

Review

An Overview of Biodiesel Production via Calcium Oxide Based Catalysts: Current State and Perspective

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Abstract: Biodiesel is a clean, renewable, liquid fuel that can be used in existing diesel engines without modification as pure or blend. Transesterification (the primary process for biodiesel generation) via heterogeneous catalysis using low-cost waste feedstocks for catalyst synthesis improves the economics of biodiesel production. Heterogeneous catalysts are preferred for the industrial generation of biodiesel due to their robustness and low costs due to the easy separation and relatively higher reusability. Calcium oxides found in abundance in nature, e.g., in seashells and eggshells, are promising candidates for the synthesis of heterogeneous catalysts. However, process improvements are required to design productive calcium oxide-based catalysts at an industrial scale. The current work presents an overview of the biodiesel production advancements using calcium oxide-based catalysts (e.g., pure, supported, and mixed with metal oxides). The review discusses different factors involved in the synthesis of calcium oxide-based catalysts, and the effect of reaction parameters on the biodiesel yield of calcium oxide-based catalysis are studied. Further, the common reactor designs used for the heterogeneous catalysis using calcium oxide-based catalysts are explained. Moreover, the catalytic activity mechanism, challenges and prospects of the application of calcium oxide-based catalysts in biodiesel generation are discussed. The study of calcium oxide-based catalyst should continue to be evaluated for the potential of their application in the commercial sector as they remain the pivotal goal of these studies.

Keywords: biodiesel production; heterogeneous catalyst; alternative fuel; renewable energy; alkaline metal oxides

1. Introduction

The rapid depletion of fossil fuel supplies affects energy security and increases greenhouse gas emissions and carbon dioxide (CO₂) concentration in the atmosphere, and these key drivers necessitate the search for alternative sources of energy [1–3]. Energy supplies have transitioned from fossil fuels since the early twentieth century to renewable sources (at a much slower rate, though) [4,5], and some of the most remarkable alternative energy

sources that can stand in for fossil fuels are wind, solar, water, and biofuel. Solar, wind, and hydro energy are the chief sources of electricity and heat generation used globally. In the United States, 20% of total electricity was produced from renewable sources in 2020; wind (8.4%), hydropower (7.3%), solar (2.3%), biomass (1.4%), and geothermal (0.5%) [6]. Biomass is a renewable organic material and bioenergy utilizes biomass, in order to produce heat, electricity, and biofuel, such as biogas and liquid fuels. The predominant types of renewable energy from biomass (i.e., biofuel) are biochar (solid), biodiesel and bioethanol (liquid), and bio-hydrogen, biogas, and biosynthetic gas (gaseous) [7,8]. Although energy sources other than biomass are preferred for electricity and heat generation, biofuels as liquid fuels serve as energy-dense fuels that can be blended with petroleum-based fuels, i.e., gasoline and diesel [9].

Petroleum diesel (petrodiesel) fuel exhausts emissions, such as particulate matter, nitrogen oxide (NO_x), and aerosols that can cause various health issues, such as respiratory diseases, allergy, cancer, and vascular diseases [10]. Unlike petrodiesel, biodiesel does not contain any metals, residues, or sulphur aromatics, and releases minimal amounts of glasshouse gases [11,12]. In this way, biodiesel can be used in combination with petrodiesel, as they have similar characteristics [13]. Biodiesel can also be used as an alternative to fossil fuel in diesel engine with no modification [14]. However, biodiesel might not be viewed as a petrodiesel substitute; rather, it can be considered as an essential component of a secure and diverse energy supply.

Transesterification is the general process for biodiesel production, in which alcohol (chiefly methanol) and oil react, and the reaction is usually catalyzed by the utilization of a homogeneous or heterogeneous catalyst [15,16]. There is some technological difficulty (corrosion and emulsification) when acid or base homogeneous catalysts are applied in the reaction [17]. On the contrary, compared to homogeneous catalysts, such as potassium hydroxide (KOH), that dissolve in the reactant [18], heterogeneous catalysts are advantageous for their easy separation, possibility of high-quality glycerol with high levels of purity ($\geq 98\%$) from the product, and possible reusability of the catalyst for several cycles. Therefore, transesterification via heterogeneous catalysis as a green process can value add to the process. Calcium oxide (CaO)-based catalysts are heterogeneous, low-cost, available material in abundance in nature that can be produced from waste feedstocks, such as seashells and eggshells [19]. CaO-based catalysts have relatively high activity, and their leaching problem can be overcome by supporting it on different carriers or mixing with other oxides [20].

This review focuses on biodiesel generation via transesterification reactions from a catalytic standpoint. In this regard, this review firstly discussed the heterogeneous and homogeneous catalysts, as well as their advantages and disadvantages; and secondly, evaluated CaO- (in the different forms of pure, supported and mixed with other oxides) catalyzed transesterification. Additionally, CaO catalysts derived from natural resources were reviewed and the effect of various parameters on the transesterification, including catalyst reusability, catalyst-loading amount, water content, total primary sites, calcination time and temperature, and reaction time were studied in brief. Moreover, the reactors in use for heterogeneous catalysts were discussed. Finally, the future perspective of the CaO-derived catalysts was reviewed to assess their capacity in biodiesel production.

2. Biodiesel

Biodiesel is a sustainable liquid fuel for transportation [21] and it has improved characteristics compared to petrodiesel, such as lower density and viscosity. The density of the fuel affects the engine's fuel injection system and the lower dense and viscous fuel leads to better atomization and mixing properties [22]. The properties of the developed biodiesel for further use as a pure compound or a blend should be tested, and the properties must be commensurate with international standards for testing biodiesel, such as EN 14,214 and ASTM D6751, according to the European Committee for Standardization and

American Standards for Testing and Materials. The biodiesel properties were compared with petrodiesel and listed in Table 1.

Table 1. Pure biodiesel properties versus petrodiesel [23–27].

	Biodiesel	Petrodiesel
Exhaust emissions	Low	High
Renewable supply	Renewable	Non-renewable
Biodegradability	Good	Poor
Toxicity	Non-toxic	Toxic
Brake thermal efficiency	Low	High
Lubricity	Good	Poor
Combustion	Complete	Incomplete
Carbon monoxide emissions	Low	High
Sulphur and aromatic content	0.0%	Sulphur dioxide: ~500 ppm Aromatics: 20–40%
Explosively	Non-explosive	Explosive
Flashpoint (K)	423	337
Cetane number	45–70	40–52
Chemical structure	C12, C14, C16, C18 and C22 fatty acid methyl esters	C12 to C25 hydrocarbons
Oxygen content (%)	11	* N/A
Cold flow properties (Solidification)	Rapid	Gradual
Conductivity	High; >500 pico S/m	Low

* N/A = not available/not applicable.

