]. However, the use of extracellular lipase as a catalyst requires complicated recovery, purification and immobilization processes for industrial application [80]. Consequently, the direct use of whole cell biocatalyst of intracellular lipases has received considerable research efforts [78]. For the industrial transesterification of fats and oils, *Pseudomonas* species immobilized with sodium alginate gel can be used directly as a whole cell biocatalyst [78].

Devanesan et al. [78] reported maximum yield (72%) of biodiesel from transesterification of *Jatropha* oil and short chain alcohol (methanol on hexane) using *Pseudomonas fluorescens* immobilized with sodium alginate gel at the optimum conditions of 40 °C, pH 7.0, molar ratio of 1:4, amount of beads of 3 g and reaction time of 48 h.

According to Parawira [32], in all the work in literature on lipases, the enzymes or whole cells are immobilized when used for catalysis. It is usually mentioned that, the advantage of

immobilization is that the enzyme can be reused without separation. In addition, the operating temperature of the process is low (50 °C) compared to other techniques which operate at harsh conditions. However, the cost of enzymes remains a barrier for its industrial implementation [81].

Most of the time, in order to tackle this cost barrier of the process, the enzyme (both intracellular and extracellular) should be reused by immobilizing in a suitable support particle, which is usually associated with considerable increase in efficiency.

Enzymes are usually immobilized for better enzyme loading, activity and stability. Selecting and designing the support matrix are important in enzyme immobilization [82]. With this respect, there are a number of ways to immobilize enzymes. These include cross-linked enzyme aggregates, microwave-assisted immobilization, click chemistry technology, mesoporous supports and most recently nanoparticle-based immobilization of enzymes [83]. Recently, the use of nanoparticles has emerged as a versatile tool for generating excellent supports for enzyme stabilization due to their small size and large surface area [82], which results in better stability and activity of enzymes immobilized on such materials. In addition, Nanoparticles strongly influence the mechanical properties of the material like stiffness and elasticity and provide biocompatible environments for enzyme immobilization [82].

However, during transesterification, the activity of immobilized enzyme is inhibited by methanol and glycerol which are always present in the reacting mixture. The use of tert-butanol as solvent, continuous removal of glycerol, stepwise addition of methanol are some of the ways to reduce the inhibitory effects thereby increasing the cost effectiveness of the process [26].

Guang Jin et al. [81] examined the use of whole-cell biocatalysts to produce biodiesel at room temperature (25 °C). They used *Rhizopus oryzae* (ATCC[®] 10260[™]) to catalyze the conversion of virgin and waste oils (triglycerides) into biodiesel fuel in the presence of 15% water. Their research results indicated that the whole-cell biocatalyst could produce about a 90% yield of fatty acid methyl ester from virgin oil, and nearly complete conversion of the remaining oil into free fatty acid, using a 96-hour reaction at room temperature (25 °C). They also reported that, in a 72 hour reaction, fatty acid methyl ester yields were about 75% for virgin oil, 80% for waste vegetable oil, and 55% for brown (trap) grease [81], which implies, whole-cell biocatalysts may be an effective way to transesterify waste oils or greases that are high in FFA and difficult to dewater [81].

Du et al. [84] developed methyl acetate, a novel acyl acceptor, for biodiesel production and carried out a comparative study on *Novozym 435* catalyzed transesterification of soybean oil for biodiesel production with different acyl acceptors. They reported that methanol has a serious negative effect on enzymatic activity as for example a molar ratio of methanol to oil of above 1:1 leads to serious inactivation of the enzyme. In their study, they used methyl acetate as the acyl acceptor, and reported that, a yield of 92% of methyl ester could be obtained with a molar ratio of methyl acetate to oil of 12:1, and methyl acetate showed no negative effect on enzymatic activity. They also mentioned that, with crude soybean oil as the oil source and methanol as acyl acceptor, a much lower methyl ester yield was obtained than that with refined soybean oil, while with methyl acetate as acyl acceptor, an equally high yield of methyl ester (92%) was achieved for both soybean oils. Lipase loses its activity very rapidly during repeated experiments with methanol as the acyl acceptor, however, according to their report, there was almost no detected loss in lipase activity, even after being continuously used for 100 batches, when methyl acetate was used for biodiesel production [84].

During enzymatic transesterification for biodiesel production, it has been demonstrated that excessive methanol present in the reaction medium would cause significant deactivation of the lipase. However, effective methanolysis using extracellular lipase has been reported to improve by stepwise addition of methanol (usually, a three-step addition of methanol in solvent-free medium) through which, according to Watanabea, 90–95% conversion can be achieved even after 50 and 100 cycles of repeated operation [85].

In another study, Li et al. [86] used tert-Butanol, as a novel reaction medium, for lipase-catalyzed transesterification of rapeseed oil for biodiesel production, with which, they claimed, both the negative effects caused by excessive methanol and by-product glycerol could be eliminated. They reported the highest biodiesel yield of 95% achieved under the optimum conditions of tert-butanol/oil volume ratio 1:1; methanol/oil molar ratio 4:1; 3% *Lipozyme TL IM* and 1% *Novozym 435* based on the oil weight; temperature 35 °C; 130 rpm, and 12 hours. According to them, there was no obvious loss in lipase activity even after being repeatedly used for 200 cycles with tert-butanol as the reaction medium [86].

Shah et al. [87] also worked on three different lipases (*Chromobacterium viscosum*, *Candida rugosa*, and *Porcine pancreas*) for a transesterification reaction of *Jatropha* oil in a solvent-free system to produce biodiesel. They reported that, only lipase from *Chromobacterium viscosum* was found to give appreciable yield. Immobilization of lipase (*Chromobacterium viscosum*) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8h at 40 °C. Further addition of water to the free (1%, w/v) and immobilized (0.5%, w/v) enzyme preparations enhanced the yields to 73% and 92%, respectively. They mentioned also that, immobilized *Chromobacterium viscosum* lipase can be used for ethanolysis of oil. According to their conclusion immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process.

Table 6. Summary of some optimized productions of biodiesel from different feedstock types using lipase-catalyzed transesterification.

Feedstock	Alcohol	Alcohol to oil Ratios	Enzymes	wt.% of Enzyme	Temp. (°C)	Stirring	Reaction time	Yield %	Remarks	Ref.
Rapeseed oil	methanol with tert-butanol as a solvent	methanol/oil molar ratio 4:1 Tert butanol/oil volume ratio 1:1	<i>Lipozyme TL IM</i> <i>Novozym 435</i>	3 wt.%	35	130 rpm	12 h	95%	No loss in lipase activity after being repeatedly used for 200 cycles with tert-butanol as the reaction medium	[86]
Soybean oil	methanol	1:1	<i>lipozyme TL</i>	0.04	40	150 rpm	-	66%	-	[89]
Soybean oil	methanol	1:1	silica gel <i>lipozyme TL</i>	0.06	40	150 rpm	-	90%	Silica gel combined with lipozyme TL and three-step addition of methanol	[89]
Soyabean oil in ionic fluid - EmimTfO	methanol	4:1	<i>Novozym 435</i> <i>Pseudomonas cepacia</i> immobilized on celite	2 wt.% 0.1	50	250 rpm	12 h	80%	High production yield in ionic liquids show that ionic liquids are potential reaction media for biodiesel production	[88]
<i>Jatropha</i> oil	ethanol	4:1			50	200 rpm	8 h	98%	With presence of 4–5% (w/w) water	[90]

Some authors also argued that using convenient reaction medium would help increase conversion of oil to biodiesel in lipase-catalyzed transesterification reactions. In this respect, Ha et al. [88] demonstrated production of biodiesel through immobilized *Candida antarctica* lipase-catalyzed methanolysis of soybean oil in 23 different ionic liquids. They reported that, the highest fatty acid methyl esters (FAMES) production after 12 h at 50 °C was achieved in EmimTfO (1-Ethyl-3-methylimidazolium trifluoromethanesulfonate). They also pointed out that around 15% higher free fatty acid production could be achieved using this ionic fluid as a reaction medium than the production system using tert-butanol as an additive. Table 6 summarizes results of some selected researches done to optimize production of biodiesel through lipase-catalyzed transesterification of different feedstock types.

According to Marchetti et al. [46], the use of lipase is a great viable method for production of ester from different sources of oil or grease even though, research on this topic is still in progress due to the enzyme flexibility and adaptability to new process.

However, when we compare enzymatic production of biodiesel with conventional chemical processes, the major obstacles repeatedly mentioned are the cost of lipases, the relatively slower reaction rate and lipases inactivation caused by methanol and glycerol. Some main advantages and disadvantages of using lipases as catalyst are summarized in Table 7.

Table 7. The advantages and disadvantages of using lipases [32].

The advantages of using lipases	
✓	Biocompatible, biodegradable and environmental acceptability
✓	Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if one keep the reactive flow
✓	Use of enzymes in reactors allows use of high concentration of them and that makes for a longer activation of the lipases
✓	Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all enzyme particles getting together
✓	Separation of product will be easier using this catalyst, producing product of very high purity with less or no downstream operations
Some disadvantages	
✓	Loss of some initial activity due to volume of the oil molecule
✓	Number of support enzyme is not uniform
✓	More expensive

In general, process optimization in lipase-catalyzed transesterification, can be done at least in the following: screening of various commercial lipase preparations; pH tuning; immobilization; adjusting water content in the reaction media; adjusting amount of enzyme used; and adjusting temperature of the reaction [90].

2.4.5. Nano catalyzed transesterification

There a number of recent developments in catalytic conversion of oils and fats to biodiesel. Among them biodiesel production using Nano catalyst and Ionic liquid catalysts are more promising in terms of few advantages over the conventional acid/base catalysts.

Nano catalysis involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Nanoscale catalysts have high specific surface area and surface energy resulting in high catalytic activity. Generally, Nano catalysts improve the selectivity of the

reactions by allowing reaction at a lower temperature, reducing the occurrence of side reactions, higher recycling rates and recovery of energy consumption [91]. With this respect, Nano catalysts are promising alternatives for efficient production of biodiesel from oils and fats as they have high specific surface area and high catalysis activities eliminating the specific problem of mass transfer resistance associated with conventional catalysts.

Wen et al. [92] studied that the solid base Nano catalyst KF/CaO can be used for biodiesel production with yield of more than 96%. This catalyst can efficiently be used to convert the oil with higher acid value into biodiesel [92,93]. It is porous with particle sizes of 30–100 nm. Wen et al. [92] could show, using X-ray powder diffraction analysis, that the Nano catalyst KF/CaO has new crystal $KCaF_3$, which increases catalytic activity and stability. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improve efficiency of transesterification [93].

Few have studied on the possible optimum conditions for production of biodiesel from different oil inputs using different Nano catalysts. Sidra et al. [94] investigated the production of biodiesel from *Jatropha* oil through transesterification process by using CaO- Al_2O_3 Nano catalyst. According to them, the optimization results for production of biodiesel from the transesterification of *Jatropha curcas* oil catalyzed by CaO- Al_2O_3 nanoparticles showed maximum yield of 82.3% at 5:1 methanol to oil molar ratio [94]. Similarly, Sivakumar et al. [95] did comprehensive study of smoke deposited Nano sized MgO as a catalyst for biodiesel production. They studied the transesterification reaction to determine the optimum conditions for different parameters like catalyst quantity, methanol oil molar ratio, reaction temperature and reaction time. A maximum conversion of 98.7% was obtained at 1.5 wt.% catalyst; 5:1 methanol oil molar ratio at 55 °C, achieved after 45 min. The conversion was three to five times higher than those reported for laboratory MgO in literature [95]. According to this study, the higher conversion was mainly due to the enhancement of surface area of the catalyst. The other advantage is that the catalyst can be easily recovered and reused up to eight times with easy regeneration steps [95]. Table 8 shows some of optimization studies on biodiesel production using Nano catalysts.

In another two separate studies Mookan et al. [96,97] conducted an investigation on the fuel quality of biodiesel produced from castor oil as well as *Pongamia pinnata* oil with methanol using iron nanoparticles as catalyst. The fuels properties that they investigated are specific gravity, kinematic viscosity, flash point, cloud point, water content, carbon residue, refractive index, copper corrosion and calorific value. They pointed out that, these properties of resulting biodiesel both from castor oil and *Pongamia pinnata* oil agree well with the specifications of biodiesel standards ASTM D6751 except for specific gravity and kinematic viscosity. According to them, most of the physico-chemical properties of castor oil biodiesel match well with the normal diesel. They also concluded that the use of iron nanoparticles as catalyst showed more advantages than the conventional acid/base catalyst for the production of biodiesel in terms of shorter reaction time as well as less amount and reusability of the catalyst.

More recently, Gupta et al. [98] did a research on the preparation and characterization of CaO nanoparticle for biodiesel production from Soybean oil. They synthesized Nanoparticle of CaO from calcium Nitrate (CaO/CaN) and Snail shell (CaO/SS) so as to investigate the performance of the catalysts in terms of biodiesel yield. According to their conclusion, the Nano catalyst from snail shell exhibits excellent catalytic activity and stability for the transesterification reaction, which suggested that this catalyst would be potentially used as a solid base Nano catalyst for biodiesel production [98].

Table 8. Summary of some optimized productions of biodiesel from different feedstock types through transesterification using Nano catalysts.

Feedstock	Alcohol	Alcohol to oil Ratios	Nano catalyst	wt.% of catalyst	Temp. (°C)	Reaction time	Yield %	Remarks	Ref.
Waste mixed vegetable oil	Methanol	5:1	smoke deposited nano sized MgO	1.5	55	45 min	98.7	The transesterification reaction was studied under constant ultrasonic mixing for different parameters	[95]
Stillingia oil	Methanol	12:1	KF/CaO–Fe ₃ O ₄ (Calcinated at 600 °C)	4	65	3 h	95	The catalyst is able to be reused up to 14 times without much deterioration in its activity	[99]
Chinese tallow seed oil	Methanol	12:1	KF/CaO	4	65	2.5 h	96.8	-	[92]
Waste cooking oil		7:1	Nano CaO	1.5	75	6 h	94.37	-	[100]
Waste cooking oil		7:1	Mixture of Nano CaO and Nano MgO	3	75	6 h	98.95	The optimum mass proportion for CaO to MgO is 0.7:0.5	[100]
Soybean oil		12:1	Nanoparticle of CaO from calcium Nitrate (CaO/CaN)	8	65	6 h	93	-	[98]
Soybean oil		12:1	Nanoparticle of CaO from Snail shell (CaO/SS)	8	65	6 h	96	-	[98]

The catalytic activity of such Nano catalysts are usually affected by calcination temperature during catalyst preparation with calcination. This is because in the preparation process of the catalyst, calcination treatment of catalyst at high temperature is favorable for the interaction between support and active ingredient, which generates new active sites for the catalyst [99]. With this respect Hu et al. [99], did an investigation on the optimum calcination temperature for the preparation of three Nano catalysts, KF/CaO–Fe₃O₄, KF/SrO–Fe₃O₄ and KF/MgO–Fe₃O₄. And they found out that the fatty acid methayl ester yield reaches the maximum value at calcination temperature of 600 °C, 600 °C, and 500 °C for KF/CaO–Fe₃O₄, KF/SrO–Fe₃O₄ and KF/MgO–Fe₃O₄, respectively [99]. Thus, calcination temperature can be taken as additional parameter to optimize biodiesel production using Nano catalysts prepared through calcination.

2.4.6. Transesterification using ionic liquids as catalysts

Ionic liquids are organic salts comprising of anions and cations that are liquid at room temperature. The cations are responsible for the physical properties of ionic liquids (such as melting point, viscosity and density), while the anion controls its chemical properties and reactivity [101]. Their unique advantage is that while synthesized, they can be moderated to suit required reaction conditions.

Another great advantage of using Ionic Liquids specifically to catalyze transesterification for biodiesel production is the formation of a biphasic system at the end of the reaction. This biphasic system occurs because the ionic liquid, insoluble in the organic phase, remains in the aqueous phase along with alcohol, the catalyst used and glycerol produced during the reaction [102]. This makes it very easy to separate the final products, because most of the top phase is biodiesel with very little amount of methanol. Pure biodiesel can then be isolated by simple vacuum evacuating of this very little amount of methanol [103]. The bottom phase contains methanol, glycerol and Ionic Liquids.

This bottom phase can then be rinsed with water for 3 to 4 cycles to separate glycerol with high purity [104], or pure glycerol can be obtained simply by distillation [103], which leaves the pure Ionic Liquid behind for further direct use for another reaction.

Among the different possible types of ionic liquids for catalysis of transesterification reaction for biodiesel production, Ionic liquids composed of the 1-n-butyl-3-methylimidazolium cation are the most widely studied and discussed compounds [105].

Very few researches are done to investigate the optimum reaction conditions for ionic liquid catalyzed transesterification with respect to temperature, molar ratio, catalyst amount, etc. Guo et al. [106] did a research to find out such optimum conditions for ionic liquid catalyzed transesterification of soybean oil with methanol by using ultrasound (24 kHz, 80 W). They found out that, at 60 °C under ultrasonic irradiation and a molar ratio of 14:1 methanol to oil, a biodiesel yield in excess of 96% can be achieved in a remarkably short time duration of 20 minutes or less in comparison to 5h or more using conventional method. They concluded that ionic liquid catalyzed transesterification is proved to be efficient and time saving for the preparation of biodiesel from soybean oil. They also mentioned the ionic liquid had a good reusability and can be easily separated from the biodiesel by simple decantation [106].

Table 9. Summary of few researches on optimized productions of biodiesel from different feedstock types through transesterification using different Ionic Liquids as catalysts.

Feedstock	Alcohol	Alcohol to oil Ratios	Ionic liquid catalyst	Wt.% of catalyst	Temp. (°C)	Reaction time	Yield %	Remarks	Ref.
Soybean oil	Methanol	8:1	Basic Ionic Liquids [Hnm]OH	4	70	1.5 h	97	The catalytic activity was affected by its alkalinity	[103]
Cottonseed Oil	Methanol	12:1	1-(4-Sulfonic acid) butylpyridinium hydrogen sulfate	0.057 ^a	170	5 h	92	The catalytic activity of the ionic liquid is dependent on its Brønsted acidic strength.	[107]
Rapeseed oil	Methanol	10:1	1-propyl-3-methyl imidazolium hydrogen sulfate ([PrMIM][HSO ₄])	10	140	5 h	19.74	-	[108]
Rapeseed oil	Methanol	10:1	1-propylsulfonate-3methyl imidazolium hydrogen sulfate ([PrSO ₃ HMIM][HSO ₄])	10	130	5 h	94.91	-	[108]
Rapeseed oil	Methanol	10:1	1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO ₄])	10	110	5 h	8.89	-	[108]
Rapeseed oil	Methanol	10:1	1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ([BSO ₃ HMIM][HSO ₄])	10	130	5 h	100	-	[108]

^a molar ratio of ionic liquid to oil

In another study, Ren et al. [103] investigated the influence of some reaction conditions, such as the amount of morpholine alkaline basic ionic liquid 1-butyl-3-methyl morpholine hydroxide ([Hnm]OH) as a catalyst, the molar ratio of methanol to soybean oil, reaction temperature and time. The optimum reaction conditions to get the maximum biodiesel yield (97.0%) were found as 4% (mass fraction) of [Hnm]OH, the methanol to soybean oil molar ratio of 8, temperature of 70 °C and reaction time of 1.5 hours. They pointed out that, the reaction exhibited high stability upon recycling, and the biodiesel yield remained more than 90% even after being

reused for five times [103]. Table 9 shows the results of some few researches done on optimized reaction conditions for ionic liquid catalyzed transesterification.

2.4.7. Supercritical transesterification

One of the approaches to overcome problems associated with poor immiscibility between the reactants and at the same time, technical problems caused by catalysts is to use supercritical method. Supercritical alcohol transesterification reaction takes place under extremely high temperature and pressure. When a gas or liquid is under high pressure and temperature beyond its critical point, unusual phenomena are exhibited on its properties. In this case, liquid and vapor phase are no longer confined under these conditions and single supercritical fluid phase is generated [19]. In the supercritical transesterification method, methanol and oil, which are immiscible liquids at room temperature, will form a homogenous fluid. This is due to the sharp drop in the solubility of methanol and reduction in dielectric constant, which makes methanol a non-polar substance [19]. In this case, the reaction will be accelerated, as there is no mass transfer limitation under such conditions.

When we consider specific application of the method for biodiesel production, super critical methanol is usually used to speed up the transesterification reaction. Using this technique, the conversion of vegetable oils into biodiesel is done in about 4 min but extremely high pressure and temperature is required for this method, which makes it highly sensitive and costly [9]. A lot of energy is required to build such a high pressure and temperature. Some authors recommend use of co-solvent to improve the conversion efficiency.

The simple chemical catalyzed transesterification processes mentioned above (Acid catalyzed and Base catalyzed) are confronted with two problems, i.e. the processes are relatively time consuming and need separation of the catalyst and saponified impurities from the biodiesel. The first problem is due to the phase separation of the oil/alcohol mixture, which can be alleviated by vigorous stirring. These problems are totally mislaid in the supercritical method of transesterification. This is perhaps due to the fact that the tendency of two phase formation of vegetable oil/alcohol mixture is not encountered and a single phase is found due to decrease in the dielectric constant of alcohol in the supercritical state [9]. In general, the supercritical methanol process, which is non-catalytic, is simpler in purification, takes lower reaction time and lower energy use than the common commercial process [16,51].

It is argued that supercritical transesterification, as an alternative technology, satisfies all the requirements to produce biodiesel suitable to be used on normal engines. In addition, it produces more than a kilo of fuel per kilo of oils used [40]. According to a study done by Marchetti et al. [109], the techno-economic analysis of the supercritical process shows that, although the supercritical alternative appears as a good technical possibility to produce biodiesel, today, it is not an economic alternative due to its high operating cost. However, there is still a possibility in reducing the operating cost and making the method more economically advantageous too. Kasteren and Nisworo [110] have proved this by using one reaction step in the process as well as propane as a co-solvent in supercritical biodiesel production plant so as to decrease operating cost.

In another view, Atabania et al. [111] pointed out that, supercritical methanol method uses lower energy and completes in a very short time (2–4 minutes) compared to catalytic transesterification. According to them, since no catalyst is used, the purification of biodiesel and the

recovery of glycerol are much easier, trouble free and environment friendly. However, the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1) [9].

Similarly, Marulanda [13] carried out a lab scale experiment on biodiesel production process by supercritical transesterification in a continuous reactor working at a 9:1 methanol to triglycerides molar ratio and 400 °C. The results of this study showed that for a specified biodiesel production plant capacity set at 10,000 tons/year the total energy consumption of this specific process (573 kW) was considerably lower than another supercritical process working at a 42:1 molar ratio and 300 °C (2407 kW), and the conventional base catalyzed process (2326 kW).

Different studies done on investigation of optimum condition for supercritical transesterification process agree that among the determinant variables temperature has the highest impact on yields, followed by reaction time and pressure. Kiss et al. [112] have done a series of experiments with ethyl alcohol to the effect of temperature, time and pressure. They found that, by increasing the reaction time at 350 °C and 12 MPa, yield increases during the whole range (from 63.36% to 93.22%). After reduction of pressure at 350 °C temperature, the maximum yield (80.1%) was reached within 30 min. They concluded that, in general, lowering the pressure would result in yield decrease. By reducing the reaction temperature (350–250 °C), the yield decreases which can in general be compensated with prolonging the duration of reaction. They attained lowest yield at a minimum temperature, minimum pressure and short reaction time (250 °C, 8 MPa, 7 min; the yield is 14.8%) [112]. Table 8 summarizes the results of some selected researches done on optimization of reaction conditions for supercritical transesterification of different feedstock types.

Table 10. Summary of the optimum reaction conditions for supercritical transesterification of different feedstock types for biodiesel production.

Feedstock	Alcohol	Process variables					Methyl ester %	Ref
		Alcohol to oil ratio	Temperature (°C)	Reaction time (min)	Stirring speed (rpm)	Pressure (MPa)		
Refined lard	Methanol	45:1	335	15	500	20	89.91%	[14]
Rapeseed oil	Methanol	45:1	350	4	-	14	95%	[113]
Coconut oil	Methanol	42:1	350	7	-	19	95%	[114]
Palm kernel oil	Methanol	42:1	350	7	-	19	96%	[114]
Rapeseed oil	Methanol	42:1	350	15	-	12	93%	[115]
Rapeseed oil	Ethanol	42:1	350	20	-	12	91.9%	[115]
Rapeseed oil	1-propanol	42:1	350	25	-	12	91.1%	[115]
Jatropha oil	Methanol	43:1	320	4	-	8.4	100%	[116]
Sunflower seed oil	Methanol	41:1	252	20	-	24	95%	[117]
Sunflower seed oil	Methanol with 0.3% CaO	41:1	252	17	-	24	95%	[117]
Sunflower seed oil	Methanol with 5% CaO	41:1	252	13	-	24	100%	[117]
RBD ^a Palm oil	Methanol	45:1	350	5	-	40	95%	[118]
Vegetable oil	Ethanol with C ₂ O Co-solvent	25:1	200	6	-	20	80%	[119]

^a Refined, Bleached and Deodorized

2.4.8. Comparison between transesterification techniques

As it has been tried to clearly put in the different research works reviewed in this paper, the different transesterification techniques do have their own advantages and disadvantages. These advantages and disadvantages can be seen with respect to cost of input material, degree of waste

generation, cost of production, product purity, yield percentage, environmental and health hazard and the like. Table 9 shows a summary on advantages and disadvantages of these major transesterification techniques as well as required character of suitable feedstock for each method.

Table 11. Summary of the advantages and disadvantages of the different techniques for transesterification of oil and/or fat for biodiesel production.

Transesterification method	Suitable feedstock character	Advantages	Disadvantages	Ref
Homogeneous Acid catalyzed	Any type of oil/fat feedstock including those with high free fatty acid.	<ul style="list-style-type: none"> ✓ Gives relatively high yield ✓ Insensitive to FFA content in feedstock, thus preferred-method if low-grade feedstock is used ✓ Esterification and transesterification occur simultaneously ✓ Less energy intensive 	<ul style="list-style-type: none"> × Corrosiveness of acids damage equipment × More amount of free glycerol in the biodiesel × Requires higher temperature operation but less than supercritical × Relatively difficult to separation of catalyst from product. × Has slower rate of production (relatively takes longer time) 	[22,40,43,44,120]
Homogeneous Base catalyzed	Oil/fat feedstock with FFA content less than 0.5% by weight of the oil	<ul style="list-style-type: none"> ✓ Faster reaction rate than acid catalyzed transesterification ✓ Reaction can occur at mild reaction condition and less energy intensive ✓ Common catalysts such as NaOH and KOH are relatively cheap and widely available ✓ less corrosive 	<ul style="list-style-type: none"> × Sensitive to FFA content in the oil × Saponification of oil is the main problem due to quality of feedstock × Recovery of glycerol is difficult, × Alkaline wastewater generated requires treatment 	[19,32,46,48,52,120]
Heterogeneous Base Catalysis	Oil/fat feedstock with FFA content less than 0.5% by weight of the oil	<ul style="list-style-type: none"> ✓ Improved selectivity ✓ Easy to separate catalyst from reaction mixture ✓ Reduced process stages and wastes ✓ Enable to regenerate and reuse the catalyst ✓ Reaction can occur at mild reaction condition and less energy intensive 	<ul style="list-style-type: none"> × Catalyst might be poisoned when exposed to ambient air × Sensitive to FFA content in the oil so selective to feedstock type × Soap will be formed if there is high FFA content × Soap formation associated with reduced biodiesel yield and problem in product purification × Leaching of catalyst active sites may result to product contamination 	[32,66,69,71,120]
Heterogeneous Acid Catalysis	Any type of oil/fat feedstock including those with high free fatty acid.	<ul style="list-style-type: none"> ✓ Catalyst separation from reaction mixture is easy ✓ Has reduced process stages and wastes ✓ Insensitive to feedstocks' FFA content. ✓ Preferred-method if low-grade oil is used ✓ Esterification and transesterification occur simultaneously ✓ Solid acid catalyst can be easily removed recycled 	<ul style="list-style-type: none"> × Complicated catalyst synthesis procedures lead to higher cost × Requires high reaction temperature, high alcohol to oil molar ratio and long reaction time. × Relatively energy intensive 	[69,75,76,120]

Lipase catalyzed transesterification	Any type of oil/fat feedstock including those with high free fatty acid and water content.	<ul style="list-style-type: none"> ✓ Insensitive to FFA and water content in the oil, thus preferred when low grade feedstock is used ✓ It is carried out at low reaction temperature ✓ Purification requires simple step, by enabling easy separation from the by-product, glycerol ✓ Gives high purity product (esters) ✓ Enables to reuse immobilized enzyme 	<ul style="list-style-type: none"> × The cost of enzyme is usually very high × Gives relatively low yield × It takes high reaction time × The problem of lipases inactivation caused by methanol and glycerol 	[19,22,26,46,78,79,120]
Nano catalyzed transesterification	Any type of oil/fat feedstock including those with high free fatty acid and water content	<ul style="list-style-type: none"> ✓ Relatively with shorter reaction time ✓ Less amount of catalyst can be enough since has high specific surface area ✓ Catalyst can be reused many times ✓ Wide range of catalyst choice 	<ul style="list-style-type: none"> × Requires relatively more alcohol for effective yield × In some cases preparation of appropriate catalysts costs more 	[91–97]
Ionic liquid catalyzed transesterification	Any type of oil/fat feedstock including those with high free fatty acid and water content but dependent on which type of ionic liquid is used (Acidic/basic)	<ul style="list-style-type: none"> ✓ Easy to separate final products due to formation of biphasic. ✓ Efficient and time saving ✓ While preparing catalysts their properties can be designed to suit a particular need ✓ Catalyst can be easily separated and reused many times ✓ High catalytic activity, excellent stability 	<ul style="list-style-type: none"> × High cost of ionic liquid production × Requires relatively more alcohol for effective yield 	[101–106]
Supercritical transesterification	Any oil and fat with greater range and water content and high FFA content (in particular, used cooking oil)	<ul style="list-style-type: none"> ✓ It takes very less time to complete ✓ Insensitive to greater water content of the feedstocks ✓ Produces more than a kilo of fuel per kilo of feedstock ✓ No need of washing the product as there is no catalyst used ✓ It is more easier to design as a continuous process 	<ul style="list-style-type: none"> × Requires higher temperature and pressure × It is not an economic alternative due to its high operating cost, due to high pressures and high temperatures × Relatively there is high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1) 	[9,40,111,112,115,118,119]

3. Conclusion

Even though biodiesel is a good alternative over petroleum diesel in various aspects, it is always jeopardized by the high cost of feedstock and absence of economically and technically viable technology for its efficient production from any feedstock type.

Different researchers recommend different methods of biodiesel production, which are usually dependent on properties of the feedstock. Among the methods to change fat and oil to biodiesel, the most convenient one is the transesterification or also called alcoholysis reaction. There are a number of techniques used to carry out transesterification of fat/oil for biodiesel production, each of which requiring specific feedstock property and optimum operating condition for efficient production of biodiesel.

From the review of different works, it can be concluded that:

- (1) Homogenous acid catalyzed transesterification is relatively insensitive to FFA content of the feedstock, is relatively less energy intensive but requires higher temperature operation and the biodiesel produced usually has more amount of free glycerol (low purity percentage).
- (2) Homogeneous base catalyzed transesterification is very sensitive to FFA and water content and thus is very selective in feedstock type. The reaction is fast, the catalysts are relatively cheap, and thus it is usually applied at industrial scale for biodiesel production.
- (3) Heterogeneous acid catalyzed transesterification avoids the problem of product separation and purification and enable reuse of the catalyst. However, it relatively requires high alcohol to oil molar ratio and long reaction time.
- (4) Heterogeneous base catalyzed transesterification reduces process stages and wastes, and enables easy catalyst separation and reuse. However, catalyst might possibly be poisoned when exposed to ambient air so that not environmentally friendly.
- (5) Lipase catalyzed transesterification is insensitive to FFA and water content, carried out at low temperature, and convert more amount of the feedstock to biodiesel. Nevertheless, it is costly due to expensiveness of the enzymes and takes longer time to have good yield.
- (6) Nano catalyzed transesterification is insensitive to FFA and water content, carried out relatively at low temperature and takes short time. The catalyst can be reused many times providing cost benefits. However, it requires more alcohol for effective yield and in some cases preparation of appropriate catalysts is expensive.
- (7) Ionic Liquids catalyzed transesterification enables easy separation of final products due to formation of biphasic thus reducing process cost and be efficient and time saving. In addition, it enables modulating desired properties of catalysts while preparing them. Catalysts have high catalytic activity, excellent stability and can also be easily separated and reused many times. However it requires relatively more alcohol for effective yield and usually expensive to have ionic liquids.
- (8) Supercritical transesterification is insensitive to FFA and water content of feedstock and thus enable to use wider feedstock types, usually takes shorter time and produces more fuel amount per feedstock mass. However, it requires higher temperature and pressure and consumes more methanol so that it is not economically profitable due to its high operating cost.

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

References

1. EIA UEIA (2016) International energy outlook 2016 With Projections to 2040. Washington, DC 20585: U.S Energy Information Administration, Office of Energy Analysis, Department of Energy.
2. Shafiee S, Topal E (2009) When will fossil fuel reserves be diminished? *Energ Policy* 37: 181–189.
3. IEA (2015) Medium term renewable energy market report 2015, Executive Summary: Market analysis and Forcasts to 2020. International Energy Agency.
4. Birol F (2014) world energy outlook 2013–2035. Rotterdam: International Energy Agency, IEA.
5. Ahmad A, Yasin NM, Derek C, et al. (2011) Microalgae as a sustainable energy source for biodiesel production: a review. *Renew Sust Energ Rev* 15: 584–593.
6. Janaun J, Ellis N (2010) Perspectives on biodiesel as a sustainable fuel. *Renew Sust Energ Rev* 14: 1312–1320.
7. Kafuku G, Mbarawa M (2010) Biodiesel production from Croton megalocarpus oil and its process optimization. *Fuel* 89: 2556–2560.
8. Satyanarayana M, Muraleedharan C (2011) A comparative study of vegetable oil methyl esters (biodiesels). *Energy* 36: 2129–2137.
9. Shahid EMJ, Younis (2011) Production of biodiesel: a technical review. *Renew Sust Energ Rev* 15: 4732–4745.
10. Carraretto C, Macor A, Mirandola A, et al. (2004) Biodiesel as alternative fuel: experimental analysis and energetic evaluations. *Energy* 29: 2195–2211.
11. Fazal M, Haseeb A, Masjuki H (2011) Biodiesel feasibility study: an evaluation of material compatibility; performance; emission and engine durability. *Renew Sust Energ Rev* 15: 1314–1324.
12. Silitonga A, Atabani A, Mahlia T, et al. (2011) A review on prospect of Jatropha curcas for biodiesel in Indonesia. *Renew Sust Energ Rev* 15: 3733–3756.
13. Marulanda VF (2012) Biodiesel production by supercritical methanol transesterification: process simulation and potential environmental impact assessment. *J Clean Prod* 33: 109–116.
14. Shin HY, Lee SH, Ryu JH, et al. (2012) Biodiesel production from waste lard using supercritical methanol. *The J of Supercrit Fluids* 61: 134–138.
15. Glisic SB, Pajnik JM, Orlović AM (2016) Process and techno-economic analysis of green diesel production from waste vegetable oil and the comparison with ester type biodiesel production. *Appl Energ* 170: 176–185.
16. Kusdiana D, Saka S (2004) Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresour Technol* 91: 289–295.
17. Meher L, Sagar DV, Naik S (2006) Technical aspects of biodiesel production by transesterification—a review. *Renew Sust Energ Rev* 10: 248–268.
18. Koh MY, Mohd. Ghazi TI (2011) A review of biodiesel production from Jatropha curcas L. oil. *Renew Sust Energ Rev* 15: 2240–2251.

19. Leung DY, Wu X, Leung M (2010) A review on biodiesel production using catalyzed transesterification. *Appl energ* 87: 1083–1095.
20. Czernik S, Bridgwater AV (2004) Overview of Applications of Biomass Fast Pyrolysis Oil. *Energ Fuels* 18: 590–598.
21. Ma F, Hanna MA (1999) Biodiesel production: a review. *Bioresource Technol* 70: 1–15.
22. Mahanta P, Shrivastava A (2004) Technology development of bio-diesel as an energy alternative. Available from: <http://newagepublishers.com/samplechapter/001305.pdf>.
23. Abbaszaadeh A, Ghobadian B, Omidkhah MR, et al. (2012) Current biodiesel production technologies: A comparative review. *Energ Convers Manage* 63: 138–148.
24. French R, Czernik S (2010) Catalytic pyrolysis of biomass for biofuels production. *Fuel Process Technol* 91: 25–32.
25. Singh SS, Dipti (2010) Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. *Renew Sust Energ Rev* 14: 200–216.
26. Ranganathan SV, Narasimhan SL, Muthukumar K (2008) An overview of enzymatic production of biodiesel. *Bioresource Technol* 99: 3975–3981.
27. Slomkowski S, Alemán JV, Gilbert RG, et al. (2011) Terminology of polymers and polymerization processes in dispersed systems (IUPAC Recommendations 2011). *Pure Appl Chem* 83: 2229–2259.
28. Chiaramonti D, Bonini M, Fratini E, et al. (2003) Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines—Part 1 : emulsion production. *Biomass Bioenerg* 25: 85–99.
29. Schwab A, Bagby M, Freedman B (1987) Preparation and properties of diesel fuels from vegetable oils. *Fuel* 66: 1372–1378.
30. Srivastava A, Prasad R (2000) Triglycerides-based diesel fuels. *Renew Sust Energ Rev* 4: 111–133.
31. Bart JCJ, Palmeri N, Cavallaro S (2010) 14-Sustainability and use of biodiesel. *Biodiesel Sci Technol* 4: 625–712.
32. Pairiawi W (2010) Biodiesel production from *Jatropha curcas*: A review. *Sci Res Essays* 5: 1796–1808.
33. Bilgin A, Durgun O, Sahin Z (2002) The Effects of Diesel-Ethanol Blends on Diesel Engine Performance. *Energ Source* 24: 431–440.
34. Lokanatham RPRK (2013) Extraction and Use of Non-Edible Oils in Bio-Diesel Preparation with Performance and Emission Analysis on C.I. Engine. *Int Eng Res Develop* 6: 35–45.
35. Gerhard Knothe JVG, Jürgen Krahl (2005) *The Biodiesel Handbook*; Gerhard Knothe JVG, Jürgen Krahl, editor: AOCS Press, Champaign, Illinois.
36. Zhang Y, Dube M, McLean D, et al. (2003) Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technol* 89: 1–16.
37. Park JY, Wang ZM, Kim DK, et al. (2010) Effects of water on the esterification of free fatty acids by acid catalysts. *Renew Energ* 35: 614–618.
38. Zheng S, Kates M, Dube M, et al. (2006) Acid-catalyzed production of biodiesel from waste frying oil. *Biomass Bioenerg* 30: 267–272.
39. Soriano Jr NU, Venditti R, Argyropoulos DS (2009) Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* 88: 560–565.

40. Marchetti J, Miguel V, Errazu A (2008) Techno-economic study of different alternatives for biodiesel production. *Fuel Process Technol* 89: 740–748.
41. Miao X, Li R, Yao H (2009) Effective acid-catalyzed transesterification for biodiesel production. *Energ Convers Manage* 50: 2680–2684.
42. Ganesan D, Rajendran A, Thangavelu V (2009) An overview on the recent advances in the transesterification of vegetable oils for biodiesel production using chemical and biocatalysts. *Rev Environ Sci Bio* 8: 367.
43. Farag HA, El-Maghraby A, Taha NA (2011) Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. *Fuel Process Technol* 92: 507–510.
44. Guan G, Kusakabe K, Sakurai N, et al. (2009) Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. *Fuel* 88: 81–86.
45. Kulkarni MG, Gopinath R, Meher LC, et al. (2006) Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chem* 8: 1056–1062.
46. Marchetti J, Miguel V, Errazu A (2007) Possible methods for biodiesel production. *Renew Sust Energ Rev* 11: 1300–1311.
47. Díaz GC, Tapanes NdICO, Câmara LDT, et al. (2014) Glycerol conversion in the experimental study of catalytic hydrolysis of triglycerides for fatty acids production using Ni or Pd on Al₂O₃ or SiO₂. *Renew Energ* 64: 113–122.
48. Demirbas A (2009) Progress and recent trends in biodiesel fuels. *Energ Convers Manage* 50: 14–34.
49. Fadhil AB, Ali LH (2013) Alkaline-catalyzed transesterification of *Silurus triostegus* Heckel fish oil: Optimization of transesterification parameters. *Renew Energ* 60: 481–488.
50. Atadashi IM, Aroua MK, Abdul Aziz AR, et al. (2013) The effects of catalysts in biodiesel production: A review. *J Ind Eng Chem* 19: 14–26.
51. Leung D, Guo Y (2006) Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Process Technol* 87: 883–890.
52. Dias JM, Alvim-Ferraz MCM, Almeida MF (2008) Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. *Fuel* 87: 3572–3578.
53. Boyce ABMSHaAN (2009) Biodiesel Production from Waste Sunflower Cooking Oil as an Environmental Recycling Process and Renewable Energy. *Bulgarian J Agricul Sci* 15: 312–317.
54. Meher L, Dharmagadda VS, Naik S (2006) Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. *Bioresource technol* 97: 1392–1397.
55. Ojolo S, Ogunsina B, Adelaja A, et al. (2011) Study of an effective technique for the production of biodiesel from *jatropha* oil. *JETEAS* 2: 79–86.
56. Barnwal B, Sharma M (2005) Prospects of biodiesel production from vegetable oils in India. *Renew Sust Energ Rev* 9: 363–378.
57. Sinha S, Agarwal AK, Garg S (2008) Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. *Energ Convers Manage* 49: 1248–1257.
58. Ouanji F, Kacimi M, Ziyad M, et al. (2016) Production of biodiesel at small-scale (10 L) for local power generation. *Int J Hydrogen Energ* 42: 8914–8921.
59. Ojolo SJ OBS, Adelaja AO, Ogbonnaya M (2011) Study of an effective technique for the production of biodiesel. *JETEAS* 2: 79–86.

60. Keera ST, El Sabagh SM, Taman AR (2011) Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst. *Fuel* 90: 42–47.
61. Uzun BB, Kılıç M, Özbay N, et al. (2012) Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties. *Energy* 44: 347–351.
62. Chung K-H, Kim J, Lee K-Y (2009) Biodiesel production by transesterification of duck tallow with methanol on alkali catalysts. *Biomass Bioenerg* 33: 155–158.
63. Chen KS, Lin YC, Hsu KH, et al. (2012) Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system. *Energy* 38: 151–156.
64. Brito JQA, Silva CS, Almeida JS, et al. (2012) Ultrasound-assisted synthesis of ethyl esters from soybean oil via homogeneous catalysis. *Fuel Process Technol* 95: 33–36.
65. Karavalakis G, Anastopoulos G, Stournas S (2011) Tetramethylguanidine as an efficient catalyst for transesterification of waste frying oils. *Appl Energy* 88: 3645–3650.
66. Jagadale SSJLM (2012) Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel. *IJMERE* 2: 407–411.
67. Baskar G, Aiswarya R (2016) Trends in catalytic production of biodiesel from various feedstocks. *Renew Sust Energ Rev* 57: 496–504.
68. Dell'Anna MM, Capodiferro VF, Mali M, et al. (2016) Esterification, transesterification and hydrogenation reactions of polyunsaturated compounds catalyzed by a recyclable polymer supported palladium catalyst. *J Organomet Chem* 818: 106–114.
69. Borges ME, Díaz L (2012) Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renew Sust Energ Rev* 16: 2839–2849.
70. Bournay L, Casanave D, Delfort B, et al. (2005) New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catal Today* 106: 190–192.
71. Furuta S, Matsushashi H, Arata K (2006) Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor. *Biomass Bioenerg* 30: 870–873.
72. Zhu H, Wu Z, Chen Y, et al. (2006) Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. *Chinese J Catal* 27: 391–396.
73. Sánchez M, Avhad MR, Marchetti JM, et al. (2016) Enhancement of the jojobyl alcohols and biodiesel production using a renewable catalyst in a pressurized reactor. *Energ Convers Manage* 126: 1047–1053.
74. Avhad MR, Sánchez M, Bouaid A, et al. (2016) Modeling chemical kinetics of avocado oil ethanolysis catalyzed by solid glycerol-enriched calcium oxide. *Energ Convers Manage* 126: 1168–1177.
75. Melero JA, Iglesias J, Morales G (2009) Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chem* 11: 1285–1308.
76. Peng BX, Shu Q, Wang JF, et al. (2008) Biodiesel production from waste oil feedstocks by solid acid catalysis. *Process Saf Environ* 86: 441–447.
77. Melero JA, Bautista LF, Morales G, et al. (2009) Biodiesel production with heterogeneous sulfonic acid-functionalized mesostructured catalysts. *Energ Fuel* 23: 539–547.
78. Devanesan M, Viruthagiri T, Sugumar N (2007) Transesterification of Jatropha oil using immobilized *Pseudomonas fluorescens*. *Afr J Biotechnol* 6: 2497–2501.

79. Bajaj A, Lohan P, Jha PN, et al. (2010) Biodiesel production through lipase catalyzed transesterification: an overview. *J Mol Catal B Enzym* 62: 9–14.
80. Ban K, Kaieda M, Matsumoto T, et al. (2001) Whole cell biocatalyst for biodiesel fuel production utilizing *Rhizopus oryzae* cells immobilized within biomass support particles. *Biochem Eng J* 8: 39–43.
81. Guang Jin TJB (2010) Whole-cell biocatalysts for producing biodiesel from waste greases. Illinois State University Normal, Illinois.
82. Meryam Sardar RA (2015) Enzyme Immobilization: an overview on nanoparticles as immobilization matrix. *Anal Biochem* 4: 178.
83. Ansari SA, Husain Q (2012) Potential applications of enzymes immobilized on/in nano materials: A review. *Biotechnol Adv* 30: 512–523.
84. Du W, Xu Y, Liu D, et al. (2004) Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *J Mol Catal B Enzym* 30: 125–129.
85. Yomi Watanabea YS, Akio Sugiharaa, Hideo Nodab, Hideki Fukudac, and Yoshio Tominagaa (2000) Continuous Production of Biodiesel Fuel from Vegetable Oil Using Immobilized *Candida antarctica* Lipase. *J Am Oil Chem Soc* 77: 355–360.
86. Li L, Du W, Liu D, et al. (2006) Lipase-catalyzed transesterification of rapeseed oils for biodiesel production with a novel organic solvent as the reaction medium. *J Mol Catal B Enzym* 43: 58–62.
87. Shah S, Sharma S, Gupta MN (2004) Biodiesel Preparation by Lipase-Catalyzed Transesterification of *Jatropha* Oil. *Energ Fuel* 18: 154–159.
88. Ha SH, Lan MN, Lee SH, et al. (2007) Lipase-catalyzed biodiesel production from soybean oil in ionic liquids. *Enzyme Microb Tech* 41: 480–483.
89. Du W, Xu YY, Liu DH, et al. (2005) Study on acyl migration in immobilized lipozyme TL-catalyzed transesterification of soybean oil for biodiesel production. *J Mol Catal B Enzym* 37: 68–71.
90. Shah S, Gupta MN (2007) Lipase catalyzed preparation of biodiesel from *Jatropha* oil in a solvent free system. *Process Biochem* 42: 409–414.
91. Sharma N, Ojha H, Bharadwaj A, et al. (2015) Preparation and catalytic applications of nanomaterials: a review. *RSC Adv* 5: 53381–53403.
92. Wen L, Wang Y, Lu D, et al. (2010) Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. *Fuel* 89: 2267–2271.
93. Chaturvedi S, Dave PN, Shah NK (2012) Applications of nano-catalyst in new era. *J Saudi Chem Soc* 16: 307–325.
94. Sidra HSG, Tariq Mahmood³, Umar Nawaz, et al. (2016) Biodiesel Production by using CaO-Al₂O₃ Nano Catalyst. *Int J Eng Res Sci* 2: 2395–6992.
95. Sivakumar P, Sankaranarayanan S, Renganathan S, et al. (2013) Studies on sono-chemical biodiesel production using smoke deposited nano mgo catalyst. *Bull Chem React Eng Cataly* 8: 89–96.
96. Mookan RSM, Senthilkumar HV, Ravichandran B, et al. (2014) Transesterification of castor oil using nano-sized iron catalyst for the production of biodiesel. *J Chem Pharm Sci* 2: 108–112.
97. Mookan RKA, Sundaresan M, Velan P (2014) Biodiesel production from *Pongamia pinnata* oil using synthesized iron nanocatalyst. *Int J ChemTech Res* 6: 4511–4516.

98. Gupta J, Agarwal M (2016) Preparation and characterization of CaO nanoparticle for biodiesel production. 2nd International Conference on Emerging Technologies. Jaipur, 302017, India: American Institute of Physics.
99. Hu S, Guan Y, Wang Y, et al. (2011) Nano-magnetic catalyst KF/CaO-Fe₃O₄ for biodiesel production. *Appl Energ* 88: 2685–2690.
100. Tahvildari K, Anaraki YN, Fazaeli R, et al. (2015) The study of CaO and MgO heterogenic nano-catalyst coupling on transesterification reaction efficacy in the production of biodiesel from recycled cooking oil. *J Environ Health Sci Eng* 13: 73–81.
101. Earle MJ, Plechkova NV, Seddon KR (2009) Green synthesis of biodiesel using ionic liquids. *Pure Appl Chem* 81: 2045–2057.
102. Gamba M, Lapis AA, Dupont J (2008) Supported ionic liquid enzymatic catalysis for the production of biodiesel. *Adv Synth Catal* 350: 160–164.
103. Ren Q, Zuo T, Pan J, et al. (2014) Preparation of biodiesel from soybean catalyzed by basic ionic liquids [Hnmm]OH. *Materials* 7: 8012–8023.
104. Dupont J, Suarez PA, Meneghetti MR, et al. (2009) Catalytic production of biodiesel and diesel-like hydrocarbons from triglycerides. *Energ Environ Sci* 2: 1258–1265.
105. Andreani L, Rocha JD (2012) Use of ionic liquids in biodiesel production: a review. *Braz J Chem Eng* 29: 1–13.
106. Guo W, Leng Y, Ji G, et al. (2014) Ionic liquids-catalyzed transesterification of soybean oil under ultrasound irradiation. International Conference on Materials for Renewable Energy and Environment. IEEE, 295–297.
107. Wu Q, Chen H, Han M, et al. (2007) Transesterification of cottonseed oil catalyzed by brønsted acidic ionic liquids. *Ind Eng Chem Res* 46: 7955–7960.
108. Fan P, Xing S, Wang J, et al. (2017) Sulfonated imidazolium ionic liquid-catalyzed transesterification for biodiesel synthesis. *Fuel* 188: 483–488.
109. Marchetti J, Errazu A (2008) Technoeconomic study of supercritical biodiesel production plant. *Energ Convers Manage* 49: 2160–2164.
110. van Kasteren JMN, Nisworo AP (2007) A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. *Resour Conserv Recy* 50: 442–458.
111. Atabani AE, Silitonga AS, Badruddin IA, et al. (2012) A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew Sust Energ Rev* 16: 2070–2093.
112. Kiss FE, Micic RD, Tomić MD, et al. (2014) Supercritical transesterification: Impact of different types of alcohol on biodiesel yield and LCA results. *J Supercrit Fluid* 86: 23–32.
113. Kusdiana D, Saka S (2001) Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel* 80: 693–698.
114. Bunyakiat K, Makmee S, Sawangkeaw R, et al. (2006) Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol. *Energ Fuel* 20: 812–817.
115. Micic RD, Tomić MD, Kiss FE, et al. (2014) Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification. *Energ Convers Manage* 86: 717–726.
116. Hawash S, Kamal N, Zaher F, et al. (2009) Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. *Fuel* 88: 579–582.

117. Demirbas A (2007) Biodiesel from sunflower oil in supercritical methanol with calcium oxide. *Energ Convers Manage* 48: 937–941.
118. Song ES, Lim JW, Lee HS, et al. (2008) Transesterification of RBD palm oil using supercritical methanol. *J Supercrit Fluid* 44: 356–363.
119. Santana A, Maçaira J, Larrayoz MA (2012) Continuous production of biodiesel using supercritical fluids: A comparative study between methanol and ethanol. *Fuel Process Technol* 102: 110–115.
120. Lam MK, Lee KT, Mohamed AR (2010) Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol Adv* 28: 500–518.



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