Comprehensive Review on Biodiesel Production from Palm Oil Mill Effluent

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Abstract

Biodiesel synthesis processes including pyrolysis, direct blending, transesterification, and advanced technologies such as microwave- and ultrasound-assisted and supercritical processes from palm oil mill effluent (POME) are reviewed to highlight the significance and advances in terms of process sustainability and cost. POME as the most contaminated waste can be effectively utilized for biodiesel production. Supercritical transesterification offers more advantages over the other processes including higher reaction rate, without catalyst constraint, producing pure glycerol, and simple product separation process. The addition of co-solvents like CO_2 should be investigated for supercritical biodiesel production from POME. Although POME is an inexpensive source to synthesize biodiesel, innovative processes are needed to maximize the oil recovery from POME. Optimization of transesterification parameters is required for high production yields and sustainable processing.

Keywords: Biodiesel, Palm oil mill effluent, Supercritical biodiesel production, Transesterification

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1 Introduction

The demand of the world's energy is rising steeply due to massive economic and population growth. Therefore, the reliability of energy on fossil fuel usage for economic growth having environmental issues is a question on its extensive usage [1]. The increase in oil prices, depletion of fossil fuel, low engine performance, threats of global warming, and crude oil reserves require better alternatives that must be renewable, economic, and environmentally friendly [2]. With the increase in pollution due to fossil-based fuels, mainly coal and natural gas, renewable sources such as biofuels are currently under consideration [3]. There has been a continuous increase in pollution and ozone depletion caused by these non-renewable energy fuels. The usage of fossil fuels-based energy reserves over many years has led to a rising global temperature, causing global warming due to the extensive release of carbon dioxide (CO_2).

There are two solutions recommended by researchers to overcome these issues. The first solution is to implement the use of renewable energy sources including wind, solar, tidal, nuclear, and geothermal energy to minimize the emission of greenhouse gases. The second way is to produce renewable fuels from wastes to minimize pollution [4]. Industrialists and researchers are more concerned with renewable energy resources to meet the energy demand as well as secure energy supply for an improved standard of living and environmental protection [5].

Among all renewable energy resources, biodiesel is a significant substitute fuel for conventional engines, being one of the biofuels with numerous advantages over fossil fuel diesel. It is biodegradable, nontoxic, and free from polluting compounds

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such as oxides of sulfur and aromatics. The characteristics of a fuel largely affect engine performance and emissions. The burning of fossil fuels is responsible for 85 % of the CO_2 emissions and 64 % of the total greenhouse gas emissions. The use of renewable and sustainable fuel such as biodiesel can lower the emission of toxic compounds due to complete combustion, thus having a strong potential to eliminate the energy crisis [6].

The release of the carbon-based compounds from the burning of biodiesel in the engines is less and has a much lower contribution in the emissions as compared to petroleum diesel. The burning of biodiesel emits CO_2 by 4.5 and 3 times lesser than gasoline and petroleum diesel, respectively [7]. However, despite less CO_2 emission, the NO_x emission from the combustion of biodiesel is slightly higher than that of petroleum diesel [8]. Nevertheless, biodiesel is an environmentally friendly fuel that significantly reduces the overall carbon emission and protects the climate. Moreover, it contains enough amount of oxygen needed for complete combustion. The characteristics of biodiesel are presented in Tab. 1.

Table 1. Physicochemical characteristics of biodiesel [9, 10].

Properties	ASTM D6751	ASTM D6751
Density at 15 °C [kg m^{-3}]	820–900	837.90
Cetane number, min	58	53.30
Acid number, max [mg KOH g^{-1}]	0.50	0.12
Water and sediment, max [vol %]	0.05	–
Pour point [°C]	–15 to –16	–13
Kinematic viscosity at 40 °C [mm^{2}s^{-1}]	1.9–6.0	2.67
Flash point, min [°C]	100–170	68

Tab. 1 presents the physiochemical characteristics of standard and pure diesel. The density, pour point, kinematic viscosity, and flash point of biodiesel and pure diesel are in a similar range. However, biodiesel has a higher cetane number in comparison with conventional petroleum diesel. There are plenty of feedstocks that can be utilized for the synthesis of biodiesel including algae oil, animal fats, vegetable oil, palm oil mill effluent (POME), and microbial sources [11]. Biodiesel produced from diverse feedstocks has different properties, e.g., structure, composition, purity, and cetane number [12]. Therefore, feedstock selection is the strategic stage for the biodiesel production process, which affects various factors, e.g., composition, cost, yield, and purity of biodiesel. A list of commonly used substrates for biodiesel synthesis is given in Tab. 2.

Biodiesel can be synthesized from numerous substrates including edible oils, non-edible oils, and waste oils as presented in Tab. 2. But, the use of edible oils is always an argument and creates a competition between food availability and fuel [19]. The use of edible oils as a substrate has negative effects on the environment due to its requirement of a larger area of land for feedstock cultivation. This causes deforestation especially in tropical regions including Indonesia and Malaysia, supplying more than 75 % of the total palm oil supply to the world. Continuation of this practice would damage flora and fauna, with influences culminating in weather changes. The application of non-edible oils to synthesize biodiesel is considerably beneficial in comparison with edible oils to avoid food crisis and make biodiesel a cost-effective process. However, oil extraction and processing for biodiesel synthesis is a complex process that increases the overall production cost [20].

Table 2. Commonly used feedstocks for sustainable biodiesel synthesis [13–18].

Edible oil	Non-edible oils	Animal fats	Other oil sources
Canola	Mahua	Fish	Poplar
Palm	Castor	Poultry fat	Microalgae
Peanut	Jatropha	Pork lard	Fungi
Soybean	Karanja	Chicken fat	Algae
Sunflower	Neem	Beef tallow	Olive stones
Barley	Rubber seed	Animal tallow	Biomass pyrolysis
Groundnut	Tall		Miscanthus
Wheat	Petroleum nut		
Rice bran	Jojoba		
Sesame	Babassu tree		
Tigernut	Silk cotton tree		
Walnut	Sylbum marianum		
Rapeseed	Linseed		
Olive	Pumpkin seed		
Raddish	Tobacco seed		
Mustard			

Waste/crude oils are the cheapest feedstocks available for biodiesel synthesis. The reason behind using these feedstocks is to divert the attention of using edible and non-edible feedstocks because of the higher cost of biodiesel synthesis. Nowadays, research is conducted on the utilization of waste resources as feedstocks for energy production as well as for the synthesis of catalysts to commercialize biodiesel production and minimize its cost. Waste oils are broadly classified into three groups, i.e., waste oil generated from food factories, non-food industry, and from houses and restaurants. Various types of waste oils, e.g., waste cooking oil (WCO), waste frying oil (WFO), crude palm oil, and grease oil have been utilized.

1.1 Palm Oil Mill Effluent

Waste oils including WCO and POME generated from palm oil mills can be utilized for biodiesel synthesis. The production of POME is directly dependent on the production of palm oil

using fresh palm fruit bunches. The global palm oil production is high and Malaysia and Indonesia are the top two suppliers of palm oil to the world by contributing 55.3 % and 33.7 % (27 million MT and 16 million MT), respectively, to the palm oil export globally in 2017/18 [21]. Palm tree cultivation and oil production was started in Malaysia in 1960. Palm oil production significantly increased from 0.1 million MT in 1960 to 16.05 million MT in 2018. Malaysia is exporting palm oil to more than 190 markets worldwide including West Asia, Africa, and the Indian subcontinent [22].

The exponential positive growth of the palm oil sector has made the palm oil industry to be one of the largest contributors to Malaysia's export, contributing more than 5 % to Malaysia's gross domestic product (GDP) [23]. The export revenue of Malaysia from palm oil is RM 64.24 billion, annually. The palm oil exports are expected to increase to 25.6 million MT annually in 2050. Palm oil requires less cultivation land, i.e., 0.26 ha, to produce 1 t of oil as compared to soybean, sunflower, and rapeseed requiring 2.2, 2.0, and 1.5 ha, respectively [24]. Malaysia exhibited an overall palm oil export of 29.4 %, utilizing 0.1 % of the global agricultural land. The higher demand for palm oil has increased the number of palm oil-producing mills in Malaysia. At present, more than 500 palm oil mills are operating. The palm oil sector provides job opportunities and supports two million livelihoods [10, 25].

The types of products obtained from palm oil mills, namely, palm oil and palm kernel oil, have a wide range of applications in food industries. The cost of palm oil is influenced by several factors including export duty, demand and supply, and nature of the palm oil production process. The price per ton of palm oil was RM 2136 and RM 2664 in 2015 and 2018, respectively [26]. The increment in cost was observed due to the rising demand for oil from importers including Egypt, the Philippines, and Pakistan. Due to the high price of palm oil in 2018, industrial biodiesel production decreased [27]. However, the production of biodiesel from palm oil was raised to 1 million MT in 2020.

It is clear that POME production will be proportionally increased by the supply of palm oil to the world [28]. About 90 wt % of fresh fruit bunches are discarded as wastes after palm oil production [29]. Moreover, only 10 wt % of palm fresh fruit bunches are converted to palm oil and the remaining 90 wt % goes directly to the waste in the form of sludge palm oil, palm fatty acid distillate, and POME. POME is a pollutant containing a high amount of oil and grease (4000–8000 mg L^{-1}), which is extremely high as compared to the allowable discharge limit, i.e., 50 mg L^{-1}. POME is a colloidal suspension containing 95–96 % water, 0.6–0.7 % oil, and 4–5 % total solids including 2-4 % suspended solids. The pH and total solids in POME are 4.7 and 40 500 mg L^{-1}, respectively. The physicochemical characteristics of POME are given in Tab. 3.

To reduce the oil content to the acceptable limit, several innovative technologies were considered by palm oil industries to process POME including aerobic and anaerobic decomposition or facultative digestion. Other than the organic treatment, the evaporation process has been recommended to process POME. Generally, the palm oil industrial waste is discharged into open ponds, allowing anaerobic digestion which produces methane. However, anaerobic digestion releases greenhouse gases like CO_2 into the atmosphere [31]. Nevertheless, methane is a valuable energy source; its application is limited to electricity production in industries and domestic purposes. Tab. 4 compares the both wastes, POME and WCO. WCO has a lot of disadvantages besides its benefits such as complex oil extraction process and difficult waste oil collection.

Table 3. Characteristics of POME as a biological waste [30].

Parameter/element	Value
pH	4.7
Chemical oxygen demand (COD) [mg L^{-1}]	50 000
Oil and grease [mg L^{-1}]	4000–8000
Biochemical oxygen demand (BOD) [mg L^{-1}]	25 000
Total solids [mg L^{-1}]	40 500
Suspended solids [mg L^{-1}]	18 000
Total volatile solids [mg L^{-1}]	34 000

One ton of palm oil produced from fresh fruit bunches (FFB) gives 240 L of POME. The amount of POME produced every year in Malaysia is increasing, i.e., in 2015, 60.88 million tons of POME was produced in Malaysia. The anaerobic digestion of POME leads to the formation of methane gas. Approximately 1 t of POME generates 28 m^3 of methane gas. The inappropriate methane gas release causes global warming. Therefore, researchers are searching for an alternative process to utilize POME waste to synthesize biodiesel.

1.2 POME as an Industrial Waste

As discussed in the previous section, the palm oil sector is considered as the backbone of the Malaysian economy, and the enormous quantity of POME has raised public and government concerns [10]. The current research is focused on the proper handling of this waste generated due to the synthesis of palm oil [32]. The implementation of significant techniques to convert the high quantity of biomass into valuable green energy sources or by-products are important for various applications. The residual material and energy sources of processed waste are taken for biomass production, fertilizers, animal feedstock, carbon capturing, fermentation medium, and biofuel and biogas production [33].

The generated waste from the palm oil industry can be classified into four main classes, i.e., POME, sludge palm oil, palm acid oil, and palm fatty acid distillate. POME is directly produced from palm oil mills while palm acid oil is extracted from POME. The palm fatty acid distillate is considered as a co-product of the palm oil industry rather than a generated waste. Similarly, sludge palm oil is contemplated as residual oil having different compositions of free fatty acid. Therefore, the wastewater and by-products can be produced as renewable energy sources [34]. They have the potential to generate renewables like biodiesel at reasonable cost of the overall process.

There are two types of palm oil industries including processing plants and refining plants. The wastewater produced from

Table 4. Comparison of POME and waste cooking oil as a potential substrate.

Palm oil and its waste	Waste cooking oil
Advantages	
4000 kg ha^{-1} of palm oil is produced.	It gives food security a guarantee and energy security.
Indonesia and Malaysia contribute 85 % of palm oil production.	Direct and indirect jobs.
The high amount of palmitic acid is suitable to produce biodiesel. It gives a biodiesel yield of ~ 96.5 %.	70 % of waste cooking oil can be recovered and converted to biodiesel.
Palm biodiesel shows good storage properties.	Emission of gases is low, 48 % less CO, 47 % less particulate matter, and 67 % less HCs.
The CO_2 emission from the burning of palm biodiesel is 38 % lower as compared to waste cooking oil biodiesel [9].	
Good low-temperature flow properties.	
Palm trees can be an excellent sink of CO_2 than rainforests. It consumes 64.5 t CO_2 ha^{-1}.	
Waste of palm oil industry (POME) can be utilized as a low-cost feedstock to produce biodiesel.	
POME is available in large amounts and recovery of crude palm oil is higher.	
Palm oil-related industrial sectors have given benefits to six million people around the world.	
Disadvantages	
Biodiesel from palm oil is not enough to compensate for global biofuel production.	Waste cooking oil to biodiesel conversion process is complex.
It creates competition between food sources and oil prices.	The storage properties of WCO biodiesel are poor.
Land disputes and social challenges	The flow properties of WCO biodiesel are not poor as compared to palm biodiesel.
Balance is needed between market demands and consumer perceptions.	Manpower is required for transportation, storage, and installation purposes.
	Low recovery rate.
	Limited availability of feedstock.
	Lack of efficient economic incentives.
	The biodiesel cost synthesized from waste cooking oil will be higher.
	Biodiesel purification is needed which diminishes the advantage of waste cooking oil.

the refining plant is less polluted as compared to that of the milling plant due to the unavailability of oil, grease content, and less organic content. The wastewater produced from the milling plant is more contaminated due to the presence of water, palm waste oil, microorganisms, solid fats, and other toxic impurities [35]. Although wastewater generated from palm oil milling plant is nontoxic, it must be processed due to the high acid content and biological oxygen demand.

In the synthesis of biodiesel, 75 % of production cost is covered by the feedstock itself. Therefore, the use of low-grade industrial waste palm oil can significantly decrease the production cost. The sludge palm oil recovered from POME has a high oil content that can be processed for biodiesel synthesis [36]. The remaining POME has biological components that can be further converted into biogas. The positive energy yield ratio is one of the major factors to consider the sustainability of biodiesel. The palm biodiesel exhibits an output to input energy of 3.53 which is significantly higher as compared to other substrates used for biodiesel production [37]. Moreover, palm biodiesel production is environmentally safer and releases 38 % less CO_2 per liter of burning.

The present review highlights comparative studies on biodiesel production processes along with the research gaps for POME as a substrate [33]. The advantage of supercritical technology is also emphasized, and recommendations to utilize the POME as a feedstock are critically reviewed and focused on.

The advantages of using palm oil waste effluent for biodiesel synthesis are discussed in detail along with techno-economic analyses. The economic factors affecting biodiesel production using supercritical technology are comprehensively described, expressing the suggestions to utilize it in an effective way of synthesizing biodiesel. Therefore, the originality of this overview lies in the economic feasibility as well as future recommendations based on supercritical biodiesel synthesis.

2 Processes of Biodiesel Synthesis from POME

Various technologies have been developed for producing biodiesel from POME. The POME can be processed as a substrate via various transesterification technologies such as direct blending, microemulsion, pyrolysis, microwave-ultrasound-assisted, and supercritical methods as illustrated in Fig. 1 (see Sect. 2.4).

2.1 Direct Blending

The application of pure edible oils and residual palm oil extracted from POME as a diesel fuel blend was common in the 19th century. But research in the mid of the 20th century proved that the direct usage of blending of edible oils and residual oil extracted from POME is inappropriate for engines causing intrinsic failure [38]. Gad et al. [39] reported the performance of blending pure palm oil and biodiesel synthesized from it with various blending ratios. The volume percentages of diesel, biodiesel, and palm oil blends were kept at 20 % and 100 % as B20, B100, and PO20. The physicochemical characteristics were analyzed and found to be identical to pure diesel. The thermal stability of biodiesel and its blends were reported lower than that of conventional diesel [39].

Fuel consumption via direct blending was higher because of the lower energy value of biodiesel and its various mixtures. The toxic emissions were found to be lowered for biodiesel blends but enhanced for palm oil blends compared to petroleum diesel [40]. This occurred due to the cleaner and environmentally safer nature of biodiesel and its blends. Prabhu et al. [41] investigated the performance of diesel engines using palm oil blending with pure diesel. The palm oil was continuously heated at 60 °C to ensure the homogeneity of the blended mixture [41]. The study was focused on the exhaust emissions to compare the performance with the engine working on pure diesel. It conducted for palm oil subjected to heat, diesel blends (PO20, PO30, and PO40), and pure diesel under a constant stirring of 1500 rpm [41]. The results indicated that PO20 was the appropriate blend among the blends studied.

Ge et al. [42] investigated the performance of diesel engines operated on palm oil recovered from POME via blending with conventional diesel. The engine performance and combustion properties of the B30 blend showed the potential to effectively reduce the particulate matter emissions and simultaneously kept NO_x emissions at minimized levels. Bari and Hossain [43] studied the physicochemical characteristics of biodiesel derived from palm oil and evaluated the engine exhaust characteristics operating on sludge palm oil. The emissions of carbon monoxide (CO) and unburnt hydrocarbons (HC) were better with sludge palm oil diesel (POD) having CO 51 % and HC 55 % lesser emissions as compared to the petrodiesel operating engine, respectively [43]. However, the NO_x emission with POD was 33 % higher than that with petrodiesel. The engine operated with POD performed smoothly, did not show any startup problems, and no audible engine knocking was observed.

Uslu [44] studied the performance of direct blending with various palm oil-diesel blends tested on single-cylinder diesel engines under the influence of various engine loads. This study was conducted for optimization using response surface methodology. The responses were observed as 69.11 %, 196.25 ppm, 0.126 %, and 189.764 ppm, respectively, for smoke, NO_x, CO, and HC with 17.88 % blending [44]. The energy consumption for the engine using unblended oils was identified as fossil fuel diesel because both exhibit the same calorific value (45.5 MJ kg^{-1}). The oil-to-diesel blending ratio of 1:10 to 1:20 is successful for proper combustion in the engines [45]. However, the use of residual palm oil extracted from POME as a direct fuel in diesel engines demands engine modifications, including change of construction material, otherwise the engine operation time is lowered, maintenance costs are also higher due to the increase in wear, and the chances of engine failure are augmented. Some diesel engines run on unblended edible oils like direct fuel ignition and compression engines, but these are not commonly applied in public transport vehicles which limits the use of this technique.

2.2 Microemulsion

The application of vegetable oil as a direct fuel is not safe for engines due to their high viscosity that can damage the engine through choking and incomplete combustion. This problem was solved by microemulsions using methanol, ethanol, and 1-butanol of biodiesel. In biodiesel microemulsion, there are different components present like a surfactant, alcohol, vegetable oil, and cetane improver. Short-chain alcohols are generally used as viscosity-suppressing agents. Similarly, the longer-chain alcohols are commonly applied as surfactant agents and alkyl-based nitrates are added to increase the cetane number. For this purpose, the microemulsion process with the help of some alcoholic solvents has been investigated.

Devarajan et al. [46] analyzed the combustion characteristics and exhaust properties of a refined palm oil biodiesel (POBD) blended with pure diesel using silver oxide (Ag_2O) as a fuel additive [46]. The experimental findings exhibited that the addition of Ag_2O particles to POME enhanced the combustion characteristics due to the increased surface area. Besides, the addition of Ag_2O nanoparticles to POME resulted in enhanced brake thermal efficiency [46]. The findings also indicated that Ag_2O nanoparticles improved the emission levels of smoke, NO_x, HC, and CO [46]. Prabhu et al. [41] reported on the influence of microemulsion on palm oil blending with conventional diesel. For this purpose, *n*-butanol (20 vol %) was mixed with a 20 % palm oil diesel blend [41]. The CO emission from palm oil diesel and butanol was observed to be 37.5 % lower,

whereas the NO_x release was 1.9 % higher than from conventional fuel. Moreover, the smoke emission was found 13 % lower, compared to petroleum diesel [41].

Charoensaeng et al. [47] studied the combustion characteristics of palm-biodiesel blends using ethanol as a microemulsifier, methyl oleate as a surfactant, and alkanols as a cosurfactant. The evaluated microemulsion enhanced the burning of fuel and decreased the NO_x emissions and exhaust gas temperature. However, no considerable change in CO emission was observed. Apart from various advantages, the drawback of using the microemulsion process is carbon deposition and incomplete combustion of fuel in the diesel engines. The incomplete fuel combustion in the engine leads to huge energy loss and higher consumption of fuel.

2.3 Pyrolysis

Pyrolysis is the breakdown of a longer-chain molecule into smaller-chain molecules using thermal energy in the absence of oxygen or employing heat using the catalyst. In this technique, larger molecules are broken, and the formation of smaller molecules takes place. This technique is more prominent in the areas where the hydroprocessing industry is well grown because of the similar nature of technology to the petroleum refining process [48]. The pyrolysis of soybean, palm, POME, and castor oils have been evaluated in the past [49–51]. Yang et al. [52] studied the pyrolysis of palm oil to produce CO, CO_2, H_2, and CH_4. The yield of H_2, and CH_4 increased with residence time. However, the overall yield of pyrolysis was 70 %. This happened due to the side reactions taking place, produced CO and CO_2 which were not the desired products [52].

Chow et al. [53] studied the pyrolysis of empty fruit bunches and POME to produce bio-oil. Due to the sludge present in POME, a lower bio-oil yield was observed as the sludge percentage was increased from 0 % to 100 %. Teoh et al. [54] studied the co-pyrolysis of empty fruit bunches and palm kernel shell (PKS) with POME pyrolysis. Pyrolysis and co-pyrolysis were performed at 60 °C. The bio-oil yield obtained from PKS was 44.5 $\pm$ 0.7 wt %. The bio-oil yield for co-pyrolysis of PKS and POME sludge showed a negative effect on bio-oil.

Lam et al. [55] conducted pyrolysis to effectively utilize POME. The biochar was produced and then utilized as an adsorbent to remove the impurities from POME. A removal efficiency of 57 % was achieved for POME. Thermal cracking and pyrolysis are disadvantageous for a moderate biodiesel production capacity, especially for developing countries. The pyrolysis process is considered a multipart process because of various complex reaction paths [56].

2.4 Transesterification

The most commonly applied way of synthesizing biodiesel is transesterification, in which the alcohol and oil reaction takes place using a catalyst to synthesize biodiesel and glycerol [57]. The common reaction between oil and alcohol to produce biodiesel is depicted in Fig. 1.

Fig. 2 demonstrates the common transesterification reaction for biodiesel synthesis. The conversion of triglycerides to diglycerides is the first step of alcoholysis, which are then converted into monoglycerides. Monoglycerides are finally converted into glycerol, yielding one mole of fatty acid methyl ester in each step.

2.5 Catalytic Transesterification of POME

Transesterification of triglycerides occurs by heating them with alcohol as a catalyst. The catalysts are generally categorized in two general classifications, i.e., homogeneous and heterogeneous types as presented in Fig. 3. The homogeneous and heterogeneous transesterification can be catalyzed by acid and alkali catalysts. The enzymatic-catalyzed transesterification involves the use of extracellular and intracellular enzymes to boost up the biodiesel yield [59].

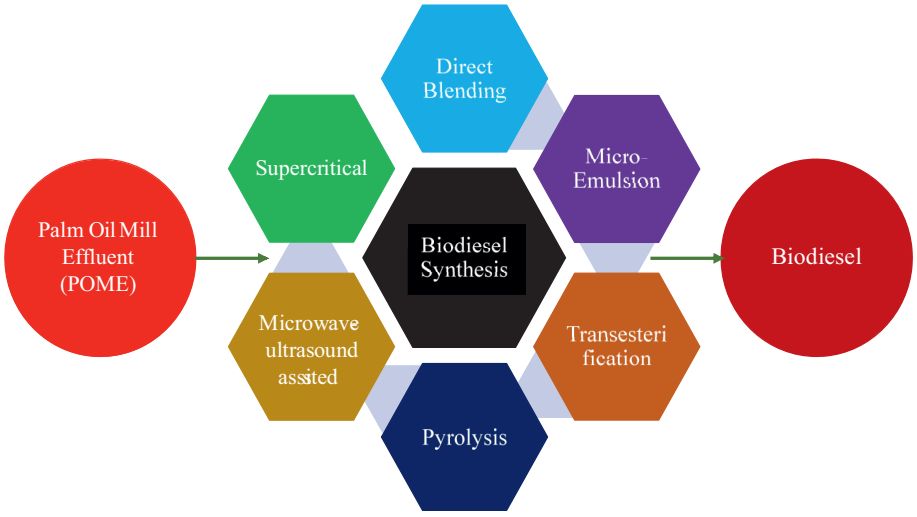


Figure 1. Production of biodiesel from POME using various technologies.

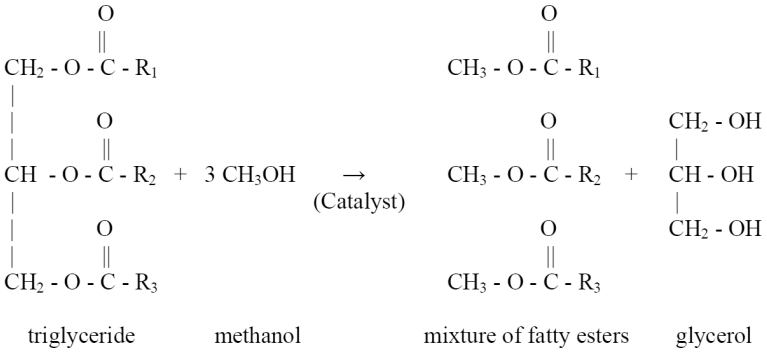


Figure 2. Transesterification process to produce biodiesel [58].

2.5.1 Homogeneously Catalyzed Transesterification

A biodiesel yield of more than 99 % can be obtained using homogeneous catalysts [60]. There are two types of homogeneous catalysts that are employed to synthesize biodiesel including, namely, homogeneous alkali catalysts and homogeneous acid catalysts. Fig. 4 displays a schematic flow diagram for generalized homogeneously catalyzed transesterification.

According to Fig. 4, base-catalyzed transesterification involves the use of a base catalyst to enhance the productivity of the reaction. However, the application of such catalyst causes soap formation due to the presence of triglycerides, contaminating the product [61]. Therefore, glycerol and alcohol are separated by gravity separation and vacuum distillation following the separation of soap from the product.

2.5.1.1 Homogeneous Alkali-Catalyzed Transesterification

Biodiesel production commonly takes place using base catalysts because of several advantages over acid catalysts. The base-catalyzed transesterification provides a faster reaction rate, it is 4000 times faster than acid-catalyzed transesterification if the same amount of acid catalyst is used [62, 63]. The homogeneous alkali-catalyzed transesterification is applied for industrial biodiesel production due to several reasons: faster reaction rate, higher activity of catalyst, and widely available and economically feasible process [64]. The most commonly used alkali catalysts are NaOH, KOH, and sodium methoxide. Other alkali catalysts include sodium ethoxide [65], potassium methoxide [66], sodium iso-propoxide [67], and sodium butoxide [60].

Metawea et al. [68] investigated the use of sludge palm oil to produce biodiesel via homogeneous alkali catalysis. The operating parameters were analyzed and optimized in a batch reactor. The effect of extended baffles present in the reactor on the yield of biodiesel was evaluated. The optimized transesterification conditions giving the highest biodiesel yield (97 %) were methanol-to-oil molar ratio of 6:1, 60 °C reaction temperature, catalyst concentration 1 wt % NaOH, and a mixing speed of 250 rpm [68]. Mujtaba et al. [69] examined the influence of KOH on the transesterification of residual palm oil using response surface methodology. The biodiesel yield was 96.61 % under the optimized parameters of reaction time of 38.96 min, methanol-to-oil ratio of 60 vol %, and KOH loading of 0.70 wt %.

Manurang et al. [70] reported on the synthesis of biodiesel using sludge palm oil via NaOH-catalyzed transesterification. The operating conditions for transesterification reaction were: 1 wt % NaOH catalyst, mixing rate of 400 rpm, and 1 h reaction time. The biodiesel yield of 83.19 % was achieved under the optimized conditions. In another study, Boonpoke et al. [71]

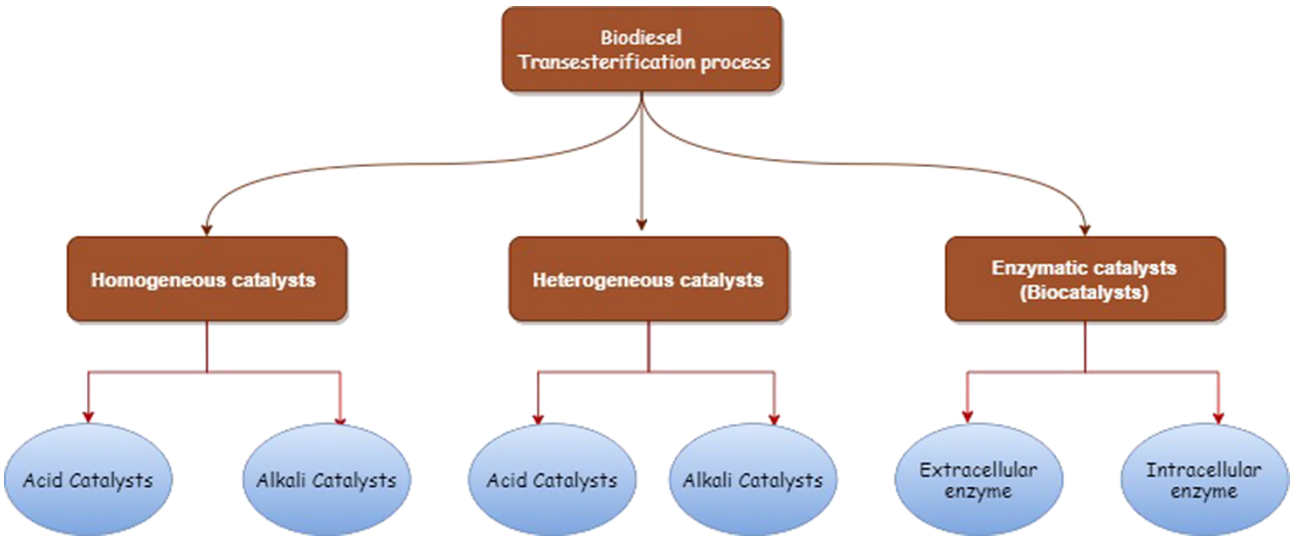


Figure 3. Classification of transesterification for biodiesel production [58].

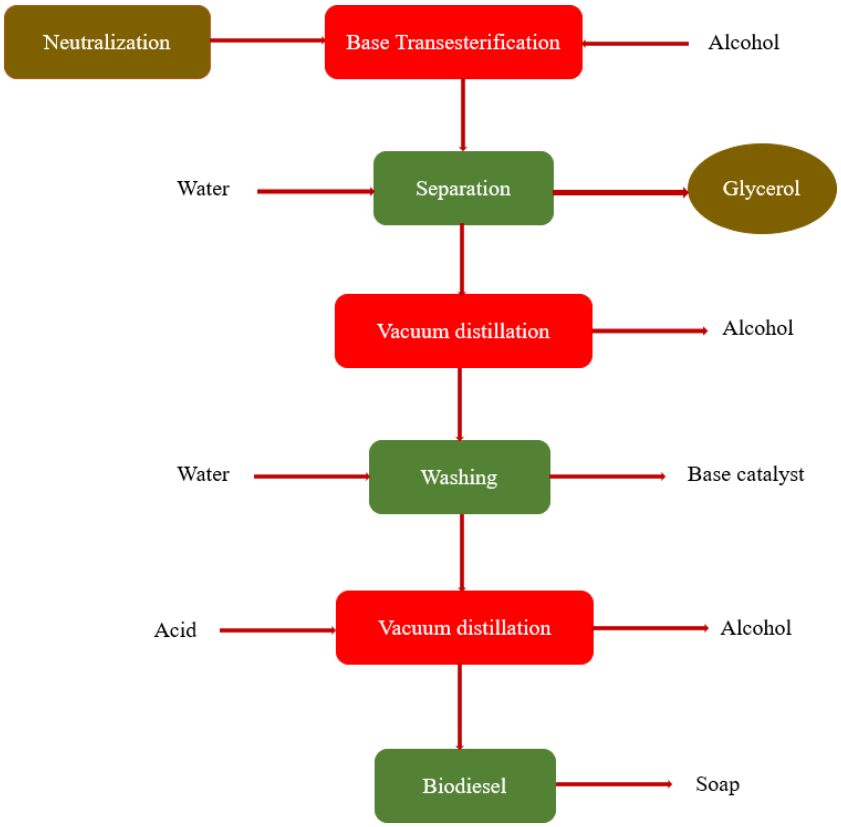


Figure 4. Schematic diagram for homogeneously catalyzed transesterification.

evaluated the influence of alkali-catalyzed transesterification of residual palm oil. The operating conditions were 1 wt % KOH catalyst, reaction temperature of 60 °C, agitation rate of 300 rpm, and 60 min reaction time resulting in the optimized yield of 84.0 % [71]. It can be noted that the biodiesel yield using KOH was higher as compared to NaOH due to the lower KOH affinity towards soap formation.

Hayyan et al. [72] determined the effect of *p*-toluene-4-sulfonic monohydrate acid to synthesize biodiesel from residual palm oil for the reaction conditions of 1 wt % KOH, reaction temperature of 60 °C, agitation speed of 400 rpm, and 60 min reaction time, resulting in the optimized yield of 76.60 %. A significant lower yield was observed as compared to Boonpoke et al. [71]. Sianipar et al. [73] studied the homogeneous alkali-catalyzed transesterification of sludge palm oil recovered from palm oil mill waste. Transesterification was performed by varying the reaction conditions of KOH loading of (0.5–2.5 wt %) at 60 °C and an agitation speed of 300 rpm for 1 h reaction time. The optimum molar ratio of methanol to palm oil sludge was 20:1 resulting in 93 % biodiesel yield.

Ilham et al. [74] investigated the production of fatty acid methyl esters via alkaline transesterification of residual palm oil. The maximum biodiesel yield of 95 % was achieved under the optimum transesterification conditions of alcohol-to-oil molar ratio of 6:1, 1 wt % NaOH loading, reaction temperature of 60 °C, and reaction time of 30 min. Aworanti et al. [75] described the production of biodiesel from POME in the presence of KOH. The process parameters were varied including methanol-to-oil ratio (1:1–12:1), catalyst loading (0.1–2 wt %), and reaction time (30–150 min). The optimized conditions were a molar ratio of 12:1, catalyst loading of 1.5 wt %, and 30 min reaction time. A biodiesel yield of 61.20 % was achieved under the optimized conditions [75].

The limitations of the process include its sensitive nature to the purity of reactants, free fatty acid (FFA) content as well as the moisture content of the feedstock. The basic catalyst that affects the separation of biodiesel and glycerine cause to increase in the wastewater generated during the purification step [76, 77].

2.5.1.2 Homogeneous Acid-Catalyzed Transesterification

The homogeneous acid catalysis includes hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sulfonic acid, ferric sulfate, and organic sulfonic acid. Among these acids, HCl [78], H_2SO_4 [79], and sulfonic acid are the most commonly used [80]. Hayyan et al. [81] reported the transesterification of sludge and residual palm oil under the operating conditions of H_2SO_4 loading of 0.75 wt %, reaction temperature of 60 °C, methanol-to-oil molar ratio of 8:1, mixing speed of 400 rpm, and 60 min reaction time. The biodiesel yield of 83.1 % was achieved under these conditions.

The operating conditions of this study were kept the same as the literature work discussed for homogeneous alkali-catalyzed transesterification. The achieved biodiesel yield was comparable with homogeneous catalysts. Davies et al. [82] investigated the esterification of POME using H_2SO_4. A biodiesel yield of 89 % was attained under the optimized conditions of reaction time (15 min), catalyst loading (0.8 wt %), and reaction temperature (60 °C). The findings indicated that the optimized conditions were a methanol/oil molar ratio of 10:1 and a reaction temperature of 60 °C giving 95 % biodiesel yield.

Nikhom et al. [83] produced biodiesel from residual oil recovered from POME. The ester and FFA recovery were 56.9 wt % and 38.1 wt %, respectively, proving the potential to be used as a substrate in the esterification process. The optimized conditions for the esterification of the recovered oil were 5 wt % H_2SO_4, alcohol-to-oil molar ratio of 2:1, a reaction temperature of 70 °C, and a reaction time of 120 min. Under the optimum conditions biodiesel having the purity and yield of 97.7 wt % and 98.5 wt.% could be produced. dos Santos et al. [84] described biodiesel synthesis from hydro-esterification of crude palm oil using methanol as a solvent. The study was conducted in a batch reactor under the optimum conditions of reaction temperature of 250 °C, reaction time of 120 min, 100:1 water-to-oil molar ratio, and mixing speed of 700 rpm. The results indicated the highest biodiesel yield of 86 % [84].

Sundaryono et al. [85] reported on the esterification of sludge palm oil extracted from POME using H_2SO_4. The reaction was carried out varying the reaction conditions of methanol-to-oil molar ratio of 6:1, 1 wt % catalyst loading of H_2SO_4, reaction time of 3 min, and reaction temperature of 60 °C. The maximum biodiesel yield of 75.3 % was achieved under these conditions. The limitations of homogeneous acid-catalyzed transesterification lie in the corrosion of equipment, extensive waste generated from neutralization, difficult recycling, formation of by-products, elevated reaction temperature, higher reaction time, and lower catalyst activity [86, 87].

2.5.2 Heterogeneous Acid- and Alkali-Catalyzed Transesterification

Heterogeneous catalysis is more advantageous than homogeneously catalyzed transesterification. In heterogeneous catalytic transesterification, it is much easier to collect the product from the catalyst after reaction completion. The heterogeneous catalytic process is presented in Fig. 5. The series of unit operations involved in the production of biodiesel using acid as a catalyst is illustrated. Transesterification in the presence of a catalyst produces biodiesel and glycerol [88]. Glycerol is separated by a gravity separator and alcohol by vacuum distillation.

The application of alkali catalysts dominates the other techniques since the catalysts are reusable and environmentally safer than heterogeneous acid catalysts [89]. These catalysts can be easily extracted from cheaper sources like limestone and calcium hydroxide. Ho et al. [90] reported the influence of a CaO catalyst on the alcoholysis of sludge palm oil. The operating conditions of 6 wt % catalyst loading, alcohol-to-oil molar ratio of 6:1, reaction temperature of 45 °C, 3 h reaction time, and 700 rpm mixing rate led to a biodiesel yield and fatty acid methyl ester (FAME) conversion of 79.76 % and 97.09 %, respectively [90].

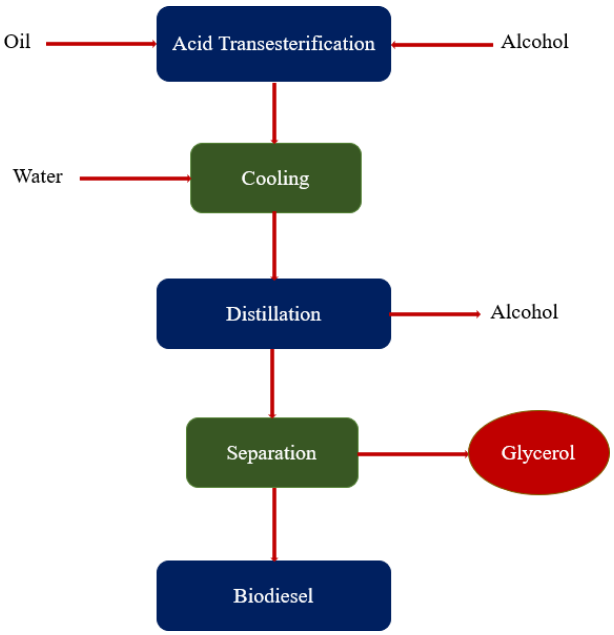


Figure 5. Schematic diagram for heterogeneously catalyzed alcoholysis for biodiesel synthesis.

Nur et al. [91] investigated the transesterification of palm oil using modified Malaysian dolomite as a catalyst and compared the findings with the inactivated ZnO catalyst. The results indicated that the maximum conversion of 99.98 % under the reaction conditions of 15:1 methanol-to-oil molar ratio in 4 h in comparison with the ZnO-doped catalyst was achieved. The biodiesel yield was quite higher as compared to other heterogeneous alkali inactivated catalysts [91]. More active sites present on the catalyst surface caused the increase in biodiesel yield.

Hidayat et al. [92] examined the influence of the catalyst ZrO_2/SO_4^{2-} on the transesterification of sludge palm oil recovered from POME. The catalyst was synthesized by sulfonation of rice husk. The influences of alcohol-to-oil molar ratio (4:1–10:1) and reaction temperature (40–60 °C) were investigated for the conversion of triglycerides to optimize the operating conditions [92]. Manurung et al. [70] produced biodiesel from SPO at an oil-to-alcohol molar ratio of 1:2, reaction temperature of 80 °C, and mixing speed of 400 rpm, and reaction time of 1 h. The maximum biodiesel yield of 83.19 % was found under the optimized conditions [70].

Uprety et al. [93] evaluated the effect of Al_2O_3 as catalyst support in the presence of CaO as a heterogeneous catalyst for the transesterification of residual palm oil. CaO/Al_2O_3 and CaO gave the highest biodiesel yields of 97.66 % and 96.75 %, respectively. The aluminum support provided to the catalyst significantly increased the biodiesel yield. Feng et al. [94] produced biodiesel from residual palm oil using acid ionic liquid $[CyN_{1,1}PrSO_3H][p\text{-TSA}]$ as a heterogeneous catalyst. The optimum operating conditions were: methanol-to-oil molar ratio of 24:1, catalyst concentration of 3.0 wt % of oil, reaction temperature of 120 °C, and 150 min reaction time, resulting in 98.4 % biodiesel yield [94]. The findings showed a significant increase in biodiesel yield in 2.5 h for a Brønsted acid ionic catalyst and proved its potential to catalyze the transesterification reaction.

Usman et al. [95] synthesized biodiesel from palm oil using ash-impregnated zeolite (Sn-PBA-zeolite) as a heterogeneous catalyst. The optimized conditions for alcoholysis by using Sn-PBA-zeolite of 1:4:1:25 weight ratio were: palm oil-to-methanol molar ratio of 1:6, catalyst loading 3 wt %, and reaction time of 3 h [95]. The maximum biodiesel yield of 76.21 % was reported under the optimized transesterification conditions.

Ngaini et al. [96] reported on the transesterification of POME using a silica-based catalyst prepared from *Imperata cylindrica* sp. imperatacid. The optimum transesterification conditions were alcohol-to-oil molar ratio of 1:1, catalyst concentration of 10 wt %, and reaction temperature of 65 °C resulting in 80 % biodiesel yield. The reported biodiesel yield is lower due to the milder reaction conditions kept during the reaction [96]. In another study, the transesterification of palm fatty acid distillate was described by Ngaini et al. [97] using the heterogeneous silica-based catalyst prepared from rice husk. A biodiesel yield of 91.6% was achieved under the optimized esterification conditions of PFAD:MeOH ratio of 1:1 and catalyst loading of 5 wt %, followed by transesterification at an oil:MeOH ratio of 1:1 giving 97.5 % biodiesel yield in 30 min.

Ding et al. [98] produced biodiesel from palm oil using [HSO_3-BMIM]HSO_4 as a heterogeneous catalyst. The transesterification reaction occurred under microwave heating. The highest yield of 98.93 % was observed when the methanol-to-oil molar ratio, catalyst concentration, microwave power, and reaction time were 11:1, 9.17 %, 168 W, and 6.43 h, respectively. Balan et al. investigated the esterification of palm oil using a heterogeneous catalyst derived from rice husk in the presence of methanol. Rice husk 600 (RH600) was employed to catalyze the esterification reaction and gave an overall biodiesel yield of 97 % [99].

Hasanudin et al. [100] obtained biodiesel from residual palm oil using tungstate-zirconia as a heterogeneous catalyst. The optimized transesterification conditions were: catalyst loading of 10 %, methanol-to-oil molar ratio of 8:1 resulting in triglycerides-to-biodiesel conversion of 74.88 %. The heterogeneous catalyst activity is similar to that of alkali catalysts under the effect of the same reaction conditions. However, heterogeneously catalyzed transesterification reaction is facing issues, i.e., it is slower in nature [101] and the catalyst is needed to activate at high temperatures.

2.5.3 Enzymatic-Catalyzed Transesterification (Biocatalysts)

The enzyme catalyst, also known as biocatalyst, is considered a green-energy method for biodiesel production. The usage of a biocatalyst is advantageous due to its capability to remove the downstream unit operations needed in base-catalyzed reactions. Biodiesel of high purity can be obtained using enzyme-catalyzed transesterification [102]. Rakkan et al. [103] optimized the synthesis of biodiesel from POME in the presence of methanol via enzymatic-catalyzed transesterification. The optimized conditions for biodiesel synthesis include enzyme concentration of 40 kUnit, methanol-to-oil molar ratio of 6:1, agitation speed of 250 rpm, reaction temperature of 40 °C, and reaction time of 12 h. The maximum biodiesel yield of 91.45 % was achieved under the optimized reaction conditions. Due to the slower nature of enzymatic-catalyzed transesterification the reaction was completed with in 12 h, making it not feasible for biodiesel synthesis.

Matinja et al. [104] produced biodiesel from POME using *Candida rugosa* lipase enzyme and methanol as a solvent. The highest triglyceride conversion was achieved at an agitation speed of 300 rpm, oil-to-alcohol molar ratio of 1:6, and 5 h reaction time. The properties of biodiesel produced using the enzymatic-catalyzed transesterification were according to the ASTM standards of biodiesel. Louhasakul et al. [105] cultivated *Yarrowia lipolytica* in POME for biodiesel production and achieved 97 % biodiesel yield at 72 h reaction time and 60 °C.

Rachmadona et al. [106] investigated the effect of lipase and ethanol to synthesize biodiesel from POME. The optimum conditions were 2100 U lipase loading, ethanol-to-triglycerides molar ratio of 4:1, 40 °C reaction temperature, 24 h reaction time, resulting in 97.43 % biodiesel yield. However, there are a lot of constraints of this process especially when implemented for commercial-scale production such as the high cost of the enzyme, slow reaction rate, and enzyme deactivation [107].

2.5.4 Microwave-Assisted Transesterification

Microwave heating is non-contact heating that avoids the chances of overheating the material. It has several advantages like direct energy transfer instead of heat transfer, reduced thermal gradients, faster response regarding the start-up and shutting, and reversible thermal effects [108, 109]. The microwave-assisted heating process is explained in Fig. 6.

The conventional heating via hot plate heats the outer layer of the bulk of the liquid and afterwards it penetrates with the help of convection. However, the microwave heating phenomenon takes place due to the effect of microwaves and heating occurs in the entire liquid at one time. Therefore, microwave heating is faster than conventional heating, causing a higher biodiesel yield in minimum time. Davies et al. [82] reported the single-step esterification-transesterification of POME for biodiesel production via microwave heating. The reaction conditions were kept at reaction temperatures of 100–150 °C, catalyst loading of 0–1, and reaction time of 0–30 min. The maximum biodiesel yield of 89 % was achieved at 150 °C and a reaction time of 15 min. The microwave heating significantly reduced the time to obtain the highest biodiesel yield as compared to conventional heating.

Muanruksa et al. [111] used sludge palm oil extracted from POME for biodiesel production to utilize it as a low-cost substrate at reaction temperatures of 30–50 °C, molar ratios of methanol to oil of 1:1 to 5:1, mixing speeds of 100–300 rpm, and reaction time of 4 h. Equilibrium was reached at the reaction temperature of 40 °C, methanol-to-oil molar ratio of 3:1, and mixing speed of 200 rpm. Under the optimized reaction conditions, a maximum biodiesel yield of 91.30 % was achieved. Rakkan et al. [103] optimized the synthesis of biodiesel from POME in the presence of methanol via enzymatic-catalyzed transesterification under the influence of microwave heating. A maximum biodiesel yield of 91.45 % was found under the optimal reaction conditions.

Bakar et al. [112] investigated the synthesis of biodiesel from sludge palm oil and compared the findings with biodiesel production using conventional heating. A maximum biodiesel yield of 95.1 % at a methanol-to-oil molar ratio of 6:1, reaction temperature of 65 °C, reaction time of 15 min, and 2 wt % KOH loading using microwave heating was achieved compared to the conventional method for which a yield of 81 % was gained under the same reaction conditions.

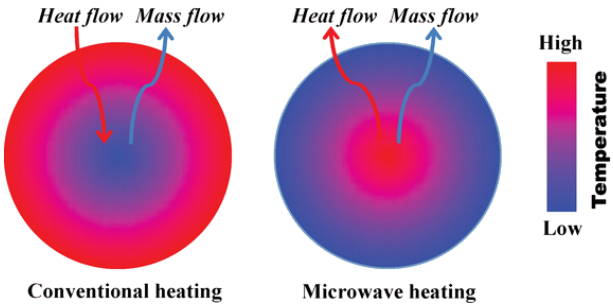


Figure 6. Heating mechanism comparison for conventional and microwave methods [110].

Apart from the advantages of microwave-assisted biodiesel production, it is not easy to upgrade from laboratory small-scale synthesis to commercial multi-ton plant capacity. The main drawback is associated with the depth of the penetration of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric characteristics [113]. A summary of biodiesel production from residual palm oil using various homogeneous and heterogeneous catalysts is presented in Tab. 5.

The maximum biodiesel yield and triglyceride conversion can be obtained using heterogeneous solid-acid catalysts in the presence of methanol at the reaction temperature of 60 °C and alcohol-to-oil molar ratio of 15:1. The application of biocatalysts is advantageous over homogeneous and heterogeneous transesterification, but the overall enzymatic catalytic transesterification process is expensive [114]. The best technology to convert POME into biodiesel known at the moment is the supercritical technology. The production of biodiesel from POME is discussed in detail in the next section.

2.5.5 Supercritical Biodiesel Synthesis Using POME

Biodiesel production using supercritical transesterification is advantageous over the other biodiesel production processes. The production of biodiesel by this technology from POME is an advanced technique that can be implemented for industrial-scale production.

Anaerobic digestion of POME produces methane and CO_2 having significant negative effects on the ozone layer. Therefore, to minimize the CO_2 emission and meet the energy demand, POME should be converted into biodiesel by using supercritical technology instead of anaerobic digestion. Among the available technologies to produce biodiesel, the supercritical technology seems to be the best option. Song et. al [115] used POME to produce biodiesel without any catalyst in a batch reaction with supercritical methanol. The methyl oleate content was increased by raising the molar ratio of the supercritical solvent. The increase in temperature beyond 350 °C resulted in a reduction in biodiesel yield due to the thermal degradation of methyl esters [115]. It can be observed that the supercritical reaction has a high energy requirement when POME was used as feedstock.

da Costa et al. [116] studied the influence of co-solvent and transesterification reaction parameters for biodiesel synthesis from residual oil extracted from palm oil waste. The yield of 99 % was achieved for FAMEs with optimum conditions of methanol-to-oil molar ratio of 42:1, 350 °C, and 5 min. The maximum biodiesel yield was obtained within 5 min which is significantly lesser time as compared to conventional catalytic transesterification.

Klabsong et al. [117] studied the supercritical methanolysis of POME without the application of a co-solvent. The reaction took place at 220–250 °C, 30 bar, and reaction times of 1–4 h. The optimum yield of 77.64 % was reported for optimum reaction conditions of 229 °C and 30 bar [117]. A lower biodiesel yield was obtained due to the lower temperature, i.e., below supercritical temperature. The most appropriate temperature for biodiesel production using supercritical technology is 350 °C.

Sootchiewcharn et al. [118] investigated the influence of temperature in the range of 330–370 °C on the transesterification of refined palm oil extracted from POME under a pressure of 200 bar and oil-to-alcohol ratio of 1:50. The optimum biodiesel yield of 78.3 % was achieved at 350 °C. Tab. 6 presents the research work done on the synthesis of biodiesel from POME using supercritical technology in the past.

Tab. 6 indicates that supercritical biodiesel production takes place at high temperature and pressure, requiring a significant amount of energy. Moreover, it also demands high startup costs and costs associated with the recovery of supercritical solvents. Therefore, the process optimization is inefficient and time-consuming because of the consumption of waste as substrate for biodiesel production. However, the presence of CO_2 as a co-solvent decreases the severity of the reaction, giving maximum biodiesel yields [45].

Table 5. Literature summary of biodiesel production using different catalysts.

Feedstock	Solvent	Catalyst	Conditions	Yield [%]	Ref.
Sludge palm oil	Methanol	NaOH	65 °C, 6:1, 250 rpm	97	[68]
Sludge palm oil	Methanol	KOH	39 min, molar ratio (60 vol %)	96.62	[69]
POME	Methanol	KOH	60 °C, 400 rpm, 60 min	76.6	[72]
Residual palm oil	Methanol	KOH	60 °C, 300 rpm, 60 min	84	[71]
POME	Methanol	H_2SO_4	60 °C, 400 rpm, 60 min	83.1	[81]
POME	Methanol	H_2SO_4	60 °C, 15 min	89	[82]
Sludge palm oil	Methanol	CaO	45 °C, 700 rpm, 180 min	79	[90]
Sludge palm oil	Methanol	Modified dolomite	60 °C, 15:1, 240 min	99.98	[95]
POME	Methanol	–	40 °C, 720 min, 250 rpm	91.45	[103]
POME	Methanol	Crude lipase	6:1, 300 min, 300 rpm	–	[104]
POME	Methanol	*Yarrowia lipolytica*	60 °C, 72 h	97	[105]

Table 6. Literature summary of POME as a substrate for biodiesel synthesis.

Feedstock	Solvent	Co-solvent	Conditions	Process	Yield [%]	Ref.
POME	Methanol	CO_2	65 °C, crude lipase catalyst	Flask reactor	92.07	[116]
POME	Methanol	–	229 °C	Noncatalytic transesterification	77.64	[117]
Refined palm oil	Ethyl acetate	–	350 °C, 20 MPa	Supercritical microreactor	78.3	[118]
Palm oil	Methanol	–	350 °C, 15 MPa	Continuous process	96	[119]
Sludge palm oil	Methanol	–	400 °C, 15 MPa	Continuous process	80	[120]
Sludge palm oil	Methanol	–	400 °C, 15 MPa	Continuous process	90	[121]

An approximately complete conversion of triglycerides can be achieved within the reaction time of 30 min without using any solvent. However, very limited work has been done on the production of biodiesel apart from the fact that it can be utilized as a cheaper feedstock [122]. Hence, biodiesel synthesis using POME as a feedstock in supercritical transesterification is an unexplored area and more research is needed to make the supercritical process cost-effective. This will help to implement this technology on an industrial level as well as to fulfil the energy needs to fully replace fossil fuel energy. Tab. 7 presents the advantages and disadvantages of biodiesel production from POME.

3 Factors Influencing the Supercritical Biodiesel Production from POME

3.1 Reaction Temperature and Time

Reaction temperature along with the reaction time plays a significant part in the reaction rate via supercritical technology. For the results reported for methanol and ethanol, triglyceride conversion to biodiesel mainly was enhanced due to the increase in reaction time and temperature. The temperature influence on the yield of biodiesel using the supercritical methanol was first studied by Kusdiana and Saka [123]. They investigated the influence of temperature and pressure ranging from 200 °C and 7 MPa to 487 °C and 105 MPa and concluded that at a temperature below 250 °C the conversion of triglycerides was lower due to the subcritical state of methanol. The maximum conversion of palm oil to biodiesel was observed at 350 °C after 4 min giving a biodiesel yield of 95 %. The complete conversion was reported for 2 min reaction time at 400 °C. However, FAMEs started decomposing at a temperature of above 400 °C.

Similar findings were reported by Rathore and Madras [124], Imahara et al. [125], and Lin et al. [126]. Almeida et al. [116] analyzed the influence of temperature and time for the supercritical alcoholysis of residual oil extracted from palm oil industrial waste. The reaction temperature and time were varied between 250–350 °C and 5–25 min, respectively. The

Table 7. Advantages and disadvantages of various transesterification processes.

Transesterification	Advantages	Disadvantages
Homogeneous acid catalytic transesterification	No soap formation takes place. Acid catalysts can catalyze the esterification and transesterification at a time.	The use of such catalysts causes corrosion to the reactors. The activity of acid catalysts is lower.
Basic-catalyzed (KOH, NaOH)	Higher catalytic activity and transesterification rate, low cost, and easier availability.	Soap formation takes place causing product contamination.
Heterogeneous acid-catalyzed	There are no chances of soap formation. Heterogeneous catalysts can be reused efficiently. They can catalyze the esterification and transesterification simultaneously.	Higher cost and lower catalyst activity. Diffusional problems are observed with such catalysts.
Basic-catalyzed (CaO, $CaCO_3$, Al_2O_3)	The use of these catalyst causes no corrosion. They are recyclable for a long time, giving higher selectivity.	Higher cost, high energy requirement, sensitivity to the presence of water, low diffusion, and hence lower yield of biodiesel.
Enzymatic-catalyzed	No side reactions take place. They can be easily separated. The enzymatic-catalyzed transesterification process is environmentally friendly.	Slow reaction rate, degradation and higher cost of enzymes used.
Supercritical	Higher reaction rate, catalyst-free process, and products can be easily separated from the reaction mixture.	Very high operating cost due to the elevated temperature and pressure needed to achieve the supercritical conditions.

biodiesel yield was 95 % at 250 °C within 5 min reaction time. When the temperature was increased to 350 °C, approximately 100 % biodiesel yield was achieved.

Sootchiewcharn et al. [118] investigated the influence of temperature and time on the alcoholysis of refined palm oil extracted from POME. A higher biodiesel yield was achieved by increasing the temperature from 330 °C to 370 °C, giving the highest fatty acid ethyl ester (FAEE) yield of 63.6 % and biodiesel yield of 78.3 %. However, the rise in biodiesel yield was observed till 350 °C. At a temperature of above 350 °C, thermal decomposition of triglycerides also took place as reported by Marulanda et al. [127].

Fig. 7 demonstrates the thermal decomposition of triglycerides under supercritical conditions. It can be observed that the decomposition of triglycerides occurs above 400 °C. Considering the decomposition effect of triglycerides on biodiesel yield, the reaction temperature of 350 °C is suggested for biodiesel production to use short-chain alcohols under supercritical conditions.

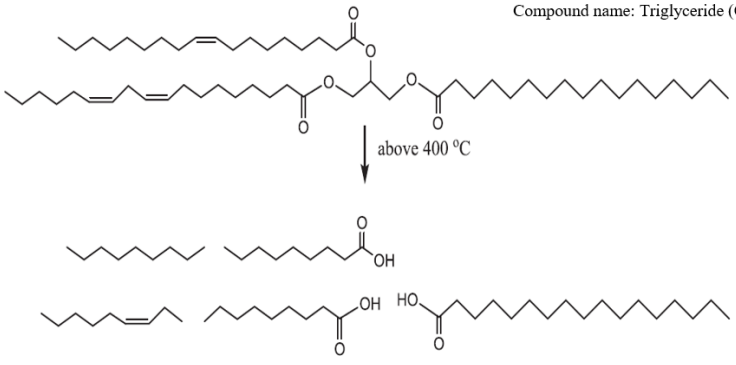


Figure 7. Thermal cracking of triglycerides above 400 °C.

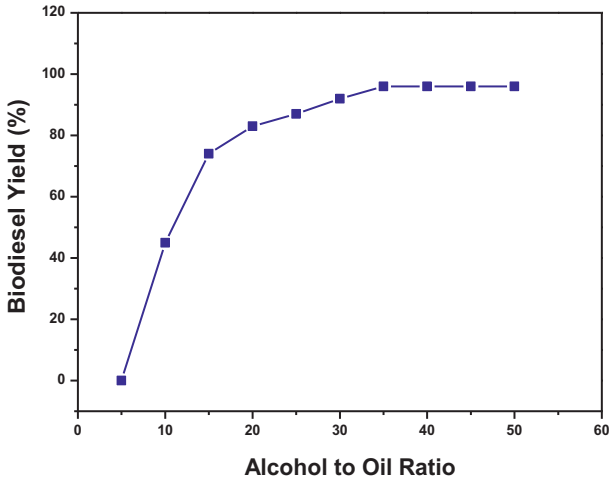


Figure 8. Effect of oil-to-alcohol ratio on biodiesel yield [116].

3.2 Effect of Oil-to-Alcohol Ratio

Triglycerides react with three moles of methanol for a complete transesterification reaction. However, since biodiesel production through transesterification is a reversible process, a higher amount of alcohol is added to avoid the reversibility of the process [116]. The study of the influence of oil-to-alcohol molar ratio ranging from 1:3.5 to 1:42 was done by Kusdiana and Saka [123]. It was found that for a lower oil-to-alcohol ratio (6 or less), incomplete conversion of triglycerides occurred. However, at a higher methanol molar ratio (42), complete conversion of triglycerides with methyl ester yield of 95 % was obtained. Similar findings were presented by Varma and Madras [128], Song et al. [115], He et al. [129], and Tan et al. [130]. The influence of oil-to-alcohol molar ratio is presented in Fig. 8.

da Costa et al. [116] investigated the influence of the alcohol-to-oil ratio on the overall yield of biodiesel production from residual oil. The alcohol-to-oil molar ratio was varied between 24:1 to 42:1. The highest yield of FAMEs was obtained at a ratio of 42:1 keeping the other process parameters constant at a reaction temperature of 350 °C and reaction time of 5 min. The oil-to-alcohol molar ratio affects the equilibrium, and a higher alcohol molar ratio for the same quantity of triglycerides shifts the chemical equilibrium to the product side. The optimum ratio of alcohol to oil of 40 is recommended in the case of supercritical biodiesel synthesis. It is important to consider that the addition of more alcohol cannot enhance the yield once the reaction has been completed, and will render the removal of alcohol from the product more difficult and energy-demanding.

3.3 Effect of Pressure

Pressure is one of the most important parameters influencing the biodiesel yield since it alters the supercritical fluid characteristics including density, viscosity, and hydrogen bond intensity. Tan et al. [130] studied the influence of pressure on biodiesel production in a batch reactor at 335 °C and oil-to-methanol molar ratio of 1:45. It was found that a pressure increase from 15 to 20 MPa resulted in the maximum biodiesel yield which was constant for pressures beyond 20 MPa. Similar findings were described by Goembira and Saka [132].

Klabsong et al. [117] determined the pressure influence on biodiesel yield for the residual oil extracted from POME and PKS. For this purpose, the pressure was varied between 10 and 30 MPa. The biodiesel yield of 80 % was observed at 14 MPa. Upon further pressure increase, no increment in biodiesel yield was achieved due to the equilibrium establishment of the reaction. The influence of pressure on supercritical biodiesel synthesis using various solvents and feedstocks is indicated in Tab. 8.

Tab. 8 demonstrates that the performance of palm oil recovered from POME was significantly higher as compared to other feedstocks. The highest biodiesel yield was observed at a relatively low temperature in comparison with rapeseed oil. The pressure effect on chemical equilibrium can be neglected due to the same number of molecules. The density dependence of the pressure affects the

Table 8. Influence of pressure on biodiesel synthesis with various solvents.

Solvent	Feedstock	*T* [°C]	*P* [MPa]	Time [min]	Molar ratio	Yield [%]	Ref.
Methanol	Palm oil	280	8.7	30	1:42	56.13	[129]
			10.5			63.87	
			12.5			76.89	
			15.5			81.76	
			21			86.55	
			25			90.92	
			36			91.51	
Ethanol	Rapeseed oil	300	10	20	1:42	76.03	[131]
			20			77.86	
			30			80.46	
			40			82.75	
Methyl acetate	POME	350	5	30	1:42	0	[132]
			10			9.85	
			15			19.37	
			20			84.31	
			30			85.71	
Methanol	POME	220	10	4	1:24	60.1	[117]
			12			63.5	
			14			67.8	
			16			70.4	
			18			70.9	

chemical reaction due to the solubility of supercritical alcohol and oil. As investigated by Anitescu et al. [133], pressure can significantly influence the mixing rate of reactants. A homogeneous phase of the reaction mixture can be attained if the operating pressure is optimized appropriately. Therefore, a pressure around 20 MPa is optimal for the production of biodiesel utilizing supercritical short-chain alcohols.

4 Techno-Economic Analysis for Biodiesel Production Technologies Using POME as Feedstock

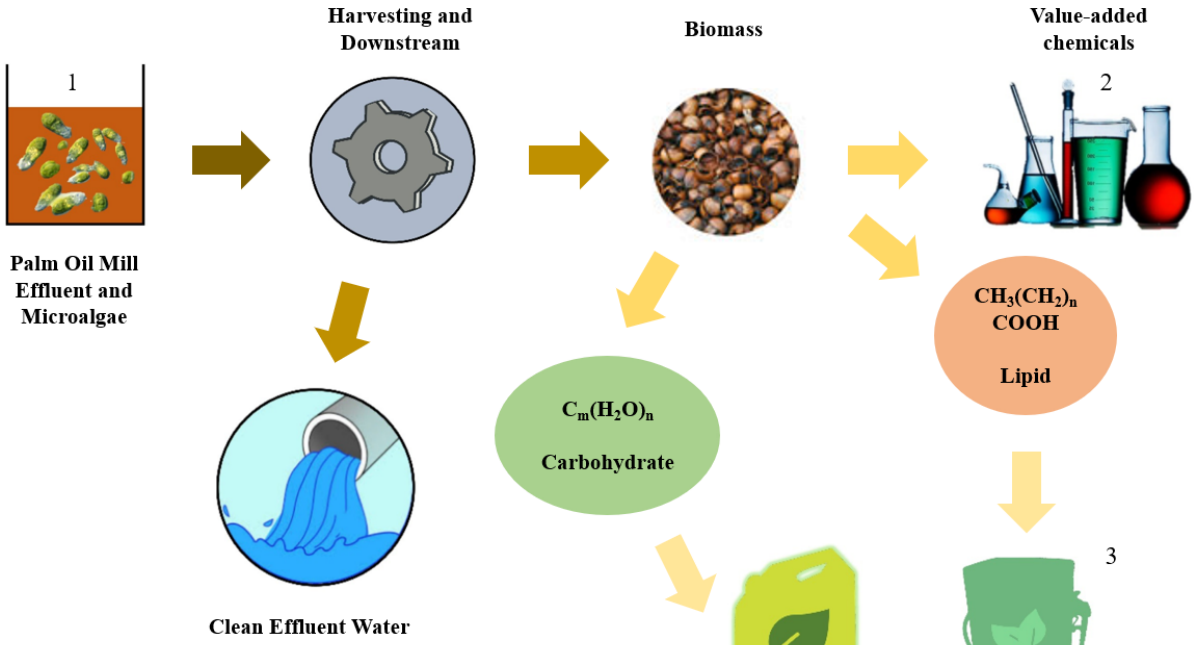
Biodiesel has become more attractive in recent years due to its availability, carbon-neutral influence, and environmental advantages. However, the economic feasibility of biodiesel is the main concern to synthesize it on an industrial scale. The processing of POME for value-added products is presented in Fig. 9.

Fig. 9 indicates the processing of POME for biodiesel and bioethanol production. POME contains a lot of solid impurities, making it necessary to perform various downstream operations such as sedimentation, filtration, and evaporation. The clean water is extracted from POME. The extracted biomass from POME during pretreatment is processed to synthesize useful chemicals such as glycerol and triacetin. The value-added chemical production depends on the nature of the solvent. The lipids and carbohydrates of biomass are converted into biodiesel and bioethanol, respectively.

4.1 Factors Affecting Biodiesel Production Economics

The economics of biodiesel depends on several factors, e.g., type of technology chosen, operating cost, type and cost of feedstock used, and biodiesel selling rate. The total capital investment includes fixed capital investment and operating cost [137]. The fixed capital investment cost contains the installation cost of the equipment with all utilities, which are necessary for smooth operation whereas the operating cost includes raw materials cost, utility cost, and labor costs for biodiesel production at a given capacity.

Currently, liquid biomass resources including palm oil by-products and effluent are gaining significant attention to meet the energy demand of the world and have been estimated



Source:

1.https://doi.org/10.1016/j.jece.2020.104519
2.https://www.indiamart.com/proddetail/laboratory-chemicals-12429583230.html
3.http://www.biodiesel-uruguay.com/uruguay-memiliki-biodiesel-dengan-bahan-yang-unik/

Figure 9. Processing of POME for value-added production [134–136].

to contribute by one-half of the total global energy needs by 2050 [138]. POME as an extensively generated waste in palm oil-producing countries can prove to be an excellent and cheaper substrate for biodiesel production. The implementation of supercritical technology can lower the cost of biodiesel synthesis from palm oil and its wastes. The separated water is used for utility purposes in distillation columns and heat exchangers. Moreover, POME can be directly employed for the transesterification reaction due to no pretreatment required in the process. The separation of the catalyst is also not needed when POME acts as a substrate. The simple processing of POME would significantly lower the cost giving a way forward to cheaper and green energy production.

4.1.1 Total Capital Investment

The total capital investment cost includes the cost of equipment and direct plant costs. The latter cover the costs related to the equipment installation, piping, instrumentation, electrical facilities, and cost of auxiliaries. The calculation of the cost of all components is based on equipment total cost and installation cost. Moreover, the estimation of total capital investment cost depends on how the purchasing cost of equipment is found. Cost estimation concerning capital investment is a crucial process. It includes designing of the process flow, selection of the equipment types and size, and type construction material.

Different researchers use various techniques to determine the total equipment cost. The formula to estimate the reactor cost made of stainless steel and having a volume from 0.1 up to 20 m^3 is $C_R = 15\,000V^{0.55}$ where V is the reactor total volume. The total capital investment cost incorporates further costs in addition to the purchasing cost of the equipment, which include labor cost, installation material costs, indirect costs such as taxes, transportation, taxes, contractor's fee, and plant overheads. For preliminary cost analysis, estimation is done based on total equipment purchasing cost [139].

Several techniques are available that can be applied to estimate the total capital investment including the Peter and Timmrhaus method, Chilton method, and Silla method [140]. The Peter and Timmrhaus technique considers the equipment purchasing cost from which the other costs can be calculated using percentages allocated based on the purchasing cost.

As discussed in biodiesel economics, the use of POME does not involve complex unit operations for biodiesel synthesis. Therefore, the maintenance cost is reduced due to the limited number of unit operations involved. This would lower the capital investment required for industrial production of biodiesel using POME. Tab. 9 presents the total capital investment cost calculation methods based on equipment purchasing cost.

Table 9. Total capital investment costs based on equipment purchasing cost [141].

Cost item	Calculation method
Raw material cost	Determined based on material balance
Utility cost	Calculated based on material balance
Maintenance cost	10 % of fixed capital investment
Labor cost	20 % of operating labor
Supervision cost	20 % of operating labor
Plant overheads cost	50 % of operating labor
Taxes	4 % of fixed capital investment cost
R&D	5 % of production cost
Unit production cost	Annual production expenses based on the capacity

4.1.2 Operating Cost

The operating cost includes the expenses for feedstocks, utilities, labor, maintenance, and depreciation costs. The raw material mainly consists of feedstock, catalyst, alcohol, and water used for washing. In all biodiesel synthesis methods, the cost of raw material includes operating cost [142, 143]. The economic analysis of biodiesel synthesis showed that raw materials and utilities covered 86 % of the total operating cost. Moreover, the mass balance is used as a reference to determine the quantity of raw material required to meet the necessary production capacity [144]. Similarly, the consumption of utilities is based on the type of process applied. It is usually calculated by the energy balance of the process.

Haas et al. [145] stated that the major contribution of the cost comes from the cost of raw materials needed, covering about 88 % of the overall cost. The overall cost was found to be linearly dependent on the feedstock quantity [146]. The total investment cost also depends on the type of process used. Harahap et al. [135] analyzed case studies to produce biodiesel from empty fruit bunches and POME. The observed operating cost for biodiesel synthesis using POME was lower as compared to other edible oils. About 80 % of the total biodiesel synthesis cost is covered by the feedstocks but POME comprised 50 % of the operating cost for biodiesel synthesis [135]. This demonstrates the cost competitiveness of biodiesel synthesis using POME as a low-cost substrate.

4.1.3 Plant Capacity/Production Scale

The profitability of biodiesel synthesis is dependent on the total production capacity of the production plant because the same substrate at different production capacities could exhibit different oil yields [141]. Very few investigations have been done on how the production capacity influences the feasibility and economics of the biodiesel synthesis process. Van Kasteren et al. [147] performed a comparative analysis using supercritical transesterification. The results of this study showed that the unitary biodiesel production cost decreased because of increasing plant capacity. The same findings were reported by Apostolakou et al. [141], who studies on vegetable oil conversion to biodiesel using alkali-catalyzed transesterification. They found that an increase of the plant capacity up to 60 000 t per year would be in favor of the sustainability of the process since the unit synthesis cost could be notably decreased. However, the increase of the capacity beyond 60 000 t per year would not be profitable.

Marchetti et. al [148] and Sakai et. al [149] conducted a sensitivity and cost-estimation analysis for biodiesel synthesis using waste cooking oil. They reported \$0.51/L and \$0.98/L cost via homogeneous catalysis and supercritical process, respectively. The investigation of transesterification of residual palm oil was done by Hass et al. [145] and You et al. [150] using homogeneous alkali-catalyzed transesterification with costs of \$0.58/L for a 36 kt biodiesel capacity plant. Sotoft et al. reported \$2.04/L cost of biodiesel with enzymatic-catalyzed transesterification.

Harahap et al. [135] analyzed case studies to produce biodiesel from empty fruit bunches and POME. The selected plant capacity was kept at 30 kt POME. The capital cost of technology or plant is annualized considering the lifetime of 25 years and 6.8 % interest rate. The total cost of production for this study was found to be 22 038 thousand USD/year. The cost to produce conventional diesel was 23 126 thousand USD/year. The cost of production using POME was significantly lower as compared to the conventional method. Tab. 10 presents the cost comparison of biodiesel using various feedstocks.

The catalyst effect is also important in considering the overall cost of biodiesel synthesis. Sundaryono et al. [85] determined the effect of catalyzing the biodiesel synthesis from palm fatty acids with a cheaper catalyst synthesized from coconut shell biochar. It was observed that sulfonating coconut shell biochar using H_2SO_4 can increase the acid activity of the prepared catalyst. This in turn enables to catalyze the low-value and cheaper substrate to produce high-quality biodiesel efficiently.

4.1.4 Market Value

The influence of a market variable would not be similar among two or more technological alternates available due to the amount and quality of the market variables, i.e., input materials and products could not necessarily be identical for different technologies available. A lot of research has been done to study the effect of variables on the sustainability of biodiesel using various technologies with varying market scenarios with respective capacities of production [157, 158]. Mulugetta et al. [159] stated that the influencing market variables, which can significantly influence the profitability of biodiesel synthesis, include the selling rate of biodiesel, purchasing cost of feedstock, and oil extraction cost. The cost of oil feedstock, as reported by many researchers, is the major market variable influencing the sustainability of the biodiesel business [160]. When supercritical transesterification of methanol is implemented for synthesizing biodiesel, the major variables that directly influence the economics are plant capacity, glycerol selling price, and capital cost.

Table 10. Techno-economic analysis of biodiesel synthesis using various feedstocks.

Plant capacity [t year^{-1}]	Feedstock	Biodiesel cost [$ L^{-1}]	Process	Ref.
36 036	Waste cooking oil	0.51	Alkali-catalyzed	[148]
36 036	Waste cooking oil	0.98	Supercritical	[149]
36 000	Waste cooking oil	0.95	Alkali-catalyzed	[151]
8000	Soybean oil	0.53	Sodium methoxide catalyst	[152]
8000	Rapeseed oil	0.78	Alkali-catalyzed	[141]
8650	Rapeseed oil	1.56	–	[153]
36 000	Palm oil	0.37	Alkali-catalyzed	[19]
1000	Palm oil	2.30	Enzymatic-catalyzed	[154]
8000	Waste cooking oil	0.86	Alkali-catalyzed	[142]
1000	Palm oil	1.12	Immobilized lipase catalyst	[155]
–	Microalgae oil	1.5	Acid-catalyzed	[156]
1452	Waste cooking oil	0.92	Heterogenous acid-catalyzed process	[149]
8000	Waste cooking oil	0.98	Lipase-catalyzed transesterification	[149]
–	Microalgae oil recycled from crude glycerol	1.76	Acid catalyzed	[156]
1000	Residual palm oil	0.29	Alkali-catalyzed	[154]
1000	POME	0.82	Enzymatic-catalyzed	[154]

Based on the techno-economic analysis, supercritical methanol transesterification could solve the problems by minimizing the pretreatment, capital, and process operational cost. It also helps to recover the high-purity glycerol as a biodiesel co-product. These are considered as the primary options to minimize the overall cost of biodiesel synthesis [161]. Biodiesel synthesis using supercritical fluids could become economically feasible and cheaper as compared to petroleum diesel. In general, supercritical fluids having low supercritical conditions will be an interesting technical and economic alternative for commercial biodiesel production in future. Therefore, more research is needed to make the supercritical technique a cost-competitive process.

5 Recommendations and Future Work

Based on the literature examined, supercritical biodiesel production is an innovative technology when implemented especially for POME as a feedstock. The recommendations based on this review study are given as:

1. It is necessary to discover some new solvents having reliable supercritical properties that can help to decrease the severity of supercritical transesterification. The solvents having low critical temperature and pressure are recommended to be used for biodiesel production since alcoholysis takes place above the supercritical properties of the solvent.
2. The addition of a co-solvent is also considered to be the appropriate option for supercritical biodiesel production technology. The recommended co-solvents include CO_2 and nitrogen gas. CO_2 has low critical properties, is nontoxic, and easily taken from the atmosphere in the form of air.
3. The addition of catalysts can boost the rate of reaction, declining the severity of the supercritical reaction as well. For this purpose, heterogeneous catalysts like ZnO and Al_2O_3 can be used in supercritical biodiesel synthesis because they can be easily separated and catalyze the reaction effectively.
4. For implementation of the supercritical technology on a commercial scale, the pinch technology should be applied to decrease the overall energy requirement of plants which will reduce the overall process cost. In this way, it can be implemented to meet the biodiesel demand. There is no single source available that can meet the biodiesel demand alone. Therefore, various feedstocks should be employed to synthesize biodiesel including edible, non-edible, and waste oils.

6 Conclusions

An overview on biodiesel production techniques including direct blending, alkali-catalyzed and acid-catalyzed transesterification, microwave- and ultrasound-assisted transesterification, and supercritical technology is presented. The supercritical process of biodiesel production seems to be the best option due to no requirement of catalyst and faster reaction rate. It can be implemented on an industrial level because of comparable cost with acid- and alkali-catalyzed transesterification. However, problems associated with the supercritical transester-

ification include the high energy requirement causing the reaction to take place at high temperature.

To decrease the severity of the supercritical process, the addition of a co-solvent is the best solution that can decrease its severity and increase the reaction rate as well. The addition of a co-solvent depends on the critical properties of the used solvent. Based on the summarized literature in this review, the addition of CO_2 as a co-solvent is better than nitrogen and helium gas due to its milder critical properties. Although the addition of a co-solvent can reduce the temperature and pressure, still future work is needed to intensify this process so that it can be implemented on an industrial scale.

POME can be utilized as a substrate for the supercritical synthesis of biodiesel, as it contains enough quantity of the oil that can be extracted for biodiesel production. It is generated in a vast amount from palm oil mills of palm oil-rich countries like Indonesia and Malaysia. According to the Malaysian palm oil board (MPOB), Malaysia is producing 10 million tons of POME annually. When it is processed via anaerobic digestion, it results in the production of biogas containing a maximum amount of CH_4 which causes ozone depletion. Therefore, instead of using it for anaerobic digestion, it can be utilized as a potential source for biodiesel synthesis. Its usage to synthesize biodiesel will decrease land and water pollution playing a positive role in the global climate.

In this study, various aspects of POME including its generation, availability, potential use, and economics were discussed in detail. POME could prove to be the cheapest feedstock to produce green energy due to its wider availability. However, to fully replace fossil fuel diesel with biodiesel, it is necessary to explore either more reliable feedstocks or increase the number of existing feedstocks. The annual production of POME can be increased by installing new palm oil mills. This can be done by planting new palm oil trees and enlarging the plantation area.

To ensure the continuous supply of feedstock, efficient trading systems for biodiesel feedstocks are required. The palm oil industrial growth will improve the job opportunities for the public in the form of labor, transport, and manpower leading to positive growth in the economy. Moreover, palm-biodiesel exhibits excellent flow and combustion properties as compared to biodiesel synthesized from other types of feedstocks. Although POME has great potential for green fuels, more research is required to reduce the overall cost of oil extraction from POME, and techno-economic analysis for various biodiesel production technologies to ensure the viability and practicability in the industry as well as optimizing the transesterification parameters, giving maximum yield.

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Conflicts of Interest

The authors declare no conflict of interest

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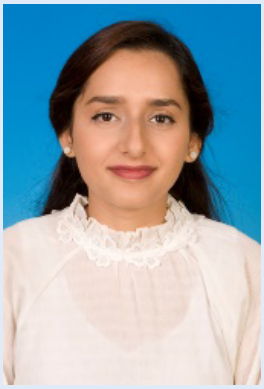

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Abbreviations

BOD	biochemical oxygen demand
COD	chemical oxygen demand
FAEE	fatty acid ethyl ester
FAME	fatty acid methyl ester
FFB	fresh fruit bunches
HC	hydrocarbons
NO_x	nitrogen oxides
PKS	palm kernel shell
POBD	palm oil biodiesel
POD	palm oil diesel
POME	palm oil mill effluent
SPO	sludge palm oil
WCO	waste cooking oil
WFO	waste frying oil

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Biodiesel is a significant substitute fuel with numerous advantages over fossil fuel diesel. Biodiesel synthesis processes such as pyrolysis, direct blending, transesterification, and advanced technologies like microwave- and ultrasound-assisted and supercritical processes from palm oil mill effluent are reviewed to emphasize the significance and advances regarding process sustainability and cost.

Comprehensive Review on Biodiesel Production from Palm Oil Mill Effluent

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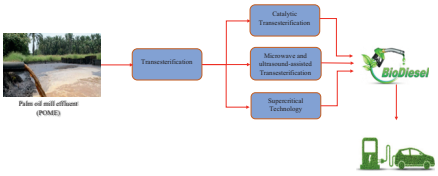

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