One of the essential factors for biodiesel generation is its capacity to be generated through a broad diversity of existing feedstocks, which are available in abundance and are at low cost [13]. The existing feedstocks for biodiesel generation are categorized into four groups; animal fat, edible vegetable oil, non-edible vegetable oil and waste cooking oil (WCO) [26,28]. Biodiesel generated from edible vegetable oils have a relatively high yield due to their lower free fatty acids (FFA) content, and their transesterification process is simpler and more accessible. However, due to the “food versus fuel” debate, which emphasizes insufficient human food supply in the future; biodiesel production from edible-plant sources is not desired [29]. On the contrary, non-edible vegetable oils are promising feedstocks for biodiesel production because they have no conflict with the stability of the food supply [30]. WCO is one example of non-edible vegetable oil with a promising choice due to its low cost as compared to fresh vegetable oil. Methanol reacts with the triglycerides of the oil process, which is usually catalyzed by a catalyst and the general equation of this reaction is shown in Figure 1. Catalysts improve the reaction time and yield, and a whole range of homogeneous and heterogeneous catalysts are applied in transesterification.

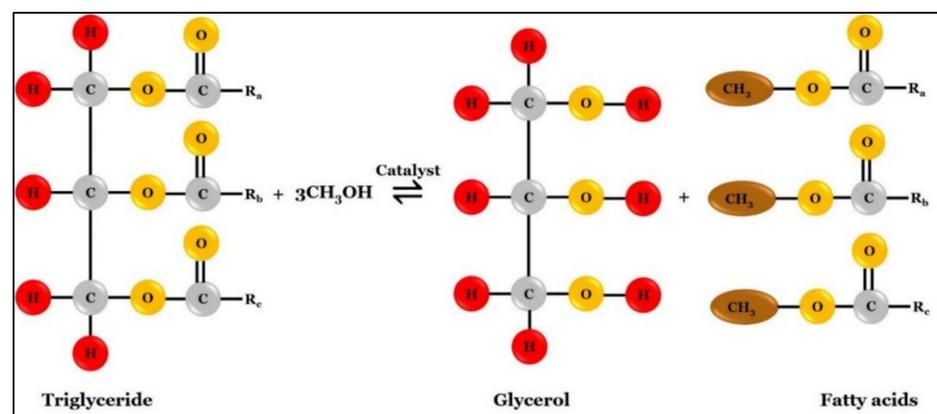


Figure 1. The transesterification process for biodiesel production [31,32].

3. Catalysts Applied in the Transesterification

Catalyst types have a crucial impact on the transesterification process as it expedites the reaction and a lower amount of alcohol is required for the conversion [33]. Therefore, the selection of an appropriate catalyst for an economic generation of biodiesel is vital. Catalysts are mostly categorized into three groups; homogeneous (alkalis and acids), heterogeneous (solid base or acid) and biocatalyst. During transesterification, homogeneous catalyst remains the same (liquid) phase to that of the reactant, while heterogeneous catalyst persists in being in a different phase (i.e., solid, immiscible liquid or gaseous) to that of the reactant. Enzyme catalysts have gained significant attention since they can hinder soap formation, and thus, the purification procedure is effortless. However, due to long-lasting reaction time and being overpriced, enzyme catalysts are less applied commercially [34].

Alkali homogeneous catalysts, including KOH and sodium hydroxide (NaOH), are conventional commercially used catalysts for being low-cost. Further, NaOH and KOH are the most viable catalysts for mass production since the transesterification process using basic catalysts is performed under low pressure and temperature conditions, and the conversion rate is outstanding with no intermediate steps. The basic homogeneous catalysts are extremely hygroscopic and able to absorb water from the air throughout the storage. The basic homogeneous also produce water when dissolved in the alcohol reactant and thus affect the yield. Application of homogeneous catalysts in transesterification has several drawbacks such as the necessity for washing the products for catalyst removal and product cleaning and thus higher costs, and an appreciable amount of product loss in some cases is inevitable. Further, the method which is used to remove the homogeneous catalyst is arduous; thus, replacing homogeneous catalysts with heterogeneous catalysts is a tactic to diminish the cost of biodiesel production [35]. Therefore, heterogeneous catalysts are promising candidates for the production of biodiesel from vegetable oils [36]. Solid heterogeneous catalysts are non-corrosive and can be utilized in a fixed-bed reactor, resulting in protected, inexpensive and more environment-friendly processes. Moreover, solid heterogeneous catalysts are recyclable and are feasible for continuous mass production. In comparison with biodiesel production by a homogeneous catalyst, less wastewater is produced by using heterogeneous catalysts, and hence the sewage treatment costs are reduced [37]. Solid heterogeneous catalysts can stimulatingly catalyze the transesterification, which can eliminate the pre-esterification stage, thus, these catalysts are especially suitable for those feedstocks with high free fatty acid (FFA) volume [37]. Solid catalysts are either acid or alkaline, and solid heterogeneous alkaline catalysts are 4000 times faster than acid catalysts in terms of reaction rate [25,38]. Heterogeneous alkali catalysts fall into one of the following categories in relation to their active basic sites: Alkaline earth metal oxides, supported alkaline earth metal oxides, supported alkali metals, alkali and alkaline earth mixed, zeolites and modified zeolites, hydrotalcite/layered double hydroxides, rare earth/lanthanide-based, ion exchange resin, zirconia-based and other materials [39]. Alkaline earth metal oxides such as CaO, magnesium oxide (MgO), barium oxide (BaO), and strontium oxide (SrO) are used in transesterification [40]; these metal oxides become active and are used in the reaction after a thermal pretreatment [41].

4. CaO-Based Catalysts

Among alkaline earth metals, CaO has received much attention due to its reasonable price, low solubility in methanol, low toxicity and high availability from natural resources [42]. The preparation of CaO is simpler compared to many other solid catalysts and its catalytic activity can be augmented by applying thermal calcination. Various precursor salts, such as carbonate, hydroxide, oxalate, and acetate monohydrate are utilized in CaO catalyst preparation [43]. It is noteworthy that exposure of CaO to air, even for a few seconds, can deactivate the catalyst [44]. However, it is possible to reactivate it by calcination in a furnace at high temperatures.

The mechanism of CaO-catalyzed transesterification is shown in Figure 2 [38]. Firstly, methoxide anion forms as a result of proton removal from methanol by basic sites. Secondly,

Table 2. Pure CaO-based catalysts type and the reaction conditions in biodiesel production.

Feedstock (Oil)	Catalyst Type	Temperature (°C)	Molar Ratio (Methanol: Oil)	Catalyst (wt%)	Time (min)	Yield (wt%)	Reusability (Cycle)	Reference
Goat fat	Nano based	70	12:1	1	180	93.7	3	[54]
WCO	Commercial	80	1:1	3.0	120	96.0	N/A	[46]
Rapeseed	Nano based	65	1:8	5	240	92.0	N/A	[55]
<i>Bombax ceiba</i>	Nano based	65	10.4	1.5	705	96.2	5	[45]
Soybean	Nanocrystalline	60	6:1	4.0	80	89.9	3	[47]
Palm	Lime based	65	15:1	6.0	120	97.0	4	[48]
WCO	Chicken manure based	65	15:1	7.5	360	90.0	N/A	[49]
Canola	FPC based	60	12:1	5.0	90	96.0	7	[50]
Canola	Dolomite based	60	9:1	5.0	90	97.4	4	[51]
Palm	Commercial	60	9:1	2.0	240	84.5	3	[52]

Commercial CaO could efficiently catalyze the conversion of WCO to biodiesel [46]. The activity of calcined CaO was significantly increased when it was added to methanol, and under the optimized conditions at 3.0% catalyst concentration at 80 °C temperature, 1:6 oil to methanol molar ratio, and 120 min reaction time showed 96% of biodiesel yield. CaO nanoparticles were used in the transesterification of *Bombax ceiba* oil and a high FAME yield of 96.2% was obtained under the following reaction conditions: At 10.4:1 methanol to oil molar ratio with 1.5% catalyst in 70.5 min at 65 °C [45]. The nanocrystalline CaO catalyst was developed by ultrasound-assisted emulsion-based method and the developed catalyst manifested 1.5 times higher surface area and 1.3 times smaller crystallite size and particle size compared to commercial CaO catalyst [47]. At optimal conditions, the synthesized catalyst exhibited an 18.9% enhanced conversion rate of oil as compared to the commercial CaO catalyst. The CaO nanocatalyst was developed and used in the transesterification of goat fat and the biodiesel yield was reported 93.72% during the transesterification for 3 h at 70 °C using 1% catalyst at molar ratio of 12:1 [54]. The assessment of catalyst reusability indicate that it can be used for at least three cycles with the biodiesel conversion efficiency of more than 80%. Nano CaO was applied in the rapeseed transesterification reaction and 92.0% yield was achieved at 1:8 methanol to oil molar ratio with 5.0 catalyst at 65 °C [55]. The activity of original hydrated lime and hydrated lime derived CaO were examined in the transesterification of palm oil and 97.0% yield was achieved when using hydrated lime derived CaO at 15:1 methanol to oil molar ratio with 6.0 catalyst at 65 °C in 2 h [48]. The hydrated lime-derived CaO presented a greater surface area and pore volume than the synthetic one.

Catalyst production from waste resources can exert influence on the environment by lowering the disposal of those wastes and the utilization of waste material for catalyst production has added benefits in terms of economics and profitability. However, very scant work has been reported on the utilization of waste-derived CaO in transesterification. CaO catalysts derived from chicken manure was developed [49]. The manure was subjected to calcination at 850 °C in order to obtain the active CaO and the developed CaO catalyst had high catalytic activity for transesterification of WCO. The optimum conditions for catalyst synthesis were 7.5% catalyst, 15:1 of methanol to oil molar ratio and 65 °C reaction temperature, and a FAME yield of 90.0% was achieved at these conditions [49]. CaO nanoparticles were produced from filter press cake (FPC) waste [56]. Managing FPC waste is a serious challenge for sugar-producing facilities, but FPC waste can be used as a source for catalyst production. The FPC was subjected to calcination at 900 °C for 2 h for activation, followed by a surfactant-hydration method for the production of CaO nanoparticles [50], and yield of over 96.0% was achieved after reacting canola oil and methanol.

Ultrasonic-assisted transesterification is an efficient method when using CaO as a catalyst as it can crush the catalyst into smaller parts, leading to more basic sites. Increased basic sites have a key role in the efficiency of CaO-catalyzed transesterification. Further, it reduces the time needed for oil conversion to biodiesel. For instance, CaO obtained from dolomite was applied in the ultrasonic-assisted transesterification of canola oil, and a yield

of 97.4% was obtained after 90 min of reaction [51]. Moreover, 84.5% yield was achieved when CaO catalyzed the ultrasound-assisted transesterification of palm oil at the following reaction conditions: 2.0% catalyst, 60 °C temperature, 9:1 methanol to oil molar ratio and reaction time of 4 h [52].

4.2. Mixed Oxides CaO Catalysts

Mixing oxides, such as CaO with other elements (e.g., Zn, Ba, Mg, Fe, etc.) is a method used for synthesizing a catalyst with increased basic sites and improved stability. In this part, the utilization of mixed CaO and their reaction conditions, as well as their preparation method, were reviewed and summarized in Table 3.

Table 3. Mixed oxide CaO catalyst and reaction conditions in biodiesel production.

Feedstock (Oil)	Catalyst	Synthesis Method	Temperature (°C)	Molar Ratio (Methanol: Oil)	Catalyst (wt%)	Time (min)	Yield (wt%)	Reusability (Cycle)	Reference
<i>Calophyllum inophyllum</i>	Zn-CaO	Precipitation Calcination	55	9:1	6.0	80	89.0	4	[65]
<i>Elaeis guineensis</i>	CaO-MgO	Co-precipitation Calcination	60	15:1	4.0	360	99.0	5	[57]
Waste edible	CaO-MgO	Wet impregnation	69.4	17:1	4.6	428	98.4	6	[58]
Soybean	MgFe ₂ O ₄ and CaO	Alkali precipitation	70	12:1	1.0	180	98.3	5	[59]
Soybean	Ca-Mg	Oxalate precipitation	70	12:1	1.0	120	98.0	5	[60]
<i>Jatropha Curcas</i>	CaO-ZnO	Co-precipitation	120	25:1	3.0	180	94.0	N/A	[61]
Karanj	CaO-La ₂ O ₃ -Al ₂ O ₃	Co-precipitation Calcination	150	9:1	5.0	180	97.0	N/A	[62]
Sunflower	CaTiO ₃ and CaO	Mechanochemical Calcination	60	6:1	10.0	600	98.1	N/A	[63]
Palm	Ca, Zn, and Al	Dissolution Precipitation	65	30:1	10.0	180	99.9	N/A	[64]

A Highly basic bimetallic alkaline earth metal oxide (CaO-MgO) (750 $\mu\text{mol g}^{-1}$) was produced by using synergistic effects [57] and the FAME yield of $\geq 99.0\%$ was obtained under the optimal condition of 4.0% catalyst at a temperature of 60 °C and 6 h reaction time. The results showed that the basicity of mixed CaO-MgO (CM-1.0) was higher in comparison with the pure CaO catalyst. The atomic absorption spectroscopy method was used to evaluate the leaching of the catalyst and the result showed that the catalyst was stable up to five cycles. CaO-MgO nanocatalyst was used to produce FAME from waste edible oils; the catalyst was successfully reused for up to six cycles and a maximum biodiesel conversion yield of 98.37% was obtained [58].

The utilization of magnetic materials eliminates the need for conventional filtration and purification. A magnetic nanoparticle catalyst (i.e., MgFe₂O₄ and CaO) was synthesized by using the synergistic effect, followed by its application in the transesterification of soybean [59] and the FAME yield obtained was 5.9% higher than pure CaO-catalyzed reaction. Additionally, the developed catalyst was found to be more active and more water and acid resistant than the neat CaO. Calcium oxalate and magnesium oxalate can be used as precursors to generate Ca-Mg mixed oxide catalyst and the bimetallic catalyst showed a better surface area than the pure CaO [60]. The FAME yield of 98.4% and 92.8% were reported for Ca-Mg, and pure CaO, respectively and the higher yield of mixed oxide catalyst was attributed to the larger surface area.

Different types of mixed earth metal oxides (e.g., CaO-MgO, CaO-ZnO, CaO-Lanthanum (III) oxide (La₂O₃), and MgO-ZnO) were investigated in terms of catalysis and it was noted that due to the increased basic density and strength, mixed metal oxides had improved activity in the transesterification than the single metal oxides [61]. The biodiesel yield of 94.0% was achieved when CaO-ZnO was applied in the transesterification of *Jatropha curcas* [61]. Transesterification of palm oil (having high acid volume) and Karanja oil (having low acid volume) CaO-La₂O₃-Aluminium oxide (Al₂O₃) catalyzed by mixed-

oxides were tested and FAME yield of 97.0% was obtained [62]. In this study, dimethyl carbonate (DMC) was used instead of methanol due to its improved properties, such as non-toxicity, non-corrosive and being active in the reaction. Calcium-containing perovskites CaTiO_3 , CaMnO_3 , and CaZrO_3 were prepared and used to catalyze the transesterification of sunflower oil [63], and the pure perovskite phase showed low or no catalytic activity. The FAME yield of 98.1% was achieved after a 10 h reaction at 60 °C when CaTiO_3 catalyzed the reaction.

On the same subject of using mixed metal oxide for biodiesel production, transesterification of refined, bleached deodorized palm oil with methanol using a new heterogeneous alkali catalyst was studied. A mixture of Ca, Zn, and Al compounds was prepared using the dissolution–precipitation method using *Meretrix meretrix* seashells as a source of CaO, in the presence of zinc nitrate and alumina as binder precursors. FAME yield of 99.9% was achieved when 30:1 methanol to oil molar ratio, 10.0% catalyst ratio, 3 h reaction time and 65 °C applied to the system [64].

4.3. Supported and Loaded CaO Catalysts

Utilization of support or carrier would improve the stabilizing characteristic of the CaO catalyst and would decrease the leaching. Various methods were applied for the development of supported CaO, including wet impregnation, precipitation and co-precipitation, followed by calcination to activate the catalyst. Alumina [66], zeolites [67], and silica [68] are the common materials for supporting CaO catalysts for biodiesel production. An overview of supported CaO catalyzed transesterification and its different parameters were listed in Table 4 and reviewed in this part.

CaO supported with Al-MCM41 was prepared via the sono-dispersion and wet impregnation method and the catalyst was used in the transesterification of sunflower oil [69]. It was found that the biodiesel conversion and quality increased as CaO was loaded due to its basicity. Diatomite supported by CaO/MgO was generated by the impregnation method and was then utilized in the transesterification of WCO, and the yield of 96.5% was obtained under the following experimental condition: temperature of 90 °C, methanol to oil molar of ratio 1:15, catalyst amount of 6.0% and reaction time of 2 h [70]. CaO, supported with silica, was successfully synthesized by using the wet impregnation method, and a yield of 87.5% was achieved, which was higher than the yield achieved when neat CaO was used [71]. Structured catalyst reactors, such as those based on the monolithic catalyst are a captivating method for biodiesel production. However, it should be noted that a high affinity between the support and catalyst could lead to the deactivation of the catalyst. The metallic citrates decomposition method was used to prepare mixed calcium/cerium oxide (CaO/Ce) both in powder and structured shapes and the Ca-Ce mixed oxides deposited on structured catalysts using Fecralloy monoliths for their use in the transesterification of sunflower oil [72]. KOH catalyst supported on CaO obtained from animal bones was utilized in the transesterification of *Jatropha curcas* oil and CaO oxide modification was carried for increasing the surface area and basicity of the catalyst [73]. The synthesized catalyst exhibited high performance and stability, which therefore led to a high FAME conversion rate of 96.1% under the following reaction condition: methanol/oil molar ratio, 9:1, catalyst concentration, 6.0% at a temperature of 70 °C at a reaction time of 3 h. Immobilization of CaO onto polymeric mats fibers was reported for biodiesel production, and this polymer had been used in the immobilization of lipase but never for loading heterogenous catalysts. The catalyst was subsequently applied in the transesterification of canola oil and methanol [74].

Zeolites have been widely used as a carrier in biodiesel production in the past decade [75–78]. Zeolites with specific pore structure and surface hydrophobicity can be modified depending on the substrate's polarity and size, and hence, molecules with diameters smaller than the proper catalyst size can enter the cavity and diffuse [38]. In this regard, how hierarchical (h) Zeolite Socony Mobil 5- (ZSM-5) supported CaO performs as a catalyst in biodiesel production from waste palm oil was investigated. The catalytic activity

of CaO was enhanced after support on h-ZSM-5, and resulted in an improvement of FAME conversion from 93.2% to 95.4% at the following reaction conditions: 6 h reaction time, 3.0% catalyst amount, 12:1 methanol to oil molar ratio and 65 °C reaction temperature [79]. CaO catalysts were supported with crystalline sodium Y (NaY) zeolite (Si/Al = 3.24), KL zeolite (Si/Al = 6.2) and NaZSM-5 zeolite (Si/Al = 40), which was prepared by microwave irradiation [67]. Further, these supported CaO catalysts were applied in the transesterification of soybean oil and their functions were compared to that of pure CaO. The results showed that the use of zeolite as support for CaO boosted the catalysis performance due to more basic sites and increased surface area. Furthermore, it was found that CaO/NaY had the best activity and a biodiesel yield of 95.0% was achieved with 3.0% catalyst, methanol to oil molar ratio of 9:1 and, reaction temperature of 65 °C within the reaction time of 3.0 h [67]. Pure cancrinite zeolitic material was utilized as catalyst support of CaO derived from waste chicken eggshells. FAME yield of 96.5% was obtained in the methanolysis of sunflower oil at 60 °C for 2 h with 4.0% of this catalyst by maintaining molar ratio of 12 [80].

Table 4. Utilization of supported CaO catalysts in transesterification.

Feedstock (Oil)	Synthesis Method	Temperature (°C)	Molar Ratio (Methanol: Oil)	Catalyst (wt%)	Time (min)	Yield (wt%)	Reusability (Cycle)	Reference
Palm	Hydrothermal	65	18:1	7.5	180	98.2	5	[81]
Sunflower	Ultrasound-dispersion	60	12:1	4.0	120	96.5	N/A	[80]
Sunflower	Impregnation and sono dispersion	70	12:1	12.0	N/A	N/A	4	[69]
WCO	Impregnation	90	1:15	6.0	120	96.5	5	[70]
Palm	Impregnation	60	20:1	3.0	120	87.5	6	[71]
Sunflower	<i>Metallic citrates</i> decomposition	60	48:1	2.0	240	99.0	N/A	[72]
Soybean	Wet impregnation	70	12:1	8.0	360	89.3	5	[84]
Soybean	Co-precipitation followed by impregnation	65	13:1	2.0	120	95.1	4	[78]
<i>Jatropha curcas</i>	Impregnation	70	9:1	6.0	180	96.1	4	[73]
Waste palm	Impregnation	65	12:1	6.0	360	95.4	N/A	[79]
Soybean	Microwave irradiation	65	9:1	3.0	180	95.0	N/A	[67]
Palm	Incipient wetness impregnation	60	12:1	9.0	360	94.1	5	[82]
Crude palm	Wet impregnation	45	12:1	6.0	180	97.1	3	[83]

CaO catalysts have few inherent issues such as leaching and diminished stability. The leaching of CaO catalysts can cause catalyst deactivation. CaO can be immobilized on a suitable carrier to improve stability and overcome the catalyst weakness. Al₂O₃ is one of the best candidates as a catalyst carrier thanks to its large surface area, fine pore distribution and structural flexibility. SrO–CaO–Al₂O₃ trimetallic oxide catalyst was reported for the first time. CaO leaching was greatly decreased and the catalyst stability increased substantially [81]. Porous materials used as carriers for CaO can boost the stability of the catalyst and the high surface area may lead to superior metal oxide dispersion, and thus, improve their catalysis activity. Bimodal meso-macroporous silica materials were made via the sol-gel method and CaO was loaded on the developed material by using the incipient wetness impregnation method [82]. The catalyst was applied in the transesterification of palm oil and a FAME yield of 94.2% was achieved. However, the low rate of dispersion of massive triglycerides through the pores can decrease the activity of the CaO load on the porous materials.

The wet impregnation method was used to make palm-oil-mill fly-ash-supported CaO to generate biodiesel from palm oil [83]. Characterization results revealed higher surface area and basic sites for the catalyst compared to the unsupported catalyst. The transesterification process was conducted at 45 °C reaction temperature, 6.0% catalyst and 12:1 methanol to oil molar ratio, and 3 h reaction time. FAME conversion and biodiesel yield of 97.1% and 79.8% were obtained when supported and unsupported catalysts were used in the reaction. The wet impregnation method was used to synthesize CaO–SnO₂ catalysts and 89.3% yield was achieved under reaction time of 6 h, 8% catalyst, the methanol to oil molar ratio of 12:1, and temperature of 343 K [84].

Activated carbon-supported CaO was developed and applied in the transesterification of WCO and the process yielded 77.3% FAME [85] and the optimum reaction conditions were 5.5% catalyst amount, 170 °C temperature, 15:1 of methanol to oil molar ratio and 2 h

and 22 min reaction time. Moreover, nanomaterials of natural or artificial origin, with one dimension of 100 nm or smaller, have been widely applied in the field of catalysts development for biodiesel production. For example, gold nanoparticles were used as support for CaO catalysts and the synthesized catalysts showed better catalytic activities [86]. The transesterification catalyzed by these gold nanoparticles-based CaO catalysts had a high yield ($\geq 85\%$) after ten cycles of recycling.

4.4. Seashell and Eggshell Derived CaO Catalysts

Seashells and eggshells are promising sources for CaO production for having calcium in their structure, given that utilization of these shells is environmentally friendly and has no detrimental effect on the ecosystem [87,88]. CaO-based catalysts were produced from abundant natural CaCO_3 origins, including mollusk shells, waste eggshells [89], ostrich eggshells, golden apple snail shells, capiz shell, meretrix shells, *Chicoreus brunneus*, shell crab shell, and clamshell. CaCO_3 obtained from these natural sources can be converted to CaO by calcination [15,41,48,90]. The retrieval of natural CaO instead of utilizing the synthetic ones is a novel way in catalyst preparation [91]. However, there are limited numbers of articles exploring the utilization of seashells and eggshells as natural, low-cost sources for CaO production. In this part, seashells and eggshells used for the CaO-based catalyst synthesis are reviewed and summarized in Table 5.

Table 5. Synthesis of seashell-derived CaO from various sources and the reaction conditions in biodiesel production.

Feedstock (Oil)	Catalyst Source	Temperature (°C)	Molar Ratio (Methanol: Oil)	Catalyst (wt%)	Time (min)	Yield (wt%)	Reference
Chicken fat	<i>Turritella terebra</i>	65	1:1	4.0	90	94.0	[92]
Leather tanning waste	Waste capiz shell	60	6:1	3.0	360	93.4	[93]
WCO	Waste oyster shell	65	9:1	6.0	180	87.3	[94]
Cotton seed	Waste mollusc shells	65	12:1	5.0	270	99.5	[95]
Palm	Waste <i>Meretrix meretrix</i>	60	30:1	10.0	180	95	[88]
WCO	mussel shell	65	9:1	10.0	180	89.0	[96]
WCO	<i>Malleus malleus</i>	65	12:1	7.5	86	93.8	[97]
WCO	<i>Donax deltooides</i>	65	63:8	7.5	129	96.5	[98]
<i>Chlorella vulgaris</i> biomass	Eggshell	70	10:1	1.4	180	92.3	[99]
WCO	<i>Meretrix meretrix</i>	60	6.0:1	0.1	180	89.0	[100]
Palm	Riversnail shell	65	12:1	1.0	90	N/A	[101]
Palm	Mixed seashells	60	30:1	10.0	180	96.0	[102]
Castor	Mud clam shell	60	14:1	3.0	120	96.7	[87]
Palm	<i>Cyrtopleura costata</i>	60	5:1	0.1	10	96.0	[103]
<i>Jatropha curcas</i>	<i>Polymesodaerosa</i>	25	5.2:1	0.02	133	98.5	[104]
Palm oil	Waste obtuse horn shell	N/A	12:1	5.0	360	86.8	[105]
WCO	Scallop shell	65	6:1	5.0	120	86.0	[106]
WCO	Eggshell	25	6:1	5.8	660	97.0	[107]
Microalgal	<i>Cyrtopleura costata</i>	65	150:1	9.0	120	84.1	[108]
Rubber seeds	Waste cockle shell	N/A	15.7:1	9.0	201	88.1	[109]

CaCO_3 is converted to CaO through the calcination process [101,110,111] and a longer calcination time results in a shorter reaction time, which is an important factor in the transesterification process [110]. The yield of transesterification catalyzed by CaO catalyst derived from river snail increased by an increase in time [101]. *Turritella terebra* was used for CaO catalyst production. The catalyst was used in the transesterification of chicken fat. A yield of 94.0% was obtained under the following experimental conditions: 4% catalyst amount, methanol to oil molar ratio of 1:12 and reaction time of 90 min [92].

The conversion of waste shells into heterogeneous inorganic catalysts is one of the principal approaches to reducing the amount of waste being disposed of in the landfill and increasing the commercial value of seafood production. CaO catalyst from waste mollusc shells exhibited better surface structural properties than commercial CaO. FAME yield of 99.5% was obtained for transesterification of cotton seed oil (reaction conditions—methanol: oil molar ratio 12:1, catalyst amount 5%, reaction temperature 65 °C for 4.5 h) [95]. CaO catalyst from waste *Meretrix meretrix* shells had 95.0% yield, and reaction conditions

for obtaining maximum conversion were 3 h reaction time, 30:1 of methanol to oil molar ratio, 10.0% catalyst amount and 60 °C reaction temperature [102]. Waste mussel shell catalyzed the transesterification of WCO and 89.0% yield was obtained after 3 h with 9:1 methanol to oil molar ratio at 65 °C [96]. Waste *Malleus malleus* shells were used for biodiesel production using WCO as feedstock; biodiesel conversion of 93.8% was achieved by using catalyst concentration of 7.5%, the methanol to oil ratio of 12:1 and reaction time of 86.25. CaO catalyst from waste capiz shells had 90.0% yield after three cycles, and reaction conditions for obtaining maximum conversion were 4 h reaction time, 6:1 of methanol to oil molar ratio, 3.0% catalyst amount and 60 °C reaction temperature [93]. Waste oyster shell catalyzed the transesterification of WCO and 87.3% yield was obtained after 3 h with 9:1 methanol to oil molar ratio at 65 °C [94]. *Donax deltooides* shells were used as a source of CaO for biodiesel production using WCO as feedstock; biodiesel conversion of 96.5% was achieved with a catalyst concentration of 7.5%, the methanol to oil volumetric ratio of 63.8% and reaction time of 129.3 min [98]. River snail shell was used as a CaO source to produce biodiesel from palm oil as a feedstock [112,113]. Furthermore, CaO catalysts are produced from mixed shells of *Meretrix meretrix*, *Amusium pleuronectes*, *Perna viridis*, *Anadara granosa* via dissolution precipitation method and by using 10.0% catalyst, 96.0% was achieved up to five cycles [102]. CaO catalyst was synthesized from clamshell and the yield was 96.7% after five times recycling [87].

The properties of catalysts can change depending on their sources. For example, CaO catalysts produced from natural dolomitic rocks had a faster conversion rate compared to the catalysts produced via same method from waste mixed seashells [114]. Moreover, reaction conditions, such as higher temperatures can increase catalytic activity, and thus, high yields can be achieved in a shorter period of time. For example, microwave-assisted transesterification catalyzed by *Cyrtopleura costata* seashell-derived CaO catalyst resulted in 96.0% yield in 10 min reaction time [103]. Moreover, basicity also improves the catalytic activity; 98% yield was obtained when the reaction was catalyzed by barium (Ba) doped CaO catalysts obtained from waste of *Turbonilla astriatula* seashells [115]. Although CaO-based catalyst, similar to other heterogeneous catalysts, can be recycled and reused up to several cycles with maintained yield, their reactivity may diminish after few cycles of reuse. The biodiesel yield decreased from 86.8% in cycle two to 70% on the third cycle when CaO catalysts synthesized from obtuse horn shells catalyzed the reaction [105].

CaO nanocatalysts from *Polymesoda erosa* seashells were synthesized using calcination, hydration and dehydration methods and were compared with the synthetic one. The transesterification process was performed using *Jatropha curcas* oil as a non-edible feedstock under the following conditions: reaction time of 133.1 min, at room temperature, and methanol to oil ratio of 5.2:1, resulting in biodiesel yield of 98.5%. In terms of reusability, the catalyst was used up to six cycles and the biodiesel yield was maintained at an average of 95.8% [104]. WCO and soybean oil were used as a feedstock for transesterification, which led to the FAME yield of 97.0%. Eggshell was used as a catalyst in this study under the reaction time of 11 h, methanol to oil molar ratio of 6:1 at room temperature. The catalyst was used up to five cycles with WCO and ten cycles with fresh soybean oil. It is noteworthy that the less reusability of the catalyst with WCO was due to the negative effect of FFA on the catalyst [107].

Waste *cyrtopleura costata* was used as CaO catalyst source to convert the microalgae oil to biodiesel and 84.1% of FAME yield was obtained at 1 h reaction time, a 150:1 weight ratio of methanol to oil at 65 °C [108]. The authors reported that the catalyst was efficient more than three times, showing the FAME yield of more than 65.0%. Waste cockle shells were utilized as a catalyst source and 88.06% biodiesel yield was obtained by using rubber seed oil as the feedstock [109]. The transesterification was carried out under the following conditions: methanol to oil molar ratio of 15.6:1, catalyst amount of 9.0%, and 168 min reaction time. Snail shells were used as feedstock for the catalyst in biodiesel production and reported a higher yield than when waste cockleshells were used. the author reported that the biodiesel yield obtained was 96.0% under conditions of methanol to oil molar

ratio of 9:1, catalyst amount of 10.0% and at 65 °C [116]. CaO was obtained successfully from seashells source through calcination in high temperature. Calcination temperature and calcination time were the most effective parameters influenced on CaCO₃ conversion to CO₂.

In most of the comparative investigations, natural CaOs obtained from seashells showed higher catalytic activity than synthetic catalysts [104,106,117]. It was found that the natural CaO had more surface area and it had a negligible amount of Mg and Sr, and due to the basicity of those alkaline metal oxides, the catalytic activity of seashell obtained catalyst increases [106]. The natural source received CaO showed better catalytic activity due to smaller particle size and larger surface area [87]. In another comparative research, hydrated lime-derived CaO presented greater surface area and pore volume than the synthetic one. Furthermore, in terms of N₂ adsorption isotherms, a small hysteresis loop was identified in hydrated lime-derived CaO, while such structure was not found in commercial CaO [48]. The preparation of synthetic CaO would be obtained only by calcination, while the development of CaO from natural sources needs other steps such as cleaning, drying, washing, dehydration, blending, and calcination. Overall, as there were limited comparative papers, it is hugely suggested to compare the naturally obtained catalyst with the synthetic one.

Characterization is an important feature for studying the spectral and structural characteristics of the catalyst, and numerous methods are used for the characterization of heterogeneous catalysts. However, choosing the best technique relies on the data presented by the methods. The common methods used for characterization are thermogravimetric analysis (TGA), Brunauer Emmet-Teller (BET) surface analyzer, X-ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). TG/DTA analyzer was used to determine the thermal stability of the synthesized zeolite-based catalyst [35,118]. BET surface analyser is used to measure the surface area, pore volume and pore diameter of the catalysts. Adsorption and desorption of nitrogen applies in the system to manifest the pore size distribution and surface area of the catalyst. In this technique, to eliminate the water and other polluting materials and let these lines become accessible to be filled with nitrogen molecules, the solid samples are discharged in a vacuum and at temperatures between 50 to 60 °C. Over a wide area, XRD is a common method to characterize the general crystalline material. This method determines the crystalline phases in bulk materials and also verifies their shape and size based on the diffraction peak attributes. Furthermore, the crystalline size of catalysts can be determined from half of the width for a (200) diffraction peak using the Scherrer equation. SEM is conducted to investigate the surface structure of the catalysts after development from seashells to confirm their structure, as well as the surface changes after reusability. Qualitative information regarding the morphology of the samples can be obtained SEM functions by focusing electron beams passing across the sample surface and imaging can be carried at different magnifications and resolutions. XPS is another method for catalyst characterization. This technique is used to determine the chemical and physical changes of catalysts upon exposure to gaseous molecules and upon different thermal treatments. Photo-ionization is applied, and after that, the kinetic energy distribution of emitted photoelectrons is analyzed to approximate the elemental constitution and chemical phase of the elements on the surface. This is obtained by discharging a soft X-ray onto the surface and identifying the energy of the photoelectrons released from areas a few nm (up to 5) from the surface of a sample [119].

5. Factors Affecting the Transesterification Catalyzed with CaO-Based Catalysts

Temperature, alcohol to oil molar ratio, catalyst amount, and reaction time are the key parameters that affect the transesterification rate and the FAME conversion. In addition to the key parameters, several specific criteria should be taken into account when using CaO or CaO-derived catalysts in the reaction, such as catalyst reusability, calcination temperature, total basic sites, water content, use of support for the catalyst, and FFA. The effect of these criteria on the reaction rate and yield are discussed in the subsequent section.

5.1. Effect of Catalyst Reusability

Catalyst reusability is an advantage of heterogeneous catalysts, and most of the alkaline metal oxides have the ability to be used several times. However, such catalysts may change during transesterification. Based on the XRD results, the crystalline structure of the reused catalyst deteriorated after four cycles [115]. The basicity of the catalyst was also diminished. Catalysts were reused for four cycles, and 90% FAME yield was maintained [101]. Catalysts obtained from waste seashells with the reusability of up to ten cycles without any apparent loss of performance were reported [120]. However, most of the research reported the reusability of CaO-based catalysts up to five cycles [87,102,118].

5.2. Effect of Catalyst Loading Amount

The catalyst loading amount is a critical factor affecting the process and catalyst amount [87]. Biodiesel yield was enhanced with increasing catalyst content from 5.0% to 10.0% [121]. On the contrary, the catalyst amount of more than 11% resulted in troubled mixing due to high viscosity, and hence the yield concentration dropped significantly [41]. Loading high concentrations of the catalysts can make the catalyst less fundamental, which then leads to low catalyst activity [115].

5.3. Effect of Water Content on Catalytic Activity

Water exerts various influences on catalytic activity and on the reaction yield. For instance, an increase in water content can increase saponification due to the hydrolysis of triglycerides to FFA [106,122]. The yield of WCO-based biodiesel decreased when water content increased from 0.6% to 2.5%. The presence of water in methanol, on the other hand, can increase the yield due to the formation of more methoxide anions as a result of water adsorption on the surface of CaO and hydroxyl groups formation [123]. However, hydration of CaO before calcination enhanced the catalytic performance [124], and hydrated CaO elevated the conversion rate and, accordingly, the biodiesel yield [125].

5.4. Effect of Alcohol to Oil Ratio

The alcohol-to-oil ratio has more effect on biodiesel yield than the catalyst loading amount yield [109,126]. An increase of yield from 55.5% to 88.1% was observed when the alcohol-to-oil ratio was increased stepwise, while the excessive rise in the alcohol-to-oil ratio decreased due to a decreased interaction of catalyst and oil [109,126]. Consequently, a higher amount of alcohol could minimize the interaction of the catalyst and oil resulting in a lower biodiesel yield. From the other point of view, the influence of impurity of source material on catalytic activity and the effect of storage conditions by FTIR and TGA were respectively studied [118,127]. In another study, the influence of adding a co-solvent on FAME yield and reaction kinetics was examined. By applying a suitable co-solvent during the biodiesel production, the reaction time and biodiesel production expenses could be reduced greatly. Thus, alcohol-to-oil molar ratio could directly impact the biodiesel yield greatly [48].

5.5. Effect of Support

Using catalyst supports can boost catalytic activity by stabilizing the catalyst and decreasing the leaching issues of CaO catalysts. CaO supported on MgO had a better catalytic activity than an unsupported catalyst due to improved basicity and increased surface area [63,117]. Scallop shell supported with $MgCO_3$ was synthesized as a catalyst with a smaller crystalline size and a better activity [127]. CaO supported with Tin oxide ($CaO-SnO_2$) had a better catalytic activity due to the improved stability as a result of supporting the catalyst [84]. Thus, using support for CaO-based catalysts can overcome their leaching problem and improve their activity in the process of biodiesel production.

5.6. Effect of FFA on Catalytic Activity

CaO-based catalysts can be affected by FFA, and oils with low FFA content serve as better feedstocks for CaO-catalyzed transesterification [128]. The presence of FFA makes the catalyst less active and affects the catalyst reusability. A high concentration of FFA in WCO exerted a negative influence on catalyst reusability and resulted in a decrease in catalyst activity after the fifth cycle, while the same catalyst with fresh soybean oil was active up to ten cycles [118].

5.7. Effect of Basic Sites

Basicity has an important role in catalyst productivity which can contribute to biodiesel production [115]. The higher the basicity of the catalyst, the higher the catalyst activity [129]. There are different ways to improve the basicity of the catalyst. Ultrasonic assisted transesterification is an efficient method when using CaO as a catalyst as it can crush the catalyst into a smaller part which leads to increased basic sites. Basic sites have the main role in CaO efficiency as a catalyst, therefore increased basic sites improves the transesterification efficiency. Further, increased basicity reduces the time needed for oil conversion to biodiesel [51]. Further, using zeolite as support can provide more surface area for the catalyst as a carrier which enhances the basicity of the catalyst. NaY, KL, and NaZSM-5 zeolites were modified by CaO via microwave irradiation to be used in the transesterification of soybean oil with methanol. The supported CaO catalyst revealed more catalytic activity than the pure CaO. The enhanced activity was due to the increase of BET values and basicity after loading on NaY zeolite [67]. Decreased catalytic activity, on the other hand, can be attributed to the blockage of basic sites due to excess Ba loading and the subsequent obstruction would pose difficulty to the diffusion of reactants throughout the catalyst [115]. However, catalyst activity does not solely rely on basic sites of the catalyst and other parameters such as feedstock used, time, temperature, etc., can affect the yield [130].

5.8. Effect of Calcination Temperature

The calcination temperature is a significant factor affecting the efficiency of the catalyst. Calcination at high temperatures increases the surface area and porosity and activates the CaO-based catalyst, and therefore results in a better catalytic effect. River snail-based CaO, produced at longer calcination temperatures, showed a better catalytic activity and higher yields were achieved.

Surface area, total pore volume, and mean pore diameter of the sample, however, will decrease by increasing the calcination temperatures to above 800 °C. It was found that the optimum calcination temperature was 600 °C, and the catalyst activity was affected by a decrease in surface area and porosity as a result of calcination at elevated temperatures [131]. The source of calcium was mixed shells of *Meretrix meretrix*, *Amusium pleuronectes*, *Perna viridis*, *Anadara granosa*. Calcium- zinc and aluminum compounds was prepared via the dissolution precipitation method and subsequently applied in transesterification and the higher calcination temperature made the catalyst more active and basic [102].

In summary, there are different criteria affecting the catalyst performance, which should be paid attention to. These criteria can significantly affect the FAME yield. Optimization is still a matter of concern while producing biodiesel. The response surface methodology RSM and central composite design (CCD), Box–Behnken factorial design and Analysis of variance (ANOVA) are general tools for optimization. In the following section, the most common reactors in use for biodiesel production by using heterogeneous catalysts have been reviewed.

6. Reactors for Heterogeneously Catalyzed Transesterification

The heterogeneously catalyzed transesterification process, including the CaO-catalyzed reactions, are typically conducted in batch stirred reactors due to their simple process. However, the implementation of these reactors leads to an increase in capital investments, as they require a large reactor volume. Therefore, a continuous process can overcome this problem

as continuous reactors can work with smaller volumes. The packed bed reactor (PBR), trickle-bed reactor (TBR), and packed bed membrane reactor are common types of reactors used in batch and continuous processes catalyzed by heterogeneous catalysis [132–134].

6.1. The Packed Bed Reactor (PBR)

PBR consists of a water-jacketed stainless-steel section. The column is packed with heterogeneous catalysts and oil and methanol will be permeated into the process by utilizing two separate raw material pumps. Blending and preheating of the reactants happens in a blending tank and the blend will be then nourished to the channel of the reactor by a pump. The reaction temperature will be managed by a heater to keep a steady temperature and the temperature indicators and pressure gauges are used to observe the system temperature and pressure. Purification is carried out by reducing the pressure distillation to eliminate the overabundance of methanol and water produced through the reaction. A methanol recovery unit does continuous distillation with a condenser and a heater. Methanol, because of having a low melting point, could be recovered via sequential processes of evaporation and distillation. The permeate stream comprising biodiesel, methanol, and glycerol will be collected [135]. Moreover, by applying a solid alkaline catalyst in a continuous flow PBR, both separation of catalyst and co-production of high pure glycerol processes were made easier, and hence it leads to a decrease in production costs and feasibility of catalysts reuse. A schematic diagram of PBR is shown in Figure 3.

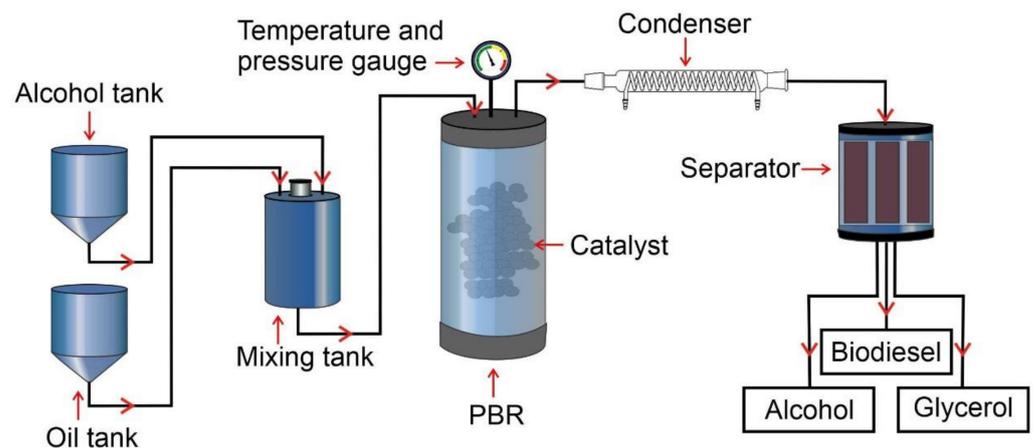


Figure 3. Schematic of packed bed reactor.

6.2. The Trickle-Bed Reactor (TBR)

In a TBR, syringe pumps are used to nourish methanol and oil into the reactor. Complete evaporation of methanol occurs in the heated part at the lowest part of the reactor, and its vapor will be moved throughout the catalyst bed. A condenser is implemented to recover the unreacted methanol. The oil is nourished through a single tube and is distributed on the catalyst bed. FAME, glycerol and unreacted oil are recovered in the product reservoir. The catalyst particles will be assembled into the base of the reactor and glass beads of the same diameter will be charged into the remainder of the reactor. An electric heater is used to heat the TBR to a designated temperature. The reaction product is then centrifuged. Deionized water will be used to rinse the upper ester layer, and the product is separated by centrifugation [133]. A schematic diagram of TBR is shown in Figure 4.

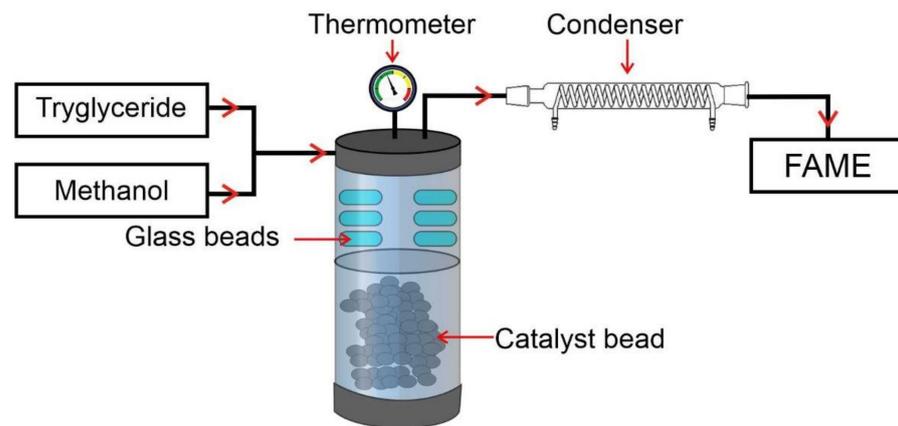


Figure 4. Schematic of trickle-bed reactor.

6.3. The Packed Bed Membrane Reactor (PBMR)

This reactor is designed to discharge the product selectively, adjust the addition of reactants to the process, and enhance the catalyst and reactants interactions [134]. Methanol molecules, biodiesel, and glycerol can pass through the membrane. Methanol should be recycled and returned to the reaction, as it is one of the essential factors for value adding to the process; thus, this reactor has a simple and efficient methanol recovery unit. This system is dependent upon continuous distillation, including a three-neck round bottom flask, thermometer and condenser. Biodiesel, methanol, and glycerol are leached through and collected in the three-neck round bottom container. Immediate methanol evaporation occurs as a result of the high temperature of the oil bath. Methanol is continuously evaporated due to its lower boiling point, followed by distillation and returning to the process to reduce its depletion. A schematic diagram of PBMR is shown in Figure 5.

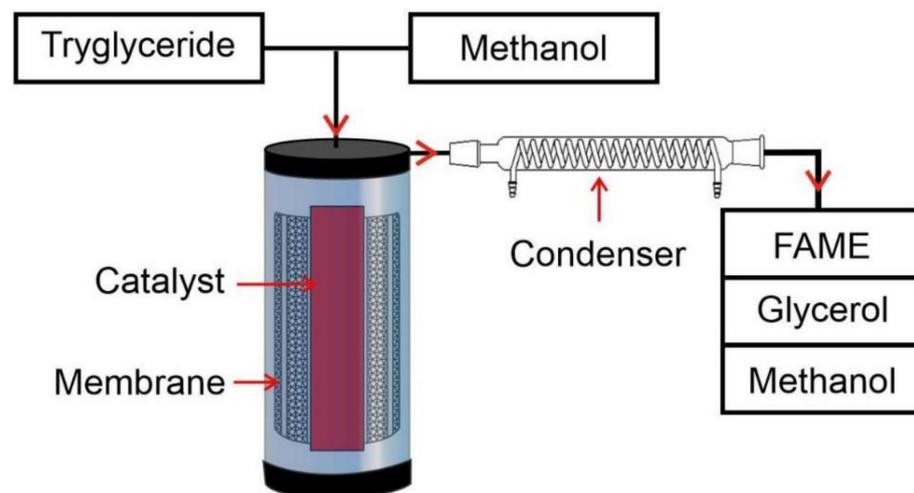


Figