

# A review on novel processes of biodiesel production from waste cooking oil



Amin Talebian-Kiakalaieh<sup>a</sup>, Nor Aishah Saidina Amin<sup>a,\*</sup>, Hossein Mazaheri<sup>a,b</sup>

<sup>a</sup> Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, Malaysia

<sup>b</sup> Department of Chemical Engineering, Faculty Engineering, Islamic Azad University, Arak Branch, Arak, Iran

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## ABSTRACT

Fossil fuel depletion, environmental concerns, and steep hikes in the price of fossil fuels are driving scientists to search for alternative fuels. The characteristics of biodiesel have made the pursuit of high quality biodiesel production attractive. Utilization of waste cooking oil is a key component in reducing biodiesel production costs up to 60–90%. Researchers have used various types of homogeneous and heterogeneous catalyzed transesterification reaction for biodiesel production. Meanwhile, the effect of novel processes such as membrane reactor, reactive distillation column, reactive absorption, ultrasonic and microwave irradiation significantly influenced the final conversion, yield and in particular, the quality of product. This article attempts to cover all possible techniques in production of biodiesel from waste cooking oil.

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\* Corresponding author. Tel.: +60 7 553 5579; fax: +60 7 558 8166.

E-mail addresses: [talebian\\_amin@yahoo.com](mailto:talebian_amin@yahoo.com) (A. Talebian-Kiakalaieh), [noraishah@cheme.utm.my](mailto:noraishah@cheme.utm.my) (N.A.S. Amin).

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## 1. Introduction

Energy consumption is inevitable for human existence. There are various reasons for the search of an alternative fuel that is technically feasible, environmentally acceptable, economically competitive, and readily available. The first foremost reason is the increasing demand for fossil fuels in all sectors of human life, be it transportation, power generation, industrial processes, and residential consumption [1]. This increasing demand gives rise to environmental concerns such as larger CO<sub>2</sub> and greenhouse gas emissions, and also global warming. World energy consumption doubled between 1971 and 2001 and the world energy demand will increase 53% by the year 2030. For instance, petroleum consumption will rise from 84.4 to 116 million barrels per day in USA until year 2030 [2,3]. The second reason is that fossil-fuel resources are non-renewable, and they will be exhausted in the near future [4]. Some reports claimed that oil and gas reserves will be depleted in 41 and 63 years, respectively, if the consumption pace remains constant [5]. The last reason is the price instability of fuels such as crude oil, which is a serious threat for countries with limited resources [6]. Several alternatives such as wind, solar, hydro, nuclear, biofuel, and biodiesel have been suggested but all of them are still in the research and development stage.

The inventor of biodiesel engines, Rudolf Christian Karl Diesel (1858–1913) demonstrated the use of vegetable oils as a substitute for diesel fuel in the 19th century [7]. He believed the utilization of biomass fuel will become a reality as future versions of his engine are designed and developed. Biodiesel is a mono alkyl ester of fatty acids produced from vegetable oils or animal fats [8,9]. In other words, when a vegetable oil or animal fat chemically reacts with an alcohol, it can produce Fatty Acid Methyl Ester (FAME), a vegetable oil which can be used in diesel engines after some adjustments and modifications. Vegetable oils contain saturated hydrocarbons (triglycerides) which consist of glycerol and esters of fatty acids. In addition, fatty acids have different numbers of bonds and carbon chain lengths. There are different kinds of modification methods, such as dilution, thermal cracking (pyrolysis), transesterification, and microemulsification. However, transesterification is the best method for producing higher quality biodiesel [10–14].

All fatty acid sources such as animal fats or plant lipids (more than 300 types of them) can be used in biodiesel production [15–19]. The utilization of these types of sources has given rise to certain concerns as some of them are important food chain materials [20,21]. In other words, the production of biofuels from human nutrition sources can cause a food crisis. Therefore, the majority of researchers have focused on non-edible oils or waste cooking oils as feedstock for biodiesel production such as algae oil [22–24], microalgae [25–29], jatropha oil [30], and grease oil [31]. Table 1 shows various feedstocks in biodiesel production [32]. The most important obstacle in biodiesel industrialization and commercialization is production costs [33,34]. Therefore, the usage of waste edible oils can reduce biodiesel production costs by 60–90% [35–39]. In an effort to produce higher quality biodiesel

at lower costs, researchers are using various novel processes to decrease the reaction time, amount of alcohol, catalyst, and particularly reaction temperature.

In this paper, an attempt has been made to review all possible methods in the production of biodiesel from waste cooking oil with emphasis on some processes in separation, purification and analysis of product quality. The downstream of biodiesel, performance of engine fuels and characterization of biodiesel exhaust have been reviewed in previous studies [40,41].

## 2. Biodiesel

The utilization of biofuels or vegetable oil in internal combustion engines was reported during 1920–1930 and Second World War from all around the world. Germany, Argentina, Japan, Belgium, Italy, France, the United Kingdom, Portugal, and China have tested and used different types of biofuels. However, petroleum fuel production costs were cheaper than alternative fuels causing to slow down production of biofuel infrastructures. Recent concerns of environmental degradation and fossil fuel depletion have again jumpstarted the production of biodiesel, because it seems to be the most feasible solution for this situation [29].

The investigation of vegetable oils as fuel started in 1978 and 1981 in the United States and South Africa, respectively. In 1982, methyl ester was produced in Germany and Austria from rapeseed oil, and a small pilot plant was built in Austria at 1985. Commercial production of methyl ester first began in Europe in 1990. More than 2.7 million tones biodiesel was produced in Europe in 2003, but their target is around 20% total diesel market in 2020. In addition, the USA future plan for biodiesel production is around 3.3 million tones in 2016 [42].

Biodiesel has significant influences in reducing engine emissions such as unburned hydrocarbons (68%), particulates (40%), carbon monoxide (44%), sulfur oxide (100%), and polycyclic aromatic hydrocarbons (PAHs) (80–90%) [43,44]. Meanwhile, it is safer to

**Table 1**  
Different feedstocks for production of biodiesel.

Conventional feedstock		Non-conventional feedstock
Mahua	Soybean	Lard
Nile tilapia	Rapeseed	Tallow
Palm	Canola	Poultry fat
Poultry	Babassu	Fish oil
Tobacco seed	Brassica carinata	Bacteria
Rubber plant	Brassica napus	Algae
Rice bran	Copra	Fungi
Sesame	Groundnut	Micro-algae
Sunflower	Cynara cardunculus	Tarpenes
Barley	Cottonseed	Latexes
Coconut	Pumpkin	Pongamina pinnata
Corn	Jojoba oil	Palanga
Used cooking oil	Camelina	<i>Jatropha curcas</i>
Linseed	Peanut	Sea mango
Mustard	Olive	Okra

**Table 2**

The structure of a typical triglyceride molecule.

Triglycerides	Diglycerides	Monoglycerides
$\begin{array}{c} \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(\text{O})\text{O}-\text{CH}_2 \\   \\ \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(\text{O})\text{O}-\text{CH} \\   \\ \text{CH}_3(\text{CH}_2)_{14}\text{C}(\text{O})\text{O}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(\text{O})\text{O}-\text{CH}_2 \\   \\ \text{HO}-\text{CH} \\   \\ \text{CH}_3(\text{CH}_2)_{14}\text{C}(\text{O})\text{O}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{HO}-\text{CH}_2 \\   \\ \text{HO}-\text{CH} \\   \\ \text{CH}_3(\text{CH}_2)_{14}\text{C}(\text{O})\text{O}-\text{CH}_2 \end{array}$

**Table 3**

The chemical structure of fatty acids.

Fatty acid (trivial name/rational name)	Structure	Common acronym	Methyl ester (trivial name/rational name)
Palmitic acid/Hexadecanoic acid	$\text{R}-(\text{CH}_2)_{14}-\text{CH}_3$	C16:0	Methyl palmitate/Methyl hexadecanoate
Stearic acid/Octadecanoic acid	$\text{R}-(\text{CH}_2)_{16}-\text{CH}_3$	C18:0	Methyl stearate/Methyl octadecanoate
Oleic acid/9(Z)-octadecenoic acid	$\text{R}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$	C18:1	Methyl oleate/Methyl 9(Z)-octadecenoate
Linoleic acid/9(Z),12(Z)-octadecadienoic acid	$\text{R}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}_3$	C18:2	Methyl linoleate/Methyl 9(Z),12(Z)-octadecadienoate
Linolenic acid/9(Z),12(Z),15(Z)octadecatrienoic acid	$\text{R}-(\text{CH}_2)_7-(\text{CH}=\text{CH}-\text{CH}_2)_3-\text{CH}_3$	C18:3	Methyl linolenate/Methyl 9(Z),12(Z),15(Z)-octadecatrienoate

store and handle, and it can be easily produced in domestic quantities.

### 2.1. Chemical composition

Natural oils and fats are the esters of glycerol and fatty acids. They are called glycerides or triglycerides. There are two kinds of fatty acids: saturated fatty acids are polarized and contain a single carbon bond, while unsaturated fatty acids include one or more carbon-to-carbon doubled bonds and are polarized. Examples of common fatty acids are stearic, oleic, linolenic and palmitic. Table 2 shows the chemical structure of triglycerides that includes triglycerides (98%), monoglycerides and diglyce-

rides. Table 3 indicates the chemical structure of fatty acids in different oils [45].

### 2.2. The properties of vegetable oils as fuels

Vegetable oils are extracted from plants and their combustion yields completely recycle carbon dioxide ( $\text{CO}_2$ ). The listing of vegetable oils along with their properties in Table 4 indicates the viscosity of vegetable oils is around 11–17 times more than diesel fuel [46]. The volumetric heating values are around 39–40 MJ/kg but for diesel fuels, it is 45 MJ/kg. The flash point for vegetable oils is very high, more than 200 °C.

**Table 4**

The properties of different vegetable oils.

Type of Oil	Species	Fatty acid composition (wt%)	Viscosity (at 40 °C)	Density ( $\text{g}/\text{cm}^3$ )	Flash point (°C)	Heating value (MJ/kg)	Acid value (mg KOH/g)	Cetane number (C)	Cloud point (°C)	Pour point (°C)
Edible oil	Soybean	C16:0, C18:1, C18:2	32.9	0.91	254	39.6	0.2	37.9	-3.9	-12.2
	Rapeseed	C16:0, C18:0, C18:1, C18:2	35.1	0.91	246	39.7	2.92	37.6	-3.9	-31.7
	Sunflower	C16:0, C18:0, C18:1, C18:2	32.6	0.92	274	39.6	-	41.3	18.3	-6.7
	Palm	C16:0, C18:0, C18:1, C18:2	39.6	0.92	267	-	0.1	42.0	31.0	-
	Peanut	C16:0, C18:0, C18:1, C18:2, C20:0, C22:0	22.72	0.90	271	39.8	3	41.8	12.8	-6.7
	Corn	C16:0, C18:0, C18:1, C18:2, C18:3	34.9	0.91	277	39.5	-	37.6	-1.1	-40.0
	Camelina	C16:0, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C20:3	-	0.91	-	42.2	0.76	-	-	-
	Canola	C16:0, C18:0, C18:1, C18:2, C18:3	38.2	-	-	-	0.4	-	-	-
	Cotton	C16:0, C18:0, C18:1, C18:2	18.2	0.91	234	39.5	-	41.8	1.7	-15.0
	Pumpkin	C16:0, C18:0, C18:1, C18:2	35.6	0.92	>230	39	0.55	-	-	-
Non-edible oil	<i>Jatropha curcas</i>	C16:0, C16:1, C18:0, C18:1, C18:2	29.4	0.92	225	38.5	28	-	-	-
	<i>Pongamia pinnata</i>	C16:0, C18:0, C18:1, C18:2, C18:3	27.8	0.91	205	34	5.06	-	-	-
	Sea mango	C16:0, C18:0, C18:1, C18:2	29.6	0.92	-	40.86	0.24	-	-	-
	Palanga	C16:0, C18:0, C18:1, C18:2	72.0	0.90	221	39.25	44	-	-	-
	Tallow	C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2	-	0.92	-	40.05	-	-	-	-
	Nile tilapia	C16:0, C18:1, C20:5, C22:6, other acids	32.1	0.91	-	-	2.81	-	-	-
	Poultry	C16:0, C16:1, C18:0, C18:1, C18:2, C18:3	-	0.90	-	39.4	-	-	-	-
Others	WCO	Depends on fresh cooking oil	44.7	0.90	-	-	2.5	-	-	-
-	Diesel	-	3.06	0.855	76	43.8	-	50	-	-16

**Table 5**  
The physical and chemical properties of vegetable oil methyl ester.

Feedstock	V <sup>a</sup>	FP <sup>b</sup>	D <sup>c</sup>	HHV <sup>d</sup>	IV <sup>e</sup>	CN <sup>f</sup>	AV <sup>g</sup>	SN <sup>h</sup>
Soybean	4.08	441	0.885	41.28	138.7	52	0.15	201
Rapeseed	4.3–5.83	453	0.88–0.888	41.55	–	49–50	0.25–0.45	–
Sunflower	4.9	439	0.88	41.33	142.7	49	0.24	200
Palm	4.42	434	0.86–0.9	41.24	60.07	62	0.08	207
Peanut	4.42	443	0.883	41.32	67.45	54	–	200
Corn	3.39	427	0.88–0.89	41.14	120.3	58–59	–	202
Camelina	6.12–7	–	0.882–0.888	–	152–157	–	0.08–0.52	–
Canola	3.53	–	0.88–0.9	–	103.8	56	–	182
Cotton	4.07	455	0.875	41.18	104.7	54	0.16	204
Pumpkin	4.41	–	0.8837	–	115	–	0.48	202
<i>Jatropha curcas</i>	4.78	–	0.8636	–	108.4	61–63	0.496	202
<i>Pongamia pinnata</i>	4.8	–	0.883	–	–	60–61	0.62	–
Palanga	3.99	–	0.869	–	–	–	–	–
Tallow	–	–	0.856	–	126	59	0.65	244.5
Nile tilapia	–	–	–	–	88.1	51	1.4	–
Poultry	–	–	0.867	–	130	61	0.25	251.23
WCO	4–5.18	148	0.878–0.887	39.26–39.48	–	48	0.15	–

<sup>a</sup> V = Viscosity (at 40 °C).

<sup>b</sup> FP = Flash Point (°C).

<sup>c</sup> D = Density (g/cm<sup>3</sup>).

<sup>d</sup> HHV = High Heat Value (MJ/Kg).

<sup>e</sup> IV = Iodine Value.

<sup>f</sup> CN = Cetane Number.

<sup>g</sup> AV = Acid Value (mgKOH/g).

<sup>h</sup> SN = Saponification Number.

It has been found that the utilization of vegetable oils in conventional diesel engines led to problems that are related to the type and grade of fuel as well as climate conditions. Some common problems are carbon deposits, plugging of the fuel lines, gelling of lubricating oils, fouled piston heads and ring sticking [47–49]. Singh and Singh [50] and Ayhan [51] identified the properties of some vegetable oil methyl esters. Table 5 tabulates the physical and chemical properties of vegetable oil methyl ester [51]. Vegetable oils have higher pour and cloud point compared to diesel fuels. Thus, it is not advisable to use them in winter. [52,53]. Furthermore, the cetane number of vegetable oils is very high hence reducing the ignition delay [54]. In addition, they have a high iodine value that increases its oxidation rate. Therefore, long time storage is not recommended for these types of fuels [55].

### 2.3. Transesterification reaction

Transesterification of vegetable oils with alcohol is the best method for biodiesel production. There are two transesterification methods, which are: (a) with catalyst and (b) without catalyst. The utilization of different types of catalysts improves the rate and yield of biodiesel. The transesterification reaction is reversible and excess alcohol shifts the equilibrium to the product side [56,57]. Fig. 1 shows the general equation of transesterification reaction.

Many different alcohols can be used in this reaction, including, methanol, ethanol, propanol, and butanol. The methanol application is more feasible because of its low-cost and physical as well as chemical advantages, such as being polar and having the shortest alcohol chain [56]. According to Fig. 2, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are long

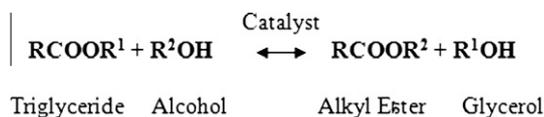


Fig. 1. General transesterification reaction equation.

chains of hydrocarbons and carbon atoms called fatty acid chains. The reaction is based on one mole of triglyceride reacting with three moles of methanol to produce three moles methyl ester (bio-diesel) and one mole glycerol.

Generally the transesterification reaction involves some critical parameters which significantly influence the final conversion and yield. The most important variables are: reaction temperature, free fatty acid content in the oil, water content in the oil, type of catalyst, amount of catalyst, reaction time, molar ratio of alcohol to oil, type or chemical stream of alcohol, use of co-solvent and mixing intensity.

### 2.4. Biodiesel production from waste cooking oil

People around the world use edible oils for cooking, after which the oil is discarded. The amount of heat and water increases the hydrolysis of triglycerides and the percent of free fatty acid (FFA) in the oil [58]. The water and FFA content have a negative influence on the transesterification reaction [59,60]. The WCO price is two to three times cheaper than vegetable oils, and it also reduces the cost of waste product removal and treatment [61]. Meanwhile, it can significantly decrease the amount of farmland, which is necessary for biodiesel producing corps. The WCO has been categorized by the FFA content to two groups: (a) yellow grease (<15%) and (b) brown grease (>15%) [46]. The prices of these types of WCO

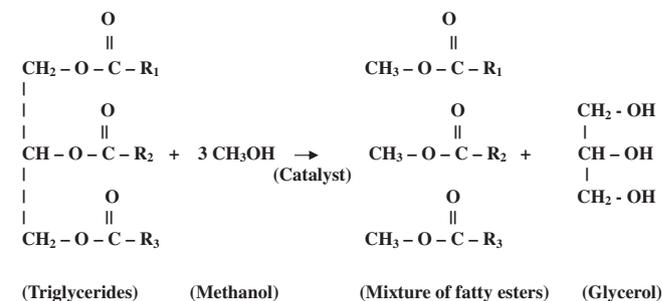


Fig. 2. Methanolysis of triglyceride.

are between (\$ 0.04 to \$ 0.09) and (\$ 0.004 to \$ 0.014) for yellow grease and brown grease, respectively [62].

Some negative effects of WCO utilization for biodiesel production include separation of fatty acid esters and glycerol and formation of dimeric and polymeric acids and glycerides. Consequently the viscosity of cooking oil increases, while the saponification process decreases the molecular mass and iodine values [58,63,64]. Meanwhile, soap formation partially consumes the catalyst and reduces the final yield. There is no systematic method for collecting waste cooking oils from households yet. The amount of WCO dumped through drains leads to water pollution. More than 80% of WCO is produced in households and controlling its disposal involves huge investments such as waste oil disposal and high water treatment cost [65,66]. There are various methods for biodiesel production from waste cooking oil which can be divided into three main groups: (a) homogeneous, (b) heterogenous and (c) non-catalytic transesterification.

### 3. Homogeneous catalytic transesterification

#### 3.1. Alkali catalyzed

Many researchers have used alkali catalysts (NaOH, KOH, CH<sub>3</sub>ONa) for production of biodiesel as these catalysts are cheap and readily available [67,68]. However, the process has some limitations such as high energy consumption which in turn causes a dramatic increase in capital equipment costs and safety issues. In addition, this process is highly sensitive to water and free fatty acid (FFA) content in the feedstock. High water content can change the reaction to saponification, which causes reductions of ester yield, difficult separation of glycerol from methyl ester, increment in viscosity, and the formation of emulsion [70,71] all of which create many problems in downstream purification and methyl ester recovery. There are various reports about the effect of oil FFA content in reaction with alkali catalysts as shown in Table 6.

Arquiza et al. [77] investigated biodiesel production from used coconut oil with methanol and NaOH as catalyst. They also evaluated the effects of some operating parameters such as the reaction temperature (30–65 °C), the molar ratio of methanol to oil (3:1, 6:1, and 9:1), and the catalyst weight (0.1%, 0.5% and 1%). The results was 94% yield at optimum condition of 60–65 °C reaction temperature, 0.5% catalyst weight and 6:1 molar ratio of methanol to oil. There are various reports of biodiesel production from used cooking oil in the presence of NaOH as catalyst [78–80]. In addition, the transesterification of waste cooking oil with ethanol and NaOH as catalyst was evaluated [81]. The result was 94.5% yield. The optimum condition of the reaction temperature was 60 °C, catalyst weight was 0.08%, and the reaction time was 20 min. Georgianni et al. [82] investigated waste soybean oil and a mixture of cottonseed oil and soybean oil with NaOH as the catalyst and methanol. They reported that the final products for both oils have the same properties, and the result was comparable with mineral diesel.

Meng et al. [83] produced biodiesel from waste cooking oil with methanol and NaOH as catalyst. They investigated the effects of different operating parameters on conversion and quality of product. These parameters include molar ratio of methanol to oil (3:1, 5:1, 6:1, 7:1, and 8:1), the amount of catalyst (0.5, 0.7, 1, 1.1, 1.2 wt%), the reaction time (30, 50, 60, 70, 90, and 110 min), and the reaction temperature (30, 40, 45, 50, 60, and 70 °C). They reached 86% conversion at the optimum condition of 6:1 molar ratio, 0.7% catalyst weights, 90 min reaction time and 50 °C reaction temperatures. Tomasevic and Siler-Morinkovic [63] reported the results of biodiesel production from waste sunflower oil with different molar ratios of methanol to oil (4.5:1, 6:1, and 9:1) and in the presence of potassium hydroxide (KOH) and sodium hydroxide (NaOH) as catalysts. The highest conversion was obtained at the molar ratio of methanol to oil 6:1, with 1% KOH/g acid value, 25 °C temperatures, and a reaction time of 30 min. Besides, they reported that good quality biodiesel was obtained with waste cooking oil by 6:1 methanol to oil molar ratio, 1% KOH, 90 min reaction time, and 25 °C reaction temperatures. However, they concluded that increasing the amount of catalyst and alcohol did not have any effect on conversion. Refaat et al. [84] investigated biodiesel production from waste cooking oil and different molar ratios of methanol to oil (3:1, 6:1, and 9:1), KOH and NaOH as catalyst with different concentrations (0.5% and 1% w/w) and reaction temperatures (25 and 65 °C). The optimum condition that produced the highest yield around 98.16% was molar ratio of 6:1, 1% w/w KOH catalyst and 65 °C reaction temperature. Meanwhile, they reported that KOH showed 1% higher conversion in comparison with NaOH. Allawzi and Kandah [85] reported the transesterification of waste soybean oil with different ethanol concentration (30–40 vol%), KOH (9–14 g/l) and reaction time (30–40 min). The results were 78.5 vol% yields at the optimum condition of 12 g/l catalyst concentration and 30 vol% ethanol. Some researchers compared NaOH and KOH catalysts activity and concluded that KOH reacted faster in comparison with NaOH catalyst [86]. However, majority of researchers have used NaOH catalyst for transesterification reaction and believed that is the best catalyst for waste cooking oil [87]. Dorado et al. [88] focused on biodiesel production from different types of vegetable oils such as palm oil and Brazilian hydrogenated fat with 5.12% FFA, Spanish olive oil with 2.24% FFA and a mixture of German vegetable oil with 1.28% FFA and KOH as catalyst during a two-step transesterification reaction. Their reported yield was 89–95%. Besides, other researchers have reported that the two-step transesterification process is better than one-step reaction since it needs a lower reaction temperature, less alcohol and amount of catalyst but reached a higher conversion [89].

The utilization of other kinds of base catalyst such as potassium methoxide (KOCH<sub>3</sub>) and sodium methoxide (NaOCH<sub>3</sub>) has been reported in various studies. Alcantara et al. [65] obtained 95% conversion with NaOCH<sub>3</sub> catalyst, with the added advantage of a reusable catalyst. Besides, Jordanov et al. [90] investigated biodiesel production from waste cooking oil with sodium methoxide as catalyst, and it has been reported to have 85.5% yields. Some researchers utilized different types of catalysts such as NaOH, KOH, NaOCH<sub>3</sub>, and KOCH<sub>3</sub> with a two-step transesterification reaction of waste cooking oil and methanol. They investigated the effect of different variables such as reaction temperature (25–65 °C), catalyst weight (0.1–1.5%), molar ratio of methanol to oil (3:1, 9:1). The results indicated that the higher yield and quality of biodiesel obtained at the optimum condition of 1% KOH, 65 °C temperature, and molar ratio of 6:1. Meanwhile, they concluded that the two-step reactions can improve the conversion up to 30% compared with one-step reaction [87].

**Table 6**  
Possible FFA content for alkali catalyzed transesterification.

Type of catalyst	FFA content	References
Alkali catalyst	Less than 0.5 wt%	[69]
	Less than 1.0 wt%	[72]
	Greater than 1 wt%	[73]
	Less than 2 wt%	[74]
	Less than 3 wt%	[75]
	Up to 5 wt%	[76]

Felizardo et al. [78] produced biodiesel from waste cooking oil with sodium hydroxide and dry magnesium sulphate. The reaction condition includes a 65 °C reaction temperature for 1 h, 3.6 and 5.4 molar ratio of methanol to oil and 0.2–1% catalyst weight. The researchers investigated variables such as oil acid value, molar ratio and catalyst weight. The results showed that the oil with lower acid value produced higher quality methyl ester than other oils with higher acid value (14%). Meanwhile, the best molar ratio of methanol to oil was 4.2% and the optimum amount of catalyst to WCO ratio was between 0.4 and 0.8 wt%. However, the authors concluded that the utilization of higher molar ratio can reduced the amount of catalyst to WCO ratio.

Wang et al. [91] reported 97.02% FAME conversion from WCO, and the optimal reaction was 1 wt% NaOH as catalyst, 6:1 molar ratio of methanol to oil for 1 h at the temperature 65 °C. Yusup and Khan [92] used waste cooking palm oil with KOH (0.5, 1, 2 wt%) as catalyst, molar ratio of methanol to oil (6:1, 8:1, 10:1), and reaction temperature (45, 55, 65 °C). The highest conversion was 96% with optimal conditions identified as 3 h reaction time, 55 °C reaction temperature, 8:1 molar ratio and 2 wt% catalysts. Meanwhile, they considered the effects of different variables on FAME conversion.

Leung and Guo [93] compared two different feedstock (canola oil and waste cooking oil) and alkali catalyst (NaOH) for biodiesel production. The optimal reaction was carried out at methanol to oil molar ratio of 7:1, 1% catalyst, 70 °C reaction temperature and 20 min reaction time to reach 90.4% conversion. However, they reported that temperature reduction from 70 °C to 40–45 °C increased the conversion up to 93.5%. Nevertheless, this reaction needs more time, which is around 60 min. Meanwhile, they obtained 88.8% FAME yield from waste cooking oil. The optimum condition was 7:1 alcohol to oil molar ratio, 1.1% NaOH, 60 °C reaction temperature, and 1 h reaction time. Dias et al. [94] evaluated the optimum amount of various base catalysts such as KOH, NaOH, and NaOCH<sub>3</sub> for waste cooking oil, soybean oil, and sunflower oil. Their result showed that 0.4–1.2% of these catalysts were sufficient for waste cooking oil and 0.2–1 was needed for neat oils. Fig. 3 indicates the homogeneous base-catalyzed transesterification mechanism which includes four steps. Firstly, the alkoxide ion formed and then directly acted as a strong nucleophile. Alkali catalysis has a direct route compare to acid. The main difference between acid and base catalytic activity in transesterification reaction is formation of electrophilic species versus stronger nucleophile formation, respectively [95].

### 3.1.1. The liquid amine

The utilization of liquid-amine based on the catalyst in transesterification process of WCO, soybean oil and tallow were reported. There are four amines based on the catalysts diethyl amine, diethyl ethanol amine (DMAE), tetra-methyl-diamino-ethane (TEMED) and tetra-methyl-ammonium hydroxide (TMAH). The best conversion of 98% was reported for TMAH when temperature was equal to 65 °C and reaction time was 90 min but this method required more liquid amine [65].

### 3.1.2. Pretreatment of WCO before alkali catalyzed transesterification

Alkali catalysts are very sensitive to water and FFA content in feedstock [96,97]. Therefore, various types of pretreatment methods are used for WCO purification, such as steam injection [98], column chromatography [99], neutralization; film vacuum evaporation [100], and vacuum filtration [101,102,47]. Meanwhile, the methods of steam distillation [103] and extraction by alcohol [104] require high temperature and large amounts of solvent, respectively making the biodiesel production process less efficient and more complicated. Dennis et al. [105] decreased the FFA content of WCO by the usual procedure of esterification of FFA with

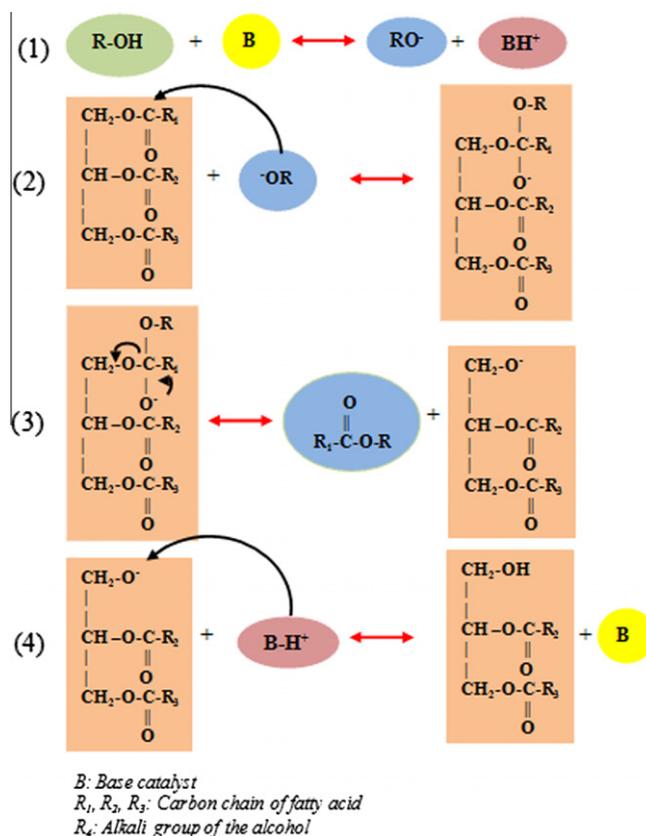


Fig. 3. Reaction mechanism of homogeneous base catalyzed transesterification.

sulphuric acid acting as catalyst. Both the homogenous and heterogeneous acid catalysts can be used in this method [106]. But, the solid acid catalysts are more advantageous compared to homogeneous catalysts [107]. In addition, some scientists have used acidic ion-exchange resins to reduce the FFA of WCO. However, the reduction of catalyst activity is the main problem in this method [108,109]. Li et al. [110] reported the esterification reaction with iodine catalyst at optimal condition of 80 °C reaction temperatures, 1.75:1 molar ratio of methanol to oil, 3 h reaction time, and 1.3 wt% catalyst. The results indicated that this type of catalyst can be recycled after reaction and can reduce the FFA content to less than 2%. The new method for pretreatment of waste oil is utilization of glycerol for acidic raw material at high temperature (200 °C) with zinc chloride as a catalyst. In this method, glycerol reacts with FFA to form monoglycerides and diglycerides. Therefore, the FFA content is reduced and biodiesel can be produced. This method needs no alcohol during the reaction, and water immediately vaporized from the mixture [111]. However, these pretreatment methods increase biodiesel production costs.

### 3.2. Acid catalyzed transesterification reaction

Acid catalysts are insensitive to free fatty acids, and they have better results for vegetable oil with FFA greater than 1% [112]. However, acids can produce a large number of salt interaction, which is a cause of corrosion. Some researchers have used inorganic acids such as sulfuric acid, phosphoric acid, sulfonated acid and hydrochloric acid in the transesterification process. The acid is mixed directly with vegetable oil. Esterification and transesterification steps occur in single stage because acids have esterification reagents and play a solvent role in this single process [113]. These

types of catalysts have a very slow reaction thus the reaction time is increased [114].

Nye et al. [114] used different types of alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-ethoxy ethanol,  $\text{H}_2\text{SO}_4$  and KOH as catalysts with waste cooking oil. They reported that acid catalyzed esters had higher yield compared to alkali catalyzed reaction. However, this reaction increased the reaction time. Recently, a large number of researchers utilized Lewis or Bronsted acids as a catalyst for biodiesel production in both kinds of homogenous and heterogeneous processes [115].

Abreu et al. [116] used Sn, Pb, and Zn complexes in the form of M (3-hydroxy-2-methyl-4-pyrone)  $2(\text{H}_2\text{O})_2$  in transesterification reaction of vegetable oils to make a four-member ring transesterification state. In addition, Di Serio et al. [106] investigated using carboxylic salts of Cd, Mn, Pb and Zn as catalysts to produce biodiesel with high FFA content. Soriano et al. [52] reported the use of homogenous Lewis acid catalyzed like THF and  $\text{AlCl}_3$  or  $\text{ZnCl}_2$  with different reaction temperatures and reaction time in the production of FAME. The results showed 98% conversion at optimum conditions with 110 °C reaction temperatures, 12–24 molar ratio of alcohol to oil, 18 h reaction time and 5%  $\text{AlCl}_3$  as catalyst. However, the maximum conversion reached 48% with optimum condition of molar ratio of 60 and reaction time of 24 h, and  $\text{ZnCl}_2$  as catalyst. Therefore, the authors concluded that  $\text{AlCl}_3$  is a stronger and more effective Lewis acid than  $\text{ZnCl}_2$ .

Freedman et al. [117] investigated the transesterification of soybean oil with methanol, 1 wt% sulfuric acid at 65 °C, molar ratio of 30:1 methanol/soybean oil and it took approximately 69 h to reach more than 90% conversion of biodiesel. Canakci and Gerpen [35] evaluated the effect of changing the molar ratio, reaction temperature, weight of catalyst and reaction time on biodiesel conversion in acid-catalyzed transesterification process, and the results showed that increasing the amount of variables caused higher conversion. One advantage of an acid catalyzed method is it is independent of free fatty acids and this method does not require pretreatment processing. These advantages make acid catalyzed the preferred method to process waste cooking oil that normally has free fatty acid of more than 2 wt% [118,119,97].

Al-Widyan and Al-Shoukh [120] demonstrated that acid catalyst is promising for transesterification of waste vegetable oils. They used waste palm oil as feedstock and sulfuric and hydrochloric acids as catalysts with different concentrations and added 100% more alcohol. The results revealed that higher concentration of acid can produce methyl ester with lower specific gravity in shorter time. The optimal condition was 2.25 M sulfuric acid, temperature 90 °C and 3 h of time. Besides, they reported sulfuric acid worked better than hydrochloric acid to produce lower specific gravity biodiesel. Meanwhile, Miao et al. [121] investigated biodiesel production through highly effective acidic reaction catalyzed by trifluoroacetic acid. They considered different ranges for molar ratio of methanol to oil (5:1–60:1), catalyst concentration (0.0, 3.0 M), temperature (100–120 °C) and reaction times (1, 7 h). They reported 98.4% conversion at optimum condition of 2.0 M catalyst concentration, 20:1 molar ratio of methanol to oil, 120 °C reaction temperatures for 5 h. Wang et al. [91] used WCO, four levels of acid catalyst (sulfuric acid 3, 4, 5, 6 w/w%), molar ratio of methanol to oil (10:1, 12:1, 16:1, 20:1, 24:1) and different reaction times (1, 2, 3, 4, 6, 8, 10 h) at 95 °C reaction temperature. The best reaction with 96% conversion was carried out at the optimum condition of 4:1 w/w catalyst, 16:1 molar ratio of methanol to oil for 10 h and 95 °C. Fig. 4 illustrates the mechanism of homogeneous acid-catalyzed transesterification of triglycerides in three steps. First, protonation of carbonyl group followed by nucleophilic attack of alcohol that produces tetrahedral intermediate. Finally, the proton migration and the tetrahedral intermediate breakdown will omit glycerol to create a new ester and reforms the catalyst [95].

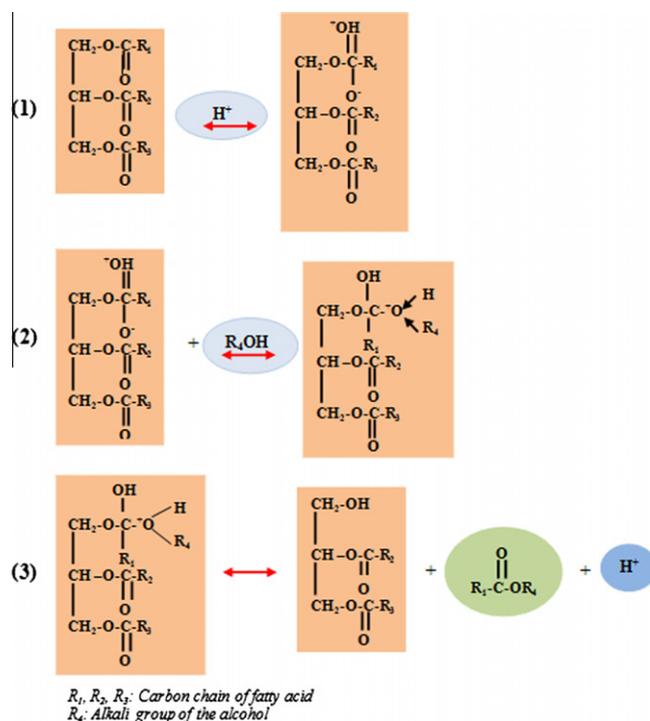


Fig. 4. Reaction mechanism of homogeneous acid catalyzed transesterification.

### 3.3. Acid and alkali catalyzed two-step transesterification

The most pressing problems of acid and alkali catalyzed transesterification are slow reaction and separation of methyl ester and glycerol (saponification), respectively. Many researchers try to use two-step acid and alkali catalyzed transesterification to eliminate these problems. In the first step, the esterification of FFA with acid catalysts to decrease FFA levels to lower than 1% and in the second step, the transesterification of WCO with alkali catalysts. Fan et al. [122] investigated the biodiesel production from recycled canola oil with a two-step acid and alkali catalyzed reaction. In the first step, they considered some variables for acid catalyzed esterification such as molar ratio of alcohol to oil (4.5:1–18:1), catalyst concentration, reaction temperature, and reaction time. The optimum condition was 40:1 molar ratio of methanol to oil and 5% sulfuric acid. The FFA level was reduced from 11% to 0.41% around 96.3% reductions at 55 °C temperature for 1.5 h. After esterification, transesterification was carried out at 6:1 molar ratio of methanol to oil with 1% potassium hydroxide. Wang et al. [91] comprised the traditional acid catalyzed transesterification reaction with sulfuric acid and the two-step transesterification which used ferric sulfate (2–0%) as catalyst followed by alkali (1.0% potassium hydroxide (NaOH)) catalyst. The results indicated that using the single step method, the highest conversion was 90%. Meanwhile, the optimum condition was 20:1 molar ratio of methanol to oil, 10 h reaction time with 95 °C reaction temperature. However, the two-step system was different. The highest conversion was 97.22% at the optimum condition of molar ratio of methanol to oil 10:1, reaction time 4 h with 95 °C reaction temperatures. With these results, the researchers argued that two-step systems have more advantages including no acidic waste treatment, high efficiency, low equipment cost and easy recovery of catalyst compared to the limitations of single step reaction.

Various researches have proven that two-step transesterification is better than the single-step process. Issariyakul et al. [123] produced biodiesel from WCO with 90% conversion in a two-step system compared to 50% conversion achieved by

single-step alkali catalyzed transesterification. In addition, Encinar et al. [124] concluded that two-step transesterification of WCO has higher conversion of up to 30% in comparison with single-step process. Cayli and Küsefoglu [125] reported the production of methyl ester is 98% in two-step transesterification compared to 86% yield in the single-step reaction. Wan Omar et al. [126] used Response Surface Methodology (RSM) for optimization of the two-stage transesterification. The results indicated the following optimum conditions: reaction temperature of 60 °C, 3 h reaction time, and 7:1 molar ratio of methanol to oil, which produced 81.3% yield.

Jain et al. [127] produced biodiesel from a high FFA value of WCO under the optimum conditions of 65 °C reaction temperature for acid and 50 °C for base transesterification reaction, 3:7 (v/v) molar ratio of methanol to oil, 400 rpm mixing intensity, and 1%w/w H<sub>2</sub>SO<sub>4</sub> and 1%w/w NaOH catalyst. The conversion was around 90.6% and 21.5% for transesterification and esterification respectively. A majority of researchers suggested two-step transesterification methods because it can produce higher yield and conversion into biodiesel production. However, the most challenging part in this reaction is the catalyst removal in both stages. This problem can be solved by neutralizing the acid catalyst but in the second step, more alkali catalyst should be used to eliminate the problems. The utilization of excess catalyst increases the biodiesel production costs. Meanwhile, the residue catalysts can be harmful for engines.

Guzatto et al. [128] used Transesterification Double Step Process (TDSP) in biodiesel production from different feedstocks. The result was exceptional because they need lower reaction time in the first step, lower the amount of catalyst used as well as mixing the methanol and acid solution directly without a cooling process between the two steps. The researchers used H NMR and a variety of biodiesel analysis methods for analyzing the quality of products. The conversion for different raw materials were high (waste cooking oil and soybean oil = 97% and linseed oil = 98%). Meanwhile, they could produce high amount of yields 87 ± 5%, 92 ± 3%, and 93 ± 3% for waste cooking oil, soybean oil, and linseed oil respectively. Thanh et al. [129] investigated two-step biodiesel production from waste cooking oil with KOH as catalyst, and also they used a continuous ultrasonic reactor to produce high quality FAME. The results indicated that 81% and 91% yields for first and second steps, respectively. Cheroenchaitrakool and Thienmethangkoon [130] optimized the optimum condition of two-step catalyzed process with MINTAB REIEASE 14 and RSM. The optimal variables were 6.1:1 molar ratio of methanol to oil, 51 °C reaction temperature, 0.68 wt% sulfuric acid as a catalyst, and 60 min reaction time in first step and 9.1:1 molar ratio of methanol to oil, 55 °C reaction temperature, 1 wt% KOH as catalyst, and 60 min reaction time for the second step. The yield was 90.56 ± 0.28%. Two-step acid and alkali catalyzed transesterification is less time consuming and less costly in contrast with the single step acid catalyst process which takes longer reaction time for its completion. Obviously, shorter reaction time required lower energy consumption. Consequently, the product cost decreases significantly [127,131].

### 3.4. The reactive extraction process

There are a lot of reports about new methods in biodiesel production using oilseeds rather than purification oils production with the transesterification reaction [132–134]. This method eliminates the expensive oil extraction process. Additionally, for recovering oils from seeds, manufactures are using hexane extraction technology which leads to smog formation and global warming. Furthermore, the utilization of high cost refined oil is the main obstacle in biodiesel production. This method is called in situ-transesterification and it works with any kind of oilseeds such as soybean, Jatropha, unwanted bran and protein meal [135,132]. Qian et al.

[136] used cottonseed oil for biodiesel production without any pre-treatment and extraction processes. The results illustrate 99% of oil was extracted at more than 98% of conversion. The optimum condition was 40 °C reaction temperature, 3 h reaction time and 0.1 mol/l of sodium hydroxide in methanol. Meanwhile, the size range of cottonseed particles was 0.3–0.335 mm and less than 2% moisture content.

Lei et al. [132] investigated low quality rice bran with in situ-transesterification process. Rice bran contains 15–23% of triglycerides and is a cheap feed stock for methyl ester production. They evaluated the effects of alkaline and acid catalysts on yield. The optimum yield was 95% with 75 ml methanol, 0.75 g sulfuric acid, 150 ml petroleum as co-solvent and 0.71 g of sodium hydroxide. Biodiesel production from rice bran with in situ-transesterification can reduce total production costs and make it economically competitive against regular diesel fuel.

## 4. Heterogeneous catalyzed transesterification

### 4.1. Solid catalyst

The homogenous reaction has some disadvantages such as low tolerance towards FFA, and water content and the purification process is complicated. Meanwhile, researchers have focused on the heterogeneous reaction with solid catalysts to eliminate these factors. Ideally, solid catalyst should have characteristics such as an interconnected system of large pores [137,138], a medium to high concentration of strong acid sites, hydrophobic surface [139], and the ability to regulate the hydrophobicity of the surface to prevent the deactivation process [95,140]. Various types of heterogeneous catalysts such as ion exchange resins [141–143], sulfated oxides [144–146], and heterogeneous base catalysts like transition metal oxide and derivatives [147,148], boron group base heterogeneous catalyst [149–155], alkaline earth metal oxides and derivatives [156–158], mixed metal oxides and derivatives [150,151,156], alkali metal oxides and derivatives [159,160], waste material based heterogeneous catalyst [161,162], carbon based heterogeneous catalyst [163,164], and enzyme based heterogeneous catalyst [165,166], have been used in various biodiesel production processes.

### 4.2. Solid acid catalysts

Wang et al. [167,91] investigated biodiesel production with two methods. The first method, involved FAME production from waste cooking oil with solid acid catalyst in a two-step process and the second feature, FAME production in a conventional acid catalyst system. Meanwhile, they compared the results of these two methods. The two-step process had 97.02% conversion with 10:1 molar ratio of methanol to oil, 4 h reaction time, and reaction temperature were 95 and 65 °C for the first and second steps, 2 wt% ferric sulfate and 1 wt% KOH as catalysts in the first and second steps. However, the conventional method had around 90% conversion with 20:1 molar ratio of methanol to oil and 10 h reaction time. The two-step system had major advantages such as absence of acidic wastewater; low equipment costs, easy recovery of catalyst, and high efficiency. The conventional method had some limitations such as no reusability of catalyst and high equipment costs.

Cao et al. [168] produced biodiesel from high acid value and water content of WCO and heteropoly acid as catalyst. This process had around 87% conversion for transesterification reaction and 97% conversion for esterification reaction. The catalyst (PW12) has some superb properties such as higher activity, easy separation from product, and is reusable for many times. In addition, FFA and water content has no effect on the catalyst activity. The

transesterification was carried out at 65 °C temperature, 70:1 molar ratio of methanol to oil, and 14 h reaction time.

Jacobson et al. [60] attempted to search for a powerful solid acid catalyst for simultaneous transesterification and esterification reactions where among (MoO<sub>3</sub>/SiO<sub>2</sub>, MoO<sub>3</sub>/ZrO<sub>2</sub>, WO<sub>3</sub>/SiO<sub>2</sub>, WO<sub>3</sub>/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, and ZS/Si) the zinc stearate immobilized on silica gel (ZS/Si) was more active than others, with 98% conversion. The optimum condition was 600 rpm mixing intensity, 18:1 molar ratio of methanol to oil, 3% w/w catalyst, and 200 °C reaction temperature. Kulkarni et al. [169] evaluated the effects of various variables on conversion of methyl ester from low quality waste cooking oil and high FFA with 12-tungstophosphoric acid (TPA) as catalyst. The results indicated that this kind of catalyst is nontoxic, recyclable, inexpensive, and user and environmentally friendly. Komintarachat and Chuepeng [170] investigated biodiesel production from WCO with different types of solid acids to evaluate the most active catalysts. They focused on parameters such as different porous support of catalyst, molar ratio of methanol to oil, catalyst weight, reaction time, reaction temperature, catalyst stability and reusability. The four types of solid acid catalysts, WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (WAL), WO<sub>x</sub>/SiO<sub>2</sub> (WS), WO<sub>x</sub>/ZnO (WZn), and WO<sub>x</sub>/SnO<sub>2</sub> (WSn) were evaluated in this research. According to the Table 7 the researchers concluded that WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (WAL) was the best catalyst and the effectiveness of others was sequenced as follows: SiO<sub>2</sub> > SnO<sub>2</sub> > ZnO. The maximum yield for WAL was 98% at optimum condition of 0.3 weight ratio of methanol to oil, 10 g WAL, 110 °C reaction temperature, and 2 h reaction time.

Ramachandran et al. [171] used heterogeneous acid catalyst (Al (H<sub>2</sub>SO<sub>4</sub>)) and prepared it by sulfonation of anhydrous AlCl<sub>3</sub> in biodiesel production from mixed waste vegetable oils. The physical and chemical properties of catalyst were analyzed using different methods such as Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis X-Ray (EDAX). The highest conversion of 81% wt was obtained at the optimum condition of 0.5 wt% catalyst, 220 °C reaction temperature, 16:1 molar ratio of methanol to oil, and 50 min reaction time. The researchers calculated that the high stability and activity of catalyst are related to the bonded hydrophilic functional groups (–SO<sub>3</sub>H) and the high acid site density.

Feng et al. [172] evaluated the utilization of cation-exchange resins (NKC-9, 001x7 and D61) as catalyst in biodiesel production from waste cooking oil. The results indicated that NKC-9 had better activity in comparison with the other ones and the esterification conversion increased by increasing the temperature, time, amount of catalyst and molar ratio of alcohol to oil. The highest conversion was 90%. Chen and Fang [173] used catalyst prepared by glucose-starch mixture composed of CS<sub>0.073</sub>O<sub>0.541</sub> for biodiesel production from waste cottonseed oil with 55.2% FFA. The highest yield was 90% for 12 h reaction time. In addition, the catalyst had a good reusability, and it can regenerate by H<sub>2</sub>SO<sub>4</sub> treatment. Corro et al. [174] reported the two-step biodiesel production from waste cooking oil. In the first step, they esterified the FFA with SiO<sub>2</sub> pretreated by HF and in the second step; they used NaOH as catalyst for transesterification of WCO by methanol. Meanwhile, GC/MS indicated that the final yield was 96% FAME. The results showed that the catalyst activity during the first step did not change even after 10 esterification runs. Zhu et al. [175] investigated Poly Styrene

Sulfonic Acid (PSSA) and Poly Vinyl Alcohol (PVA) blend membranes for biodiesel production from waste cooking oil. They reported that at temperatures higher than 80 °C, a cross linker structure emerges between PSSA and PVA. The best conversion was recorded around 80%.

Lam and Lee [176] commented that the biodiesel produced by methanol is not completely renewable since methanol is derived from petroleum fuels. They attempted to use a mixture of methanol and ethanol in biodiesel production from waste cooking oil and solid acid catalyst where the utilization of this mixture could eliminate some limitations such as long reaction time. The highest yield was 81.4% in only 1 h. Olutoye and Hameed [177] investigated biodiesel production from waste vegetable oil and solid catalyst (Mg<sub>1-x</sub>Zn<sub>1+x</sub>O<sub>2</sub>). The highest ester content of 80% was obtained at an optimum condition of 188 °C reaction temperature, 2.55 wt% catalyst, 9:1 molar ratio of methanol to oil, and 4.25 h reaction time. Park et al. [143] used WO<sub>3</sub>/ZrO<sub>2</sub> catalyst and waste cooking oil for biodiesel production. The highest conversion was 85% in a packed bed reactor, and the optimal condition was 75 °C reaction temperature and 20 h reaction time. But the conversion reduced to 65% in the next run and remained constant for up to 140 h. They concluded that the oxidation of WO<sub>3</sub> was the main reason for the low performance. Furthermore, other scientists reached similar results for this type of catalyst [139]. Park et al. [178] used three different catalysts (sulfated zirconia, amberlyst 15, and tungsten oxide zirconia) for biodiesel production from WCO. It was determined that tungsten oxide zirconia (WO<sub>3</sub>/ZrO<sub>2</sub>) had the best activity with 96% FFA conversion. The optimum reaction parameters were 150 °C reaction temperature, 9:1 molar ratio of alcohol to oil, 2 h reaction time, and 0.4 g/ml (oil). Some examples of the various heterogeneous acid catalyst applications are listed in Table 8.

The advantages of solid acid catalysts are: (1) insensitive to FFA content, (2) simultaneous esterification and transesterification reaction, (3) easy catalyst removal, (4) product, fatty acid ester, does not need water washing, (5) higher yield, (6) lower amount of catalyst required, (7) environmental-friendly, (8) eliminate or decrease corrosion.

#### 4.3. Solid base catalyst

There are different types of solid base catalysts such as calcium oxide [182], Mg–Zr [183], nano-magnetic KF/CaO–Fe<sub>3</sub>O<sub>4</sub> [184], modified CaO by trimethylchlorosilane (TMCS) [185], and supported solid base catalyst such as EU<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [186], La/β Zeolite [187], KI/Al<sub>2</sub>O<sub>3</sub> [188], Na/NaOH/γ-Al<sub>2</sub>O<sub>3</sub> [189] which researchers have used for transesterification reaction of biodiesel production. These catalysts are inexpensive and have high yield but there has been limited research on FAME from WCO using these types of catalysts.

The supported solid base catalysts are the best catalysts in biodiesel production. Guo et al. [190] investigated the use of solid base catalysts in biodiesel production and demonstrated that more than 95% yield can be achieved at optimum conditions of 3.0 wt% sodium silicate catalysts, 7.5:1 molar ratio of methanol to oil, 60 °C reaction temperature, 60 min reaction time, and 250 rpm mixing intensity. Fig. 5 exhibits the flow diagram for biodiesel production by heterogeneous catalysts.

Kondamudi et al. [191] used Quintinite-3T (Q-3T) catalyst made from sol–gel process. They evaluated the activity of this catalyst with various feedstock's such as canola, waste vegetable oils, coffee, and soybean in different FFA content (0–30%). The results indicated that FFA and triglycerides converts into biodiesel simultaneously.

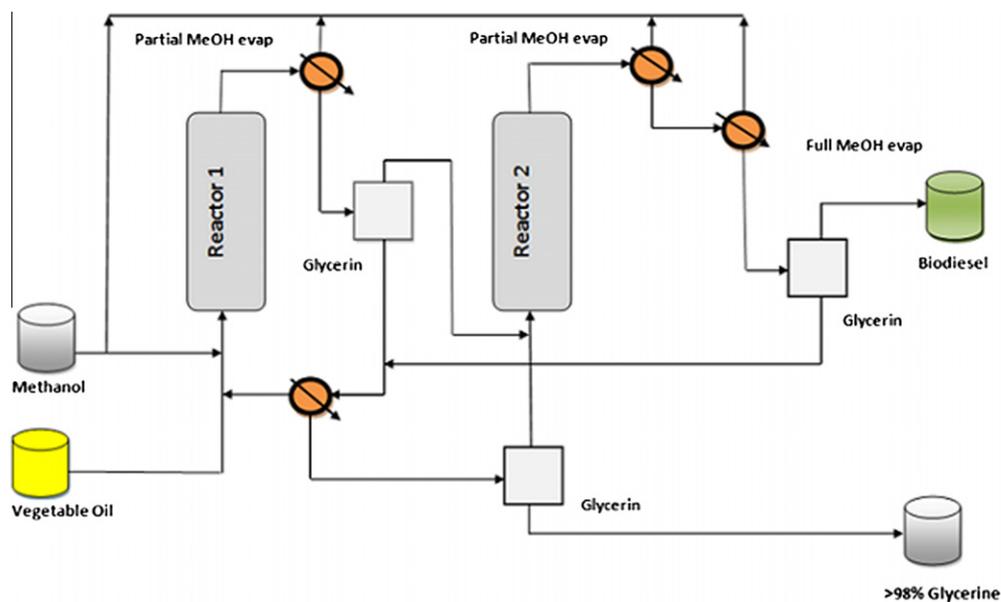
Chung et al. [192] used ZSM-5(MFI), Modern site (MOR), Beta (BEA) zeolite, Fauja Site (FAU), and silicate catalysts for reduction of FFA in waste cooking oil in esterification reaction. They

**Table 7**  
The final yields and acid values for four types of solid acid catalyst.

Entry	Catalyst	FAME yields (wt%)	Acid value (I/mg KOH)
1	WO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> (WAL)	98	4.7
2	WO <sub>x</sub> /SiO <sub>2</sub> (WS)	92	5.6
3	WO <sub>x</sub> /ZnO (WZn)	84	4.4
4	WO <sub>x</sub> /SnO <sub>2</sub> (WSn)	91	5.8

**Table 8**  
Various applications of heterogeneous acid catalysts.

Feedstock	Catalyst type	Temperature (°C)	Molar ratio	Cat (wt%)	Time (h)	Yield	Reference
Methyl soyate	Ruthenium catalysts	40	–	0.1	2	46	[141]
Waste cooking oil	Zinc stearate immobilized on silica gel (ZS/Si)	200	18:1	3	10	98	[179]
<i>Jatropha curcas</i> oil	Sulfated tin oxide (SiO <sub>2</sub> (SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> –SiO <sub>2</sub> ))	60–80	15:1	3	2	97	[180]
Ethyl propanoate and ethyl-hexanoate	Heteropoly acids (H <sub>2</sub> SO <sub>4</sub> , Amberlyst-15 and zeolites HY and H-Beta)	60	20:1	0.1	1	84	[144]
Sunflower oil/methanol mixtures	Silica functionalized with 4-ethyl-benzene sulfonic acid groups	200	6:1	1.5	–	–	[181]



**Fig. 5.** Flow diagram of biodiesel production using heterogeneous catalyst.

**Table 9**  
Various applications of heterogeneous solid base catalysts.

Catalyst	Reaction condition				Yield (%)	Conversion (%)	Reference
	Temperature (°C)	Molar ratio	Time (min)	Catalyst (wt%)			
Al/Mg hydrotalcite	100	60:1	180	10	<80	–	[193]
KNO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	70	12:1	420	6	87	–	[194]
Montmorillonite KSF	190	8:1	180	3	79.6	–	[195]
MgO	–	12:1	60	0.5	92	–	[196]
	300	39.6:1	–	–	91%	–	[197]
CaO	100	6:1	–	1	–	90	[198]
SnO	65	12:1	30	3	90	–	[199]
Waste eggshell	60	18:1	60	10	97	–	[200]
Golden apple	60	18:1	60	10	83	–	[200]
Meretin venus	60	18:1	60	10	78	–	[200]

**Table 10**  
Advantages and disadvantages of the acid/base catalysts tested for (trans-) esterification.

Catalyst type	Benefits	Drawbacks
Ion-exchange resins (Nafion, Amberlyst)	Very high activity easy regeneration	Low thermal stability possible leeching
Tpa (H3pw12o40)	Very high activity	Soluble in water
Tpa-Cs (Cs2.5h0.5pw12o40)	Super acid sites	Low activity per weight
Zeolites (H-Zsm-5, Y and beta)	Controllable acidity and hydrophobicity	Small pore size low activity
Sulfated metal oxides (zirconia, titania, tin oxide)	High activity thermally stable	Deactivates in water, but not in organic phase
Niobic oxide (Nb2o5)	Water tolerant	Average activity
Calcium oxide/Cao	Low temperatures	Long reaction times
Calcium methoxide/Ca(Ome)2	High yield, reusable	High reactants ratio
Calcium ethoxide/Ca(Oet)2	High yield, short times	High reactants ratio
Li-dopped zinc oxide/Zno	Low temperatures	Long reaction times
KF loaded on Eu2o3	Short reaction times	Incomplete yields

concluded that MFI zeolite improved the removal of FFA with cracking. In addition, the pore structure and acidity of catalyst affects the catalytic activity in FFA elimination. Table 9 summarizes some other studies that used various types of heterogeneous base catalysts [190]. In addition, Table 10 indicates the advantages and disadvantages of heterogeneous acid and base catalysts [201].

#### 4.4. Heterogeneous solid catalysts potential for industrial application

Biodiesel production by heterogeneous solid catalysts instead of conventional homogeneous catalyst leads to economical production costs due to catalyst recycling and reusability [202], simultaneous esterification and transesterification [203], and lower catalyst (solid base) consumption. Mbaraka and Shank [204] reported that 88 tones of homogeneous catalyst (NaOH) was necessary for 8000 tones biodiesel production. In contrast, Dossin et al. [205], used only 5.7 tones heterogeneous solid catalyst (supported MgO) for 100,000 tones FAME production. However, the main drawback of solid catalyst application is the formation of three phases mixture (catalyst, oil, and alcohol). There are two key solutions for the mass transfer problem. The first is application of co-solvents such as *n*-hexane, dimethyl sulfoxide (DMSO), ethanol, and tetrahydrofuran (THF) that improves the miscibility of alcohol and oil. The second is catalyst support utilization that increases the catalyst activity by providing larger specific surface area and pores [206].

There is only one industrial biodiesel production plant utilizing heterogeneous solid catalyst which is the Esterfif™ process. The French Institute of Petroleum (IFP) studied the fundamental of this process and the Axens developed the technology of practical usage. Bournay et al. [207] described the reaction process of zinc and aluminum (Zn–Al) mixed-oxide utilized as a heterogeneous solid catalyst. Reaction was performed at higher pressure (3–5 Mpa) and temperature (483–523 K) compared to conventional homogeneous process. Table 12 illustrates the process that includes two fixed-bed reactors with rapeseed oil as the feed and excess methanol. In addition, excess methanol was removed by partial evaporation after each reaction before biodiesel and glycerol were separated in a settler. The final products (98% FAME yield and glycerol with >98% purity) conformed to the European specifications. The main characteristics of biodiesel and glycerol are summarized in Table 11. The disadvantages of the process include: (1) it is sensitive to the FFA and water (below 1000 ppm) content [208], (2) it requires relatively high reaction temperature and pressure. Therefore, only refined oils can be used in this plant.

Kouzu and Hidaka [209] compared the application of CaO as a heterogeneous solid catalyst for biodiesel production in a laboratory scale pilot plant and (Zn–Al) solid catalyst which was utilized by Esterfif™ process. They used CaO catalyst from limestone with

particle size of 1.0–1.7 mm. The reaction process included a fixed-bed reactor located in a circulating stream of the batch transesterification system. The result was 97% FAME yield at 333 K reaction temperature and atmospheric pressure with only 2 h reaction time. They used circulating flow to provide sufficient contact time of emulsified reactant and CaO catalyst and fast feeding. Table 12 summarized the features of CaO catalyst process and (Zn–Al) Esterfif™ process.

CaO catalyst leaching was the main obstacle for industrial application of this process. However, the best solution is polishing biodiesel with absorbent to omit the catalyst leaching. However, the leaching problem has not been overcome yet. It is clear that transesterification effect decreased by reusing CaO catalyst. Nevertheless, the catalyst was reused successfully for 17 times [210]. Similarly, the solid catalyst in the Esterfif™ process was deactivated as with time [211]. However, researchers concluded that CaO solid heterogeneous catalyst was feasible for industrial biodiesel production plant. In addition, Zabeti et al. [206] reported that small amount of water could improve the CaO catalyst activity and FAME yield. They reached to 95% biodiesel yield by adding 2.03 wt% water at optimum condition of 8 wt% catalyst amount, 12:1 molar ratio of alcohol to oil, and 3 h reaction time. More importantly, the catalyst was stable even after 20 cycles.

Although the biodiesel production by heterogeneous solid catalyst has been industrialized, researchers still continue their work for improving the process. As such, the current process worked at high temperature (220–240 °C) and high pressure (40–60 bar) which consequently concurred with high industrial construction costs. Therefore, there are many research activities on new heterogeneous catalyst application that have industrial potential.

Rattanaphra et al. [212] evaluated myristic acid esterification with sulfated zirconia as heterogeneous solid catalyst. Sulfated zirconia has recently received considerable attention as a catalyst in industrial processes due to its superacid characteristics. It has higher acid strength than sulfonic ion-exchange resins, heteropolyacid, and other heterogeneous acid catalyst [213,214].

Zeolite is microporous alumina silicate mineral that is used for fluid catalytic cracking and hydro-cracking in petrochemical industry and also as adsorbent for water and waste water treatment. There are various types of zeolites with inner electric fields and pore structure for crystal and surface properties [215]. Zeolite has high potential to be used in industrial biodiesel production plants.

Lou et al. [216] investigated biodiesel production from WCO by 27.8 wt% FFA content in presence of some carbohydrate-derived catalyst produced from different carbohydrates such as starch, sucrose, *D*-glucose, and cellulose. The results showed that starch-derived catalyst was the best one due to high stability (>93%) after 50 cycles of reusability. In addition, it exhibited higher catalytic

**Table 11**  
Characteristics of biodiesel and glycerol produced from rapeseed oil with CaO heterogeneous catalyst.

Biodiesel				Glycerol	
	R <sub>1</sub>	R <sub>2</sub>	ES		Method
Weight composition (%)				Glycerol content (wt%)	BS 5711-3 >98.0
Methyl esters	94.1	98.3	>96.5	Specific gravity 25 8C (kg/m <sup>3</sup> )	ISO 3675 1264
Monoglycerides	2.0	0.5	<0.8	Refractive index 20 8C	ASTM D1747 1.4735
Diglycerides	1.1	0.1	<0.2	Acidity (mg KOH/g)	EN 14104 0.1
Triglycerides	1.6	0.1	<0.2	Ash (wt%)	ISO 6245 None
Free glycerol	–	–	<0.02	Chlorides (mg/kg)	EP5.0 <10
Metal content (mg/kg)				Chlorinated compounds (mg/kg)	EP5.0 <10
Group I (Na + K)	<2	<2	<5	Halogenated compounds (mg/kg)	EP5.0 <10
Group II (Ca + Mg)	<2	<2	<5	Heavy metals (mg/kg)	ASTM D4951 None
Zn	<1	<1	–	Arsenic (mg/kg)	ISO 11969 D18 <0.1
Phosphorus content (mg/kg)	<10	<10	<10		
Acid number (mg KOH/kg)	<0.3	<0.3	<0.5		

**Table 12**  
Comparison between CaO and Zn–Al heterogeneous catalyst industrial application [209].

	Industrial Esterfl <sup>TM</sup>	Laboratory CaO
Catalyst	Zn–Al mixed oxide	Calcined lime stone (size distribution: 1.0–1.7 mm)
Reactor	Fixed-bed reactor (continuous-flow reaction system)	Fixed-bed reactor (batch reaction system with circulating stream)
Reacting condition	Temperature: 483–503 K; Pressure: 3–5 MPa; liquid space hourly velocity: 0.3–3 h <sup>-1</sup>	Temperature: 333 K; pressure: atmospheric pressure; catalyst contact time: 2 h
Feature	Good productivity proper for mass production	Simplified system proper for on-site production
Process diagram		

R<sub>1</sub>, R<sub>2</sub>, R: fixed-bed reactor.  
PL: polisher.

activity compared to sulphate zirconia and niobic acid in both esterification and transesterification reactions. Thus researchers concluded that this catalyst is eco-friendly, recyclable, highly effective, and highly suitable for biodiesel production from WCO with high FFA.

Yan et al. [217] utilized various ratios of ZnO–La<sub>2</sub>O<sub>3</sub> catalyst for biodiesel production from waste oils. Final results indicated that the Zn–La with ratio of 3:1 was recycled for 17 times without loss of activity in batch reactors and produced 92.3% biodiesel yield for 70 days in a continuous tubular flow reactor. Meanwhile, other research showed up to 100 days activity for the same catalyst [218]. This type of ZnO–La<sub>2</sub>O<sub>3</sub> catalyst has the longest catalyst life among all heterogeneous catalyst applied for biodiesel production.

#### 4.5. Enzymatic catalyzed transesterification

Recently, it has been found that enzymatic catalyst (immobilized lipase) can be used in transesterification reaction. No by-product, easy product removal, reusability without any separation step and lower operating temperature are the key advantages of this method. However, it is found to be very expensive [219,220]. The enzymatic reaction is insensitive to water and FFA content in waste cooking oil [220,221]. Ranganathan et al. [222] compared the alkali and enzymatic transesterification process in biodiesel production. They construed that the utilization of biocatalyst can produce very high purity FAME with lower or no downstream process compared to alkali catalysts.

Some factors have significant influence on the biodiesel production with lipase such as number of cycles, types of alcohol, ratio with oil and type of lipase. There are different types of lipases that can be used as the catalyst such as: *Rhizaopusoryzae*, *Candida rugosa*, *Pseudomonas fluorescens*, *Burkholderia*, *Cepacia*, *Aspergillusniger*, *Thermomyces lanuginose* and *Rhizomucormiehei* [223]. Hsu et al. [221] investigated the production of biodiesel from waste grease with two different alcohols (methanol and ethanol) and immobilized lipase. Transesterification with methanol showed very low conversion (47–89%) but transesterification with ethanol indicated the acceptable conversion levels (84–94%). Meanwhile, researchers have reported that immobilized lipase can be used many times without a serious loss of activity. Yagiz et al. [224] used immobilized lipase on hydrotalcite and zeolite catalyst and waste oils for biodiesel production. The highest yield was 95%, and the optimum condition was 4:1 molar ratio of methanol to oil, 5 h reaction time,

and 4 wt% catalyst loading. In addition, they reported seven times reusability for catalyst.

Amount of water, temperature and pH are additional factors that affect the biodiesel yield. Chen et al. [225] investigated biodiesel production from WCO at the presence of immobilized candida lipase in fixed bed reactor. They believed that WCO utilization solve both environment pollution and energy crisis problems. The highest 91.08% FAME yield was obtained at optimum condition of 25:15:10:100 of lipase/hexane/water/WCO weight ratio, 2.1 ml/min reactor flow, and 45 °C reaction temperature. There are reports that the minimum amount of water is necessary to activate enzymes [226–229] since enzymatic activity decreases in larger amounts of water. This means the amount of water for enzymatic method must be between 0.1% and 20% [229–231]. The impact of water in enzymatic method infers that lipase acts between aqueous and organic phases. Increasing the temperature initially would increase the reaction rate, but the effectiveness may be reduced and the reaction limited by mass transfer causing the rate of reaction to decrease dramatically at high temperature [232]. In enzymatic method, solution pH increases overall production. *Pseudomonas cepacia* has a high pH of about 7, and this property makes it easier to use compared to other types of lipase and should be used whenever a researcher wants to produce high yield without pH tuning [233].

##### 4.5.1. Immobilization of lipase

The natural lipase substrates (lipids) are in-soluble; however, their globular protein nature makes lipases spontaneously soluble in aqueous solutions [234]. The utilization of proper organic solvent or an emulsifier can overcome the mistake of increasing more enzyme and substrate [232,235]. On the other hand, the usage of lipase for pseudo homogeneous reactions causes technological problems such as pollution of products with residual enzymatic activity and commercial problems such as the usage of enzyme in a single reactor pass. These problems consume a portion of the overall potential of enzymatic activity. However, lipase becomes an independent phase in the reaction system with immobilization without any problem and consumption. Furthermore, rising temperatures cause the rate of lipase-catalyzed reaction per unit value of active enzyme to increase, but this trend leads to a higher thermal deactivation rate of lipase, therefore, yielding decreasing amounts of active enzyme [232,236]. The immobilization forms a

hard external backbone lipase molecule and increases the temperature, so faster reaction rate will occur.

The best method for immobilization is physical adsorption. This method is recommended by a majority of scientists for such reasons as it is non-toxic and inexpensive, able to retain activity and able to be regenerated [237]. The immobilized lipase by physical adsorption was used successfully in biodiesel production [228,238–240]. However, lipase immobilized through entrapment is more stable than physically adsorbed lipase [241]. In addition, the application of lipase encapsulated in a sol–gel has shown good results in biodiesel production [227,242,243]. Different types of membrane reactors such as flat sheet [244], and hollow fiber form [240,245] were used to increase the conversion because the reaction and separation occurred simultaneously in these types of reactors. The cost of lipase is the main obstacle that holds back the full exploitation of enzyme potential. Therefore, reusability of lipase is necessary. Immobilized form of lipase is a suitable catalyst for economic production of biodiesel with enzymatic catalysts because it has a higher stability and rate of activity compared to the soluble form.

Mittelbach [246] investigated the transesterification of sunflower oil with *Pseudomonas lipase*, *Candida lipase*, and *Mucor lipase* as catalyst with three types of alcohols (methanol, ethanol, butanol), with and without petroleum ether as solvents. The results showed that the conversion for ethanol and butanol was high even without solvent but methanol only produced traces of FAME without solvent. Besides, Nelson et al. [247] reported that *Candida antarctica* was a suitable catalyst for secondary alcohols such as iso-propanol and 2-butanol with around 80% conversion and *Mucor miehei* was good for primary alcohols like methanol, ethanol, propanol and butanol with around 95% conversion with solvents (hexane). However, methanol only showed around 19.4% conversion without a solvent. Some researchers reported low conversion for methanol and ethanol [248–250] and reported around 90% conversion for 2-ethyl-1-hexanol and *P. fluorescens* enzyme with butanol as acyl acceptor. The low yield referred to the inhibitory effects caused by methanol in the immobilized enzymes transesterification.

Al-Zuhair et al. [251] designed a pilot plant to produce biodiesel from WCO with enzymatic catalyst (Immobilized lipase (Novozyme 435)) in a packed-bed bioreactor. The researchers used a flash drum and a vacuum distillation column to produce a higher purity of the product. The results indicated that this pilot plant required around 620,000 US\$ in capital costs which must be paid back in 4 years. Rodrigues et al. [252] investigated biodiesel production from virgin and waste sunflower oil and two types of enzymes (Lipozyme TL IM and Novozym 435) as catalyst with

supercritical carbon dioxide. The transesterification reaction with lipozyme TL IM was carried out at 40 °C reaction temperature, 20 MP pressure, 24:1 molar ratio of methanol to oil, and only 20 s reaction time. The result was around 98% yields of methyl ester. However, they then evaluated the effects of combination of Lipozyme TL IM and Novozyme 435 on the final yield in which they achieved around 99% FAME yield. Table 13 summarizes the various applications of enzymatic catalyst in biodiesel production processes.

#### 4.6. The non-enzymatic heterogeneous catalyst

This method is relatively new and includes ZrO<sub>2</sub>, ZnO, SO<sub>4</sub>, 2-/SnO<sub>2</sub>, SO<sub>4</sub> 2-/ZrO<sub>2</sub>, KNO<sub>3</sub>/KL, zeolite and KNO<sub>3</sub>/ZrO<sub>2</sub>. The main advantages of these types of catalysts are: less corrosion and being more environments friendly. These properties can reduce the cost of biodiesel production. Furthermore, they can reduce the formation of soap even in low quality oils. However, this type of reaction was carried out at 200 °C and pressure level of 50 bars, with 6:1 molar ratio of methanol to oil and 3% catalyst weight for maximum efficiency [223].

#### 4.7. Non-catalytic production

There are a large number of drawbacks in biodiesel production using conventional methods (alkali and acid catalyzed processes) such as: requires high energy to conduct, difficult recovery of glycerol, high sensitivity to water and FFA content in raw material (feedstock), and very low reaction rates. Meanwhile, the utilization of lipase (enzymatic catalyzed) has their own disadvantages such as having a high price of catalyst and being time consuming [267,268]. Researchers have attempted to find novel methods that do not need catalysts to eliminate or decrease these types of obstacles in biodiesel production [269]. Saka was the first scientist who proposed that FAME can be produced by supercritical method [270]. The supercritical method requires no catalyst and can achieve near complete conversion in a relatively short time. This method is not feasible for large scale production because it requires high temperature and pressure for biodiesel production. These reasons dramatically increase the equipment and production costs. Thus, most researchers have focused on finding new approaches in this method to decrease the reaction temperature and pressure. The utilization of co-solvents such as carbon dioxide, hexane and calcium oxide are the key components to overcome these obstacles [271,272].

Jian-Zhong et al. [273] investigated biodiesel production with a conventional supercritical method and a supercritical coupled with

**Table 13**

Some studies in biodiesel production with various transesterification enzymes.

Lipase	Oil	Alcohol	Conversion (%)	Cost	Reference
Novozyme 435	Vegetable oil	Methanol	90–93	Moderate	[253]
	Sunflower oil	Methanol	97	High	[254]
	Soybean oil	Methyl acetate	92	High	[255]
	Soybean oil	Methanol	98	High	[256]
	Rapeseed oil	Methanol	95	High	[257]
	Cotton seed	Methanol	97	High	[258]
	Jatropha oil	Ethyl acetate	91.3	high	[259]
	Canola oil	Methanol	–	–	[260]
	Rice bran oil	Methanol	–	–	[261]
	Olive oil	Methanol	–	–	[262]
<i>R. oryzae</i>	Vegetable oil	Methanol	90	–	[263]
<i>R. oryzae</i>	Soybean oil	Methanol	90	Low	[264]
<i>P. fluorescens</i>	Jatropha oil	Ethanol	–	–	[265]
<i>R. miehei</i>	Palm oil	Methanol	–	–	[266]
<i>C. rugosa</i>	Jatropha oil	Ethanol	–	–	[265]
<i>P. cepacia</i>	Jatropha oil	Methanol and ethanol	–	–	[248]

co-solvents methods. The conventional method was carried out at various reaction temperatures (260, 300, and 350 °C), constant molar ratio of methanol to oil 42:1, 300 rpm mixing intensity, and different pressure up to 20 Mpa. The results showed that at 350 °C reaction temperature, the highest yield was 95% in 10 min. Meanwhile, alcohol and oil do not mix to form a single phase; therefore, hexane was added to the mixture to solve this problem. The results indicated that the reaction yield without hexane was 67.7%, but the yield reached 85.5% with 25 wt% of hexane. The researchers concluded that mutual solubility between methanol and oil was improved with the addition of hexane. Furthermore, the researcher reported the reaction with carbon dioxide (CO<sub>2</sub>) hexane as a proper solvent for vegetable oil. However, supercritical CO<sub>2</sub> is a suitable solvent for moderate and small organic molecules, because it has low cost and available material. The supercritical condition of CO<sub>2</sub> is 31 °C and 7.38 Mpa which it is lower than the supercritical methanol conditions (239 °C and 8.09 Mpa). The reaction condition for supercritical CO<sub>2</sub> was 300 °C reaction temperatures, 0.2 ratio of CO<sub>2</sub> to methanol, and 42:1 molar ratio of methanol to oil. The highest yield achieved was 90.6% FAME in 30 min. In addition, the supercritical method coupled with potassium hydroxide (co-solvent) was also reported in this study. The results of this part of research was excellent because the highest yield in the supercritical condition without catalyst was (<5%) but when the mass ratio of KOH to oil was 0.1% with 16 °C reaction temperature and 10 Mpa pressure, the yield was 98% FAME. The results of the last part of the research showed that the temperature reduced to around 190 °C compared to the conventional method. Meanwhile, the reaction with stirring speed of 300 rpm, KOH mass 0.1 wt%, 30 min reaction time, 160 °C reaction temperature, and 24:1 molar ratio of methanol to oil reached to 100% yield. There are many researches on utilization of co-solvents with supercritical method such as using propane [274], calcium oxide [272], and carbon dioxide [271]. The third approach of non-catalytic method is the utilization of co-solvent that is soluble in methanol and oil. This type of reaction does not have residual catalyst in the glycerol and ester and also is complete in only 5–10 min. Tetrahydrofuran is a co-solvent that is used in this method. Its boiling point is near to methanol boiling point. The results indicated that the process could have around 99% conversion with high FFA raw material such as animal fat and crude palm oil [275].

Demirbas [276] compared the FAME conversion in two catalytic and supercritical methanol methods. He evaluated the effect of different variables such as temperature, catalyst weight, and molar ratio of methanol to oil in both methods. The results showed that the optimum condition for base catalyzed transesterification reaction was 90:1 molar ratio, 360 K reaction temperature, and 6% catalyst weight to produce lower than 90% yield. However, for the supercritical methanol method, the optimum condition was 560 K reaction temperature, 41:1 molar ratio, to produced high purity of FAME (99.6%) and glycerol (96.5%). Tan et al. [277] investigated the biodiesel production from waste palm cooking oil with supercritical method. They evaluated the effects of variables such as molar ratio of alcohol to oil, reaction temperature, and reaction time. The final and highest yield was around 80% at the optimum condition.

There are several advantages of supercritical method including: (1) free fatty acids and glycerides react at equivalent rates, (2) the diffusive problems are eliminated by homogeneous phase, (3) the process tolerates great percentage of water in the feedstock, (4) there is no catalyst elimination step, (5) high molar ratio of methanol to oil can produce higher conversion in short reaction time. Despite having all these advantages, this method has some significant disadvantages including: (1) The process required high pressure (25–40 Mpa), (2) high reaction temperature (350–400 °C) caused extra costs for cooling and heating processes, (3) un-reacted methanol evaporation process is expensive with the high molar ratio of methanol to oil. Table 14 compares four different transesterification methods for biodiesel production [41].

## 5. Effect of different processes in biodiesel production

### 5.1. Reactive distillation method

Fig. 6a shows the life cycle of fossil fuels versus biodiesel. It indicates that the production and consumption of biodiesel creates no pollution, but fossil fuels produce 1.55 kg of CO<sub>2</sub> per 1 l of diesel burned. Meanwhile, Fig. 6b illustrates the reactive distillation column process for biodiesel production [278]. Reactive distillation is the process where chemical reaction and distillation separation occur simultaneously in the single equipment. This process has some advantages for special reactions such as: the reaction needs one or more reactant, the reaction needs to remove some of the products for completion, and the co-product recycling or product recovery process is complicated or has the possibility for azeotrope formation [279]. A variety of reactions such as homogenous catalyst, heterogeneous catalyst and non-catalyst can be carried out in reactive distillation process, in which the reaction must show reasonable data for conversion at pressure and temperature levels that are similar (compatible) to distillation conditions [280,281].

The application of reactive distillation process has some advantages such as: continuous removal of products from reaction zone can eliminate the conversion limitations; it can also decrease capital costs because both reaction and separation processes are carried out using the same equipment. In addition, the type of integration is needed to lower costs in piping and instrumentation, heat integration and pumps. Moreover, this process can eliminate the need for a re-boiler because in exothermic reactions, the heat of vaporization provides from the heat of reaction. Meanwhile, there is no azeotrope formation in this process. The other properties of reactive distillation process are: reactive distillation includes a smaller amount of equipment, hence a lower number of connections between instruments, reducing safety issues. Meanwhile, the evaporation removes reaction heat. Generally the reactive distillation process is less severe than conventional process [281,282]. Wang et al. [283] evaluated the reactive distillation process for methyl acetate hydrolysis process. The results indicated a 10% reduction in energy consumption and a 50% increase in production, compared to conventional fixed bed reactor.

**Table 14**  
Comparison of different biodiesel production methods.

Variable	Alkali catalysis	Acid catalysis	Enzyme catalysis	Supercritical alcohol
Reaction temperature (°C)	60–70	55–80	30–40	239–385
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters
Water in raw materials	Interference with reaction	Interference with reaction	No influence	–
Yield of methyl esters	Normal	Normal	Higher	Good
Recovery of glycerol	Difficult	Difficult	Easy	–
Purification of methyl esters	Repeated washing	Repeated washing	None	–
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium

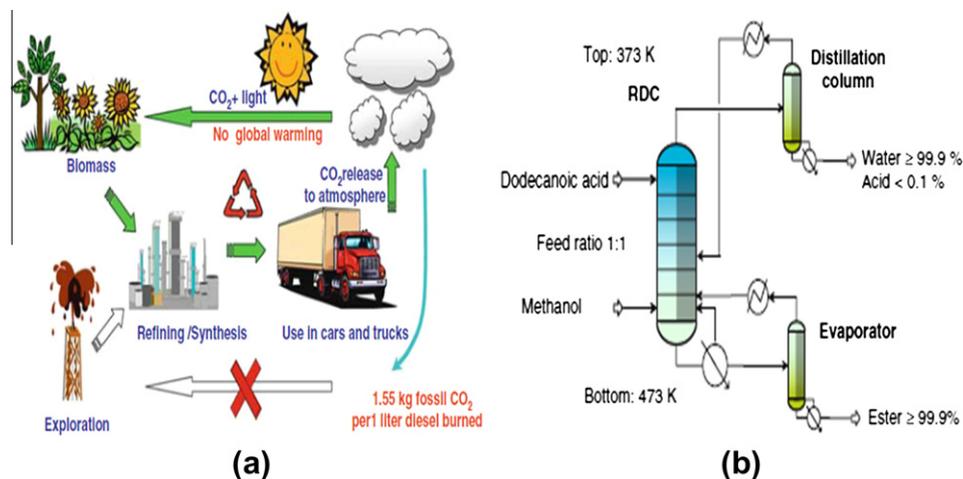


Fig. 6. (a) Life cycle of diesel versus biodiesel. (b) FAME production in RDC.

Lai et al. [284] produced high purity ethyl acetate with reactive distillation system and reached 99.5 wt% purity. He et al. [285] investigated biodiesel production from canola oil by reactive distillation process. They reported that by excising alcohol, a smaller reaction time could be achieved to the higher conversion. There are other researches in the different types of reactive distillation method such as catalytic reactive distillation, dual reactive distillation, and simulation and modeling of reactive distillation process. Da Silva et al. [280] compared the results of biodiesel production from soybean oil with reactive distillation and catalytic reactive distillation process. The results showed that the highest conversion for reactive distillation was 94.54% ethyl ester with optimum condition of 6 min reaction time, 6:1 molar ratio of ethanol to oil, and 1.5 wt% catalyst weight. However, in distillation, the best conversion was 98.18 wt% with 0.65 wt% sodium hydroxide as catalyst, 8:1 molar ratio of ethanol to oil, and 6 min reaction time.

Catalytic Distillation (CD) has received massive attention recently from both industrial and scientific researchers. Smith [286] invented this method for Methyl Tert-Butyl Ether (MTBE) synthesis. A large number of successful catalytic distillations were carried out, such as Eastman Kodak process for the methyl acetate production [287] and MTBE process [288]. The advantages of this method are: increased reaction conversion and selectivity, shifting the chemical equilibrium by continuous removal of products, significantly decreases the catalyst requirement, easy separation of the catalyst from the reaction mixture, reduces capital costs, avoidance of hot spots and runaway, heat integration benefits, and no undesired reaction. However, this method has complex interaction between vapor–liquid equilibrium, mass transfer, multiple steady state dynamics, and intra catalyst diffusion and chemical kinetic [282].

## 5.2. Dual reactive distillation

The catalytic reactive distillation method allows more opportunities in biodiesel production and specialty chemicals. Effective water removal for protecting the solid catalyst against deactivation and avoiding costly recovery of the excess alcohol are the most important problems to overcome. Dimian et al. [289] investigated a novel approach based on dual esterification of fatty acid with light and heavy alcohols. The methanol and long chain alcohol 2-ethyl hexanol have an equivalent reactive function but synergistic thermodynamic features. The reaction process takes place at moderate pressure, 130 and 200 °C temperatures compared to high pressure and vacuum by single light and heavy alcohol. The ester-

ification behaves like reactive absorption combined with reactive azeotropic distillation with water-separation agent and heavy alcohol as co-reactant. Furthermore, the researchers developed an original method in the application of a control strategy for obtaining the optimum operation condition. The most important advantages are: high flexibility in operation, multi-functional reactive distillation device, and decreased equipment costs by highly integrated design [290].

In addition, some researchers focused on integration methods to reduce energy consumption in biodiesel production. Reactive distillation, catalytic reactive distillation, and dual reactive distillation have significant effects in reduction of costs and energy consumption in fatty acid production. Meanwhile, Kiss et al. [291] reported that heat integrated reactive distillation uses much lower energy around 43% for heating and 47% for cooling compared to conventional reactive distillation. Furthermore, they used Aspen Plus for modeling and simulation of the process, and the results showed around 99.9% FAME production. The most important advantages of this method are: (1) process productivity increase up to 5–10 times higher than conventional units, (2) reactants are fed in stoichiometric ratio, without excess alcohol, (3) catalyst neutralization, salt water treatments, and soap production are eliminated, (4) sulfur eliminated from final product, (5) large range of alcohols and fatty acids are suitable, (6) investment costs decreases, (7) energy consumption significantly reduces, (8) reaction conversion and yield are very high.

## 5.3. Reaction absorption

Reactive absorption is a novel biodiesel process that offer more advantages compared to conventional methods. The advantages are: high conversion and selectivity, simple and robust process, no thermal degradation of product, omits regular catalyst-related operations and no waste streams. It can also decrease capital and operational costs. Researchers use water tolerant solid acid for catalysts in this method, so they can eliminate additional separation steps and salt waste streams.

Table 15 shows all available solid acid catalyst with their advantages and disadvantages [292–294]. Reactive absorption has some advantages in comparison with reactive distillation for instance lower temperature in the reactive separation column to avoid the thermal degradation of the FAME products. It means that without re-boilers (no product vapors return to the column) and a condenser (no reflux of water by product) the capital and operating cost can be reduced, and the process becomes simpler and more

**Table 15**  
Advantages and disadvantages of available solid acid catalysts.

Catalyst type	Benefits	Drawbacks
Ion-exchange resins (Nafion, Amberlyst)	Very high activity easy regeneration	Low thermal stability possible leeching
TPA (H3PW12O40)	Very high activity	Soluble in water
TPA-Cs (Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> )	Super acid sites	Low activity per weight
Zeolites (H-ZSM-5, Y and Beta)	Controllable acidity and hydrophobicity	Small pore size low activity
Sulfated metal oxides (zirconia, titania, tin oxide)	High activity thermally stable	Deactivates in water, but not in organic phase
Niobic oxide (Nb <sub>2</sub> O <sub>5</sub> )	Water tolerant	Average activity

robust. Meanwhile, reactive absorption can shift the chemical equilibrium to completion by continuous removal of products instead of using an excess of reactant. The main problem for esterification is the removal of effective water to protect the solid acid catalyst; excess alcohol should not be used in this method. Meanwhile, the removal of water is important for shifting the reaction to the equilibrium, resulted in higher conversion and purity [289,292,294–296].

This method is suitable for waste cooking oils, waste vegetable oils and animal fats with up to 100% FFA. Furthermore, this method works at moderate temperature and ambient pressure. The reaction condition was 160 °C temperature, 1 bar pressure, resulting in 99.9% methyl ester yield [297]. Kiss and Bildea [298] evaluated the integrated reactive absorption process for biodiesel production with solid acid catalyst and the simulation of the process. The results illustrated that the purity of production was higher than 99.9% when the productivity of reactive absorption unit was 19 (kg FAME/kg catalyst h). Table 16 shows different types of reactive separation processes for fatty acids esterification and also the amount of energy required for each method [298]. In addition, the integrated reactive absorption requires only 21.6 kW h/tonne biodiesel, which is around one ninth of energy requirement for the conventional reactive distillation.

#### 5.4. Continuous flow biodiesel production

The conventional transesterification process uses batch operation, which has some disadvantages such as: poor adaption to automation, tedious, and labor-intensive. However, a continuous flow biodiesel production has significant benefits that include low production costs and time in small-scale plant, the ability to produce higher quality biodiesel per unit of labor, and the capacity to improve the equipment design to optimize the quality of biodiesel [227]. Moreover, the continuous method increases productivity and profit while reducing costs and reaction time. The Rotating Packed Bed (RPB) has been designed to increase the micro-mixing efficiencies and mass transfer by the utilization of great centrifugal force. Various applications of this method have been reported such as the utilization of RPB as gas liquid contact in absorption [299–302], distillation [303,304], stripping [305,306], and ozonation [307–311]. Meanwhile, the RPB method has a high micro-mixing ability and can be used in a large number of applications

**Table 16**  
Energy requirement for different methods.

Method	Energy requirement (kW h/tonne biodiesel)	Reference
Reactive distillation	191.2	[276]
Dual reactive distillation	166.8	[289]
Reactive absorption	138.4	[297]
Heat integration reaction distillation	108.8	[291]
Integrated reactive absorption	21.6	[298]

[307,312,313]. In addition, the RPB reactors produce smaller particles in shorter time compared to conventional reactors [314].

Chen et al. [299] investigated biodiesel production with rotating packed bed reactors. Meanwhile, they evaluated the effects of variables such as molar ratio of alcohol to oil (4:1, 6:1, 12:1, 18:1 and 24:1), reaction time (0.43–1.67 min), mixing intensity (150, 300, 900, 1500 rpm), reaction temperature (34, 42, 60, 65 °C), and catalyst weight (0.1, 0.24, 1, 2, 3, 5%w/w). The results of this research showed a wide range of (5.5–97.3%) conversion. The optimum condition was 0.72 min reaction time, 900 rpm mixing intensity, 6:1 molar ratio of alcohol to oil, 3%w/w catalyst weight and 60 °C reaction temperature which produced the highest conversion of 97.3% ester. Komers et al. [315] reported around 98.5% conversion for biodiesel production with continuous stirred tank reactor (CSTR) from soybean oil with KOH as catalysts. Halim et al. [316] developed a continuous procedure of lipase-catalyzes transesterification of waste cooking palm oil in a packed bed reactor, raising the possibility of large-scale production. Meanwhile, the researchers used Response Surface Methodology (RSM) for process optimization. The results showed that the optimum condition was 10.53 cm packed bed height, 0.57 ml/min flow rate, Novozyme 435 as catalyst, tert-butanol as solvent, 1:1 volume ratio of solvent to oil, 4:1 molar ratio of methanol to oil and 40 °C reaction temperature and the highest FAME yield was 80.3%. In addition, they concluded that mass transfer controlled the transesterification of waste cooking oil in a continuous packed bed reactor. Table 17 shows various studies on continuous production.

#### 5.5. Membrane reactor

The most important issues in biodiesel production are the removal of residual impurities such as free glycerol, catalyst, un-reacted methanol, bound glycerol, un-reacted tri-glycerides (TG), diglycerides (DG), monoglycerides (MG), and small amounts of soap and water because these types of impurities affect engine performance significantly [323]. One approach for separation of impurities in FAME is to drive the reaction as close as possible to complete conversion of the oil. However, the transesterification of TG is an equilibrium reaction and the reaction can never reach 100% completion. The second approach is multiple water wash of product but this method requires waste water treatment process [324]. The utilization of hot water (50 °C) stream for washing showed the best results. Some solid absorbents such as activated carbon fiber, activated carbon, and activated clay can be used for purification product [325,326]. Another method for purification and separation of biodiesel is the utilization of membrane reactors. Methanol and vegetable oils are not miscible and membrane reactors take advantage of this immiscibility to create a better purification process. The separation by membrane is useful for water purification, protein separation and gas separation. The commercial application of this method is separation that involves aqueous solutions and relatively inert gases [327,328]. There are two types of membrane, organic and inorganic. Meanwhile, the inorganic membranes are suitable for use with organic solvents because they have high thermal stability and can be used at high temperatures

**Table 17**  
Continuous transesterification process.

Oil	Catalyst	Reactor	$T$ (°C) <sup>a</sup>	$V_R$ (ml) <sup>b</sup>	$t_L$ (min) <sup>c</sup>	$Y_{FAME}$ (%) <sup>d</sup>	$P_{FAME}$ (mol/ min) <sup>e</sup>	$P_{FAME}/V_R * 10^3$ (mol/ ml min) <sup>f</sup>	Reference <sup>g</sup>
Soybean oil	NaOH	Motionless mixers and high-shear reactor	80	2000	5.80–8.12	68–99.5	0.511–0.872	0.255–0.436	[317]
Palm oil	KOH	Stirred-tank reactor	60	1000	40–70	58.8–97.3	0.0252–0.0278	0.0252–0.0278	[318]
Canola oil	KOH	Reactive distillation reactor	55	10	2.67–6.67	41.5–97	0.00172–0.00931	0.172–0.931	[319]
Soybean oil	KOH	Microwave heating reactor	50	2000	0.56	94.4–95.25	4.9–17.8	1.23–4.46	[320]
Commercial oil, palm oil	KOH	Ultrasonic	38	4000	2	72–96	0.199–0.623	0.057–0.23	[321]
			40	2620					
Soybean oil	NaOH	Zigzag micro-channel reactor	40	0.0642	0.3	81.5–99.5	0.00025	3.89–8.11	[322]
			75		0.47		0.00052		

<sup>a</sup>  $T$  (°C) = the reaction temperature.

<sup>b</sup>  $V_R$  (ml) = reactor volume.

<sup>c</sup>  $t_L$  (min) = the estimated hydraulic retention time.

<sup>d</sup>  $Y_{FAME}$  = yield of the fatty acid methyl ester.

<sup>e</sup>  $P_{FAME}$  = productivity of FAME.

<sup>f</sup>  $P_{FAME}/V_R$  (mol/(ml min)) =  $P_{FAME}$  per unit reactor volume.

<sup>g</sup> Reference.

[329,330]. The advantages of membrane reactors are: (1) production cost decrease due to integrated reaction and separation step, (2) thermodynamic limited or product-inhibited reactions increase, (3) incompatible reactants controlled contact, (4) undesired reactions eliminated.

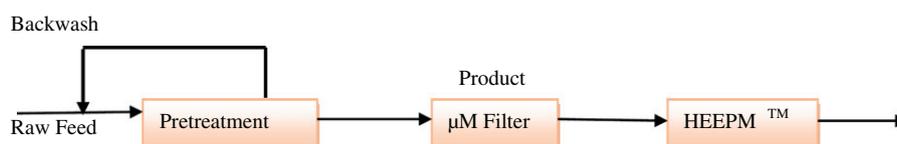
Dube' et al. [331] reported that micro-porous inorganic membrane reactor could remove FAME, glycerol, and methanol during the transesterification reaction of triglycerides. Cao et al. [332] investigated the utilization of membrane technology for biodiesel production and reductions in required molar ratio of methanol to oil. The results showed that the highest conversion was (85.7–92.4 wt%) and significant reduction for molar ratio from 15:1 to 10:1 methanol to oil. He et al. [333] compared three conventional methods of washing with distilled water, washing with acid (HCL), and extracting with solvent (*n*-hexane or petroleum ether) with a novel technology of hollow fiber membrane extraction. All conventional methods produced 97.5% purity biodiesel. However, the membrane reactor obtained around 99% purity and other properties of biodiesel such as kinematic viscosity, acid value and density were similar to standard values. Saleh et al. [323] reported the utilization of membrane reactors for separating glycerol from the product. Their experiment showed that the membrane technique only uses 2.0 g water for one liter of treated FAME (0.225 mass%). However, conventional methods use 10 liters of water for one liter of treated biodiesel.

Sdrula [334] investigated membrane separation for crude glycerides and biodiesel. Biodiesel industry produces million tons of crude glycerides waste, and this amount of glycerin is projected to increase rapidly with the significant growth of biodiesel production. The researcher used an economical solution which combines the high efficiency of electro dialysis and nano-filtration for purity and recovery of glycerin, respectively. The High Efficiency Electro-Pressure Membrane (HEEPM) can be operated in batch, semi-batch

and continuous processes. Fig. 7 illustrates the general scheme of HEEPM technology and Fig. 8 shows a schematic view of prototype biodiesel membrane separation plant [334].

Another new technology is hydrophobic porous membranes that can be used in biodiesel industry. The advantages of this method are: (1) different raw material such as recycled cooking oil, pure vegetable oil, animal fat, and some solid oils with any level of FFA can be used, (2) various types of membranes have been developed for different kinds of raw material, (3) high quality FAME according to ASTM D-6571 and EN-14214, (4) glycerin-purifying process with membrane system meets USP standard, (5) no additional chemicals needed, (6) decreased costs.

The application of various types of membrane such as ceramic separation [335], hybrid separation [336,337,103], and polymeric membrane [338] have been reported for biodiesel separation process. Wang et al. [339] evaluated ceramic membrane separation for biodiesel purification to decrease the water demand in washing process in contrast with micro-filtered and the pore sizes of 0.6, 0.2 and 0.1  $\mu\text{m}$  to separate the residual soap and free glycerol at 60 °C temperatures and 0.15 MPa pressure. The best pore size was 0.1  $\mu\text{m}$ , and this novel refining process of biodiesel did not produce wastewater compared to conventional methods. Furthermore, Gomes et al. [340] reported 99.4% glycerol retention with 0.2  $\mu\text{m}$  membrane pore size and 2.0 bar pressure. The results showed that transmembrane pressure has a significant influence on biodiesel microfiltration. In addition, they evaluated the effects of ethanol on feed mixture. The results indicated that 5% mass ethanol in feed stock gave the highest result of 99.6% glycerol retention. Buchaly et al. [341] investigated the simulation, modeling and analysis of hybrid separation process (combination of reactive distillation and membrane separation) by application of heterogeneous catalyst (*n*-propyl propionate) from 1-propanol and propionic acid. The results illustrate the process performance in terms



**Fig. 7.** General scheme by HEEPM technology (EET process).

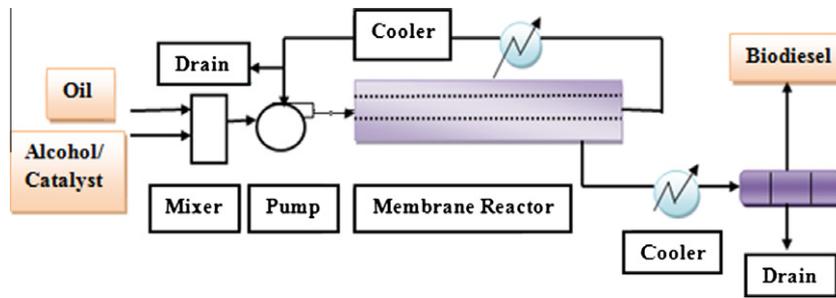


Fig. 8. Schematic view of biodiesel membrane separation prototype plant.

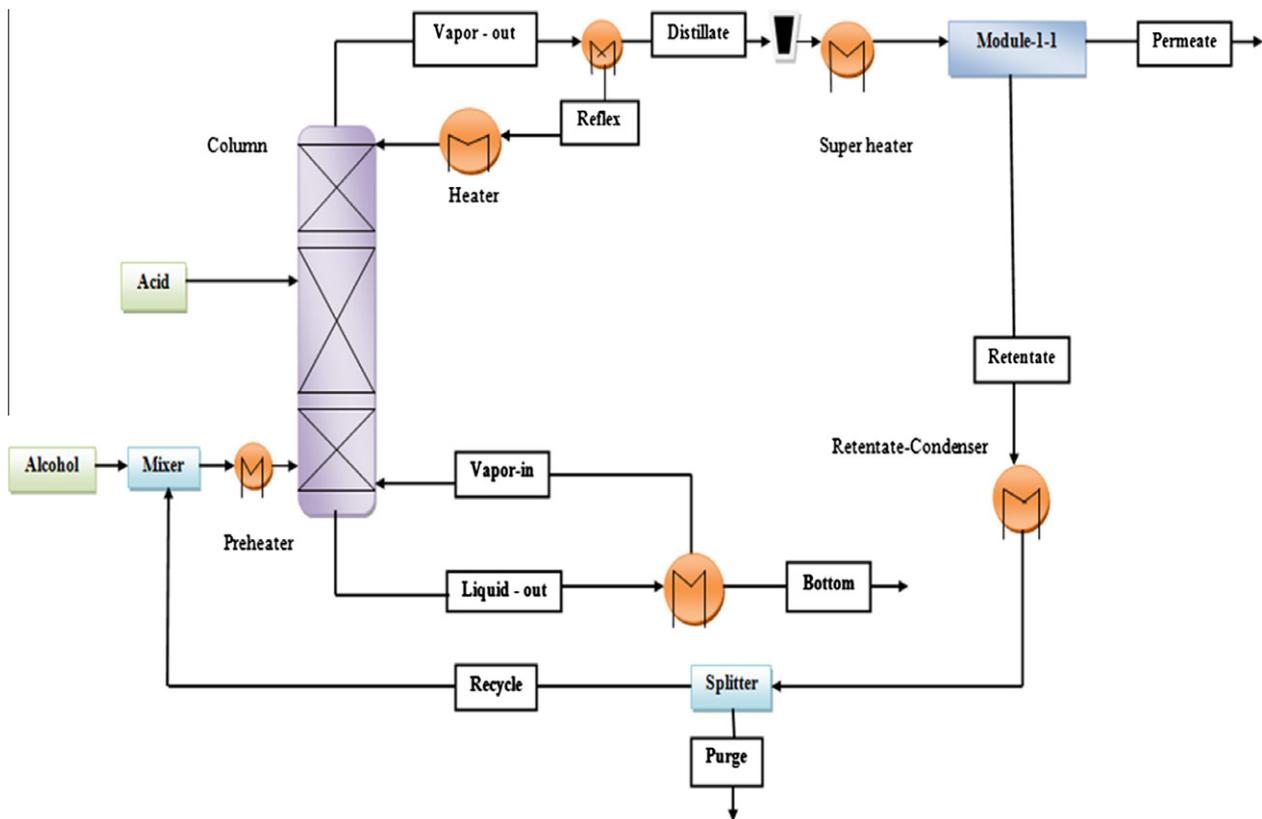


Fig. 9. Process design of hybrid process.

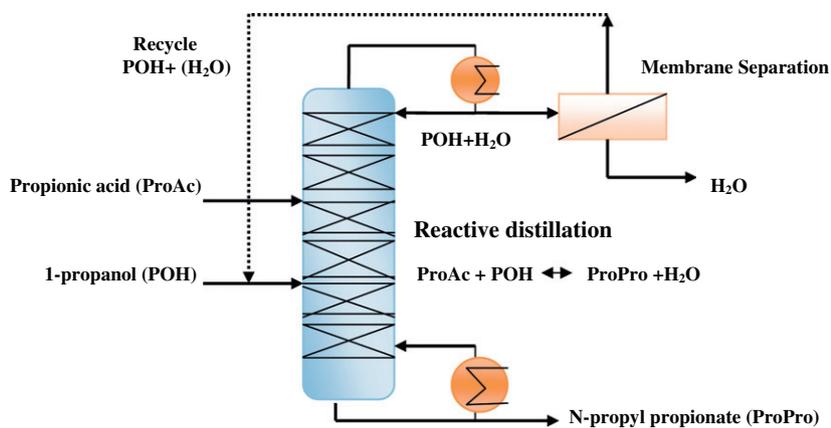


Fig. 10. Reactive distillation column with membrane separation located in distillate stream.

of acid conversion and product purity was high and feasible. Figs. 9 and 10 illustrate a design of the hybrid process, and a reactive distillation column with a membrane separator located in the distillation stream, respectively. Another approach in membrane separation is a novel process of a dual bed membrane that a few researchers have studied before, and the results show huge advantages in comparison with conventional membrane separation. It is hoped that the utilization of this process is made more mainstream in the future [342,343].

### 5.6. Ultrasonic

Ultrasonic process using sound wave energy vibrates more than 20,000 times per second. These waves are in the range of 20–100 kHz that is beyond the human hearing limit (10–12 kHz). Medical research and detection was the first application of ultrasonic waves in 1930–1940 [344]. However, the industrial application of this energy significantly increased since 1980s and today ultrasonic waves are using in wide ranges of application such as processing, extraction, and atomization [345–347]. Ultrasonic irradiation has three significant influences on reaction: (1) acoustic streaming mixing, (2) variation of sonic pressure lead to rapid movement of fluids [348], (3) cavitation bubbles formed by liquid breakdown that caused by large negative pressure gradient application in liquid. The main effect of ultrasonic waves on chemical reactions comes from formation and collapse of micro-bubbles [349]. The liquid jet effect is cavity collapse that improves the mass transfer by disrupting the interfacial boundary layers. These waves can provide high temperature (>5000 K) and pressure (>1000 atm) that has significant influence on increasing the reaction rate, mass transfer, and catalytic surface areas [350]. Mixing of oil and alcohol is the main factor that increases the biodiesel yield because both oil and alcohol cannot be miscible completely in conventional processes. Therefore, the low frequency ultrasonic waves are the best solution [351].

Ultrasonic irradiation improves the reaction characteristics by formation of smaller droplets (146–148 nm by 50–70 W) compared to conventional stirring system (340 nm by 1000 rpm) by improving the contact area between oil and alcohol [352,353]. Besides, ultrasonic energy can break catalyst to smaller particles to form new sites for subsequent reaction. Therefore, researchers concluded that solid catalysts are suitable choice for this process because the catalysts stability is expected to last longer [354]. In addition, ultrasonic irradiation can enhance the enzyme (Novozym 435) catalyst activity [355,356]. There are some reaction parameters that significantly influence the ultrasonic irradiation process: (1) ultrasonic power, (2) frequency effect, (3) catalyst type, (4) alcohol type.

The main advantages of ultrasonic irradiation process are: (1) shorter reaction time, (2) lower molar ratio of alcohol to oil, (3) less energy consumption (50%), (4) lower amount of catalyst utilization (enzyme), (5) increased reaction rate, (6) enhanced conversion, (7) improved yield, (8) different reaction path way, (9) simpler equipment setup, (10) better process economy, (11) simpler separation and purification processes, (12) higher quality glycerol production.

In contrast, this process has some disadvantages such as (1) the reaction temperature was slightly higher for long reactions, (2) higher catalyst loading compared to conventional processes, (3) the ultrasonic power must be under control due to the soap formation in fast reaction. Therefore, FAME yield can be reduced by higher frequencies (40 kHz).

Since the advantages of ultrasonic process are enormous, the process is suitable for large scale industrial plants. However, comprehensive information about all aspects of chemical reaction and application of heterogeneous catalyst and non-edible oil in continuous systems are still lacking. Definitely this process requires

additional technical and scientific enhancement to overcome the drawbacks before commercialization and industrialization can be realized.

Salamatinia et al. [357] investigated the ultrasonic process with heterogeneous transesterification of palm oil for production of biodiesel. Meanwhile, they evaluated the effect of variables such as the reaction time (10–60 min), molar ratio of alcohol to oil (3:1–15:1), catalyst weight (0.5–3.0 wt%) and ultrasonic amplitude (25–100%). Researchers used Design Expert software for statistical optimization of process. The results indicated that RSM model could be able to predict the FAME yield with the lowest error. Besides, the ultrasonic process dramatically reduced the catalyst weight and reaction time to 2.8% wt and 50 min individually, with reaching more than 95% yield. The optimum condition was 9:1 molar ratio of alcohol to oil, 70% and 80% ultrasonic amplitude for Bao and Sro catalyst, respectively. Manh et al. [358] evaluated two ultrasonic (19.7 kHz) and hydrodynamic cavitations methods in alkali catalyzed biodiesel production. The results indicated that both methods were efficient and had significant influence in saving energy and time for transesterification of soybean oil compared to conventional methods. Meanwhile, the researchers concluded that hydrodynamic cavitation has the potential for utilization in industrial scale processes [351]. Yu et al. [350] investigated the production of biodiesel from soybean oil and an immobilized form of Novozym 435 as catalyst. The transesterification reaction was carried out by two different methods (ultrasonic irradiation and ultrasonic irradiation with vibration). The enzyme activity and reaction rate are dramatically increased by ultrasonic irradiation with vibration. Some variables such as water content, ratio of solvent to oil, enzyme dosage, organic solvent, ultrasonic power, ratio of methanol to oil, and temperature were investigated in this research. The results indicated that the 96% yield of FAME was obtained under optimum conditions of 50 rpm mixing intensity, 0.5% water content, 1:1 tert-amyl alcohol to oil volume ratio, 6:1 methanol to oil molar ratio, 40 °C reaction temperature, 50% of ultrasonic power and 4 h reaction time. There are many other researches for application of ultrasonic process in production of biodiesel [359,360–364]. Figs. 11 and 12 shows a flow diagram of the ultrasonic irradiation process and schematic diagram of the experimental set up, respectively [364,357].

### 5.7. Microwave

Microwave ovens entered households in 1954 and the utilization of this equipment has increased in recent years. Microwaves can heat matter faster than conventional ovens, and this is the most important property of this type of oven. However, industrial microwave applications include product drying, moisture and fat analysis of food product, solvent application and irradiate coal to remove sulfur and other impurities.

Microwaves transfer energy to samples directly and this energy completes the reaction. Microwave irradiation has a higher frequency than radio waves and much lower than X-rays with wavelength of 1 mm–1 m and 300 MHz to 300 GHz frequency [7]. There are three microwave heating equipments patents in use in biofuel manufacturing (WO03/014272 A2, 2003; US 2005/0274065 A1, 2005; US 2006/0162245 A1, 2006). The implementation of multiple microwave process has a significant effect on land, time saving and energy in comparison with conventional single large reactor tank system.

Microwaves do not have the ability to break bonds or form energy, and are manifested as heat through interaction with the materials. This heat can be reflected (metals), transmitted (good insulators that will not heat), or absorbed (decreasing the available microwave energy and rapidly heating the samples) [365]. Refaat et al. [366] obtained the optimum parametric conditions for

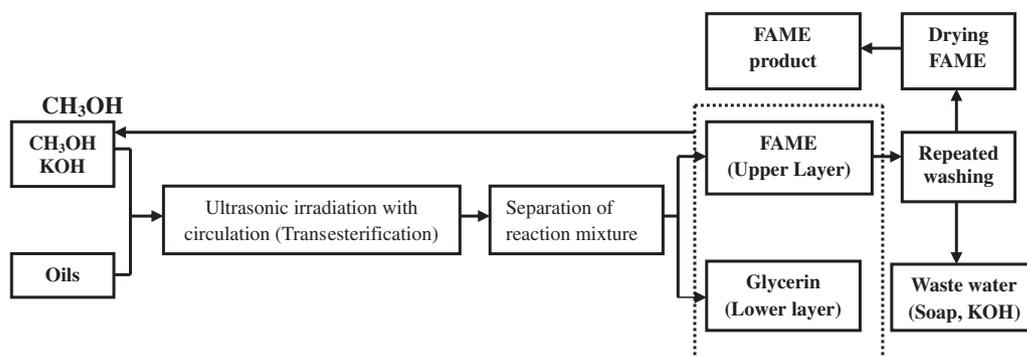


Fig. 11. Flow diagram of ultrasonic irradiation process for biodiesel production from vegetable oil in presence of a base-catalyst.

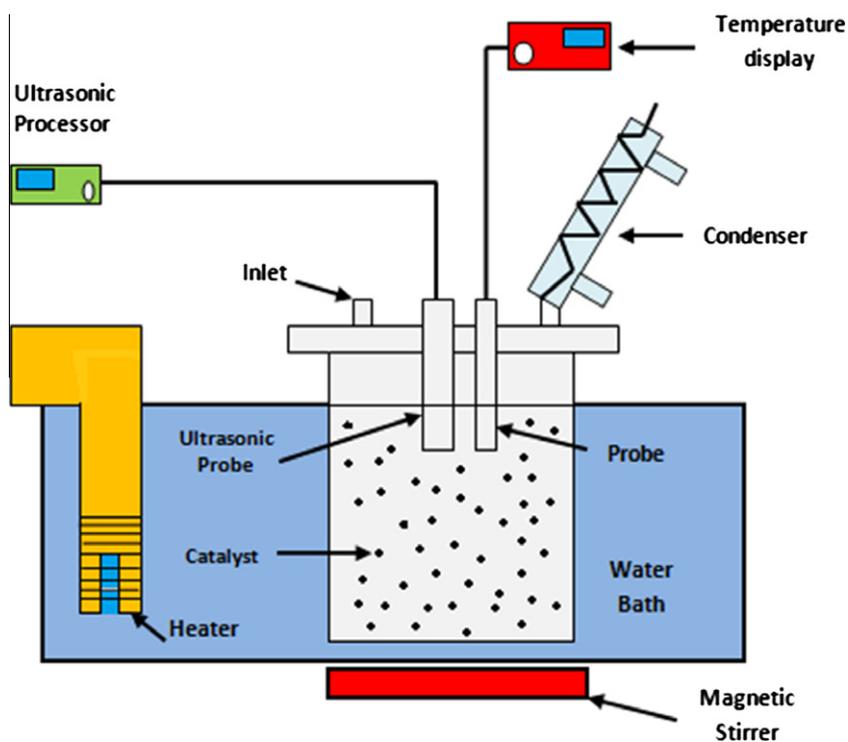


Fig. 12. Schematic diagram of an experimental set-up used for ultrasonic-assisted biodiesel production process.

conventional method with application of microwave irradiation for production of biodiesel from neat and waste vegetable oil with a high FFA content. Meanwhile, the results indicated that microwaves can easily route fuel with the added benefits of increasing the reaction reactant and improving the separation and purification process. There are a lot of reports of utilization of microwave irradiation transesterification that use domestic ovens flow system [101,367,368].

The main advantages of microwave process are: (1) higher quality and yield product, (2) minimum energy consumption (23 times lower than conventional methods) [369], (3) environmental friendly, (4) shorter reaction time, (5) lower molar ratio of alcohol to oil, (6) less quantity of by-products, (7) more effective heat transfer system (conventional methods transfer heat to the reaction by convection, conduction, and radiation from reactor surface but, microwaves transfer energy in a form of electromagnetic and not thermal heat reflux.) The microwave energy is directly delivered to the reactant and preheating step is eliminated.

In addition, Motasemi and Ani [370] reported that 1 kg biodiesel by microwave irradiation system required 0.47 kW h electricity;

however, the average 2.1277 kW h electrical energy can be produced by 1 kg biodiesel. Therefore microwave process has potential to produce about 1.6596 kW h/kg extra electrical energy that demonstrates the sustainability of the process.

Barnard et al. [371] evaluated the energy consumption of batch and continuous microwave irradiation for biodiesel production. Their results summarized in Table 18 indicated that the continuous system is more energy efficient than conventional heating and batch microwave system.

On the other hand, the main drawbacks for industrial (large-scale) application of microwave processes are: (1) high microwave output (power) may cause damage to organic molecules (triglycerides) [102], (2) safety aspects. The most important limitation of this process is the scaling-up to industrial (Large-scale) production plant from laboratory scale process, due to the low penetration depth (a few centimetres) of microwave radiation into the absorbing material [372,373].

Mazzocchio et al. [374] evaluated the production of biodiesel with  $\text{NaOH}$  (homogeneous) and  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (heterogeneous) catalysts under conventional heating and microwave irradiation.

**Table 18**

Comparison between energy consumption by conventional and microwave processes [371].

Method	Energy requirement (kJ/L) <sup>a</sup>
Conventional heating <sup>b</sup>	94.3
Microwave continuous flow (7.2 L/min feedstock flow)	26.0
Microwave continuous flow (2 L/min feedstock flow) <sup>c</sup>	60.3 (92.3) <sup>d</sup>
Microwave heating (4.6 L batch reaction) <sup>e</sup>	90.1

<sup>a</sup> Normalized for energy consumed per liter of biodiesel prepared.<sup>b</sup> On the basis of values from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998 study into life cycle inventory of biodiesel and petroleum diesel for use in an urban bus.<sup>c</sup> Assuming a power consumption of 1700 W and a microwave input of 1045 W.<sup>d</sup> Assuming a power consumption of 2600 W and a microwave input of 1600 W.<sup>e</sup> Assuming a power consumption of 1300 E, a microwave input of 800 W, a time to reach 50 °C of 3.5 min, and a hold time at 50 °C of 1 min.**Table 19**

The ethyl ester yield percentage by microwave method.

Reaction time (s)	% Yields of fatty acid ethyl ester at molar ratio					
	3:1 (%)	6:1 (%)	9:1 (%)	12:1 (%)	15:1 (%)	18:1 (%)
10	7.19	23.90	100	100	100	100
20	5.44	34.27	100	100	100	100
30	3.82	27.84	100	100	100	100
40	5.93	31.32	100	100	100	100
50	6.69	39.21	100	100	100	100
60	6.67	32.31	100	100	100	100
80	2.52	41.16	100	100	100	100
100	8.67	24.87	100	100	100	100

The results showed that the microwave was faster and obtained higher activity and yield compared to conventional methods. Meanwhile, under microwave irradiation both catalysts exhibited the same results. However, the  $\text{Ba}(\text{OH})_2\text{H}_2\text{O}$  catalyst gave easier separation, recycling and no soap formation. Lertsathapornasuk et al. [375] investigated the production of biodiesel from waste palm oil with domestic microwave (800 W) in a continuous transesterification reaction and sodium hydroxide as catalyst. The highest conversion was 97% FAME with optimum condition of 12:1 molar ratio of ethanol to oil, 30% catalyst and 30 s reaction time. In addition, they evaluated the effects of variables such as molar

ratio of ethanol to oil (3:1, 6:1, 9:1, 12:1, 15:1, and 18:1), 1% NaOH as catalyst, and reaction time (10–100 s). The complete conversion (100%) was carried out at 9:1 molar ratio of ethanol to oil and only 10 s reaction time. The researchers reported that the reaction time with microwave irradiation was 10 times shorter than conventional methods. Table 19 indicates the yield percentages of fatty acid ethyl ester from UVO [375]. They compared the fuel properties (kinematic viscosity, cetane number, pour point, copper correlation, sulfur content, cloud point, high heating value) with standard biodiesel (B100). The results indicated that the product properties were similar to high speed diesel. Besides, these researchers used a continuous method in production of biodiesel by microwave irradiation (800 Watts) from different feed stocks (coconut, rice bran, and used cooking palm oil). The optimum condition was 1.0% sodium hydroxide as catalyst, 9:1 molar ratio of ethanol to oil, and only 30 s reaction time. The results was amazing because they achieved 100%, 94%, and 83% conversion for coconut oil, rice bran oil, and used cooking oil, respectively. Fig. 13 indicates the schematic diagram of continuous microwave process [32].

Yaakob et al. [376] evaluated the effect of methanol to oil molar ratio, amount of catalyst, reaction time and temperature on biodiesel production from *Jatropha* oil and waste cooking oil. The results indicated that 12:1 methanol to oil molar ratio, 1% NaOH, 7 min reaction time and 65 °C reaction temperatures were the optimal condition. The highest yield was 88% for both feedstocks. Safiuddin and Chua [101] used 0.5% NaOH, 100% excess anhydrous ethanol and 750 W microwave irradiation for production of ethyl ester. Also, they evaluated the amount of microwave exit power and reaction time. The results showed 4 min reaction time in comparison with 75 min for conventional method and 50% exit power of 750 W microwave. Chen et al. [377] investigated biodiesel production from WCO at the presence of NaOH and  $\text{CH}_3\text{ONa}$  as catalysts. They examined the effect of microwave irradiation on these processes. The results indicated that the FAME yield for  $\text{CH}_3\text{ONa}$  catalyst was higher than NaOH catalyst, by similar amount of 0.75 wt%. In addition, they concluded that biodiesel yield increased by increasing the reaction time from 1 to 3 min and increasing the microwave irradiation power. The optimum reaction conditions were 0.75 wt%  $\text{CH}_3\text{ONa}$  catalyst amount, 6:1 molar ratio of methanol to oil, 750 W microwave powers, and only 3 min reaction time.

## 6. Conclusions

Alternative fuel production from renewable resources poses many challenges. Depletion of fossil-fuel resources, unstable price

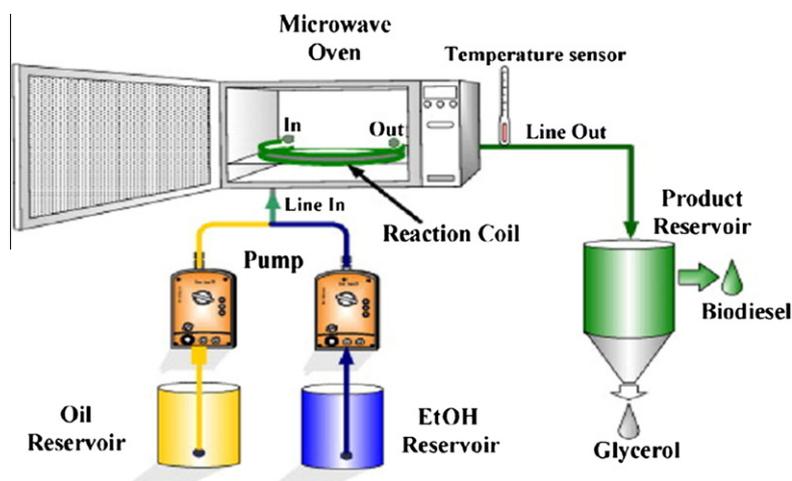


Fig. 13. Schematic diagram of a continuous microwave biodiesel production process.

of crude oil and other fossil fuels, and environmental concerns are the main reasons for finding a new fuel which should be environmentally friendly, cheap, widely available, and technically acceptable. Biodiesel is one of the best fuel alternatives that researchers are focused on and efforts are being made to produce it at a lower cost and with outstanding fuel properties. The transesterification reaction is the best method for production and modification of biodiesel. Acid, alkali, or enzymatic catalyzed, and non-catalyst transesterification are different approaches that have been tried for biodiesel production. However, all of them have their own advantages and disadvantages. The type of feed stock is the most important factor in the production of biodiesel. There are various types of vegetable oils and animal fats that can be used in this process. Utilizing waste cooking oil can decrease biodiesel production costs. However, the cooking process has negative influences on oil properties and can create different types of impurities in the oil and can also increase the FFA and water content of oil. Therefore, these obstacles increase the cost for the purification and separation process in the downstream of biodiesel production. The transesterification with alkali catalysts is the conventional method for biodiesel production, but this method causes serious problems in the purification part since they are highly sensitive to FFA and water content in the raw material. The acid catalyzed process is not sensitive to FFA and water content like base catalysts. However, the production process is much longer. The utilization of enzymatic catalysts showed very good results, but they are expensive and for the industrial production of biodiesel, this is not acceptable. In addition, the non-catalyst method or supercritical method requires high temperature and pressure, and this is obviously not economical. Therefore, scientists focus on the utilization of heterogeneous acid and base catalysts in biodiesel production since the catalysts may be reusable many times. The reusability of catalyst is the most important property which can make them economical for industrial production in a continuous process. Hence, various methods such as membrane reactor, reactive distillation, reactive absorption, microwave, and ultrasonic to reduce production costs, reaction time, catalyst and alcohol requirements have been used in transesterification reactions. These methods can increase the quality of FAME for applications to diesel engines without any kind of engine modification.

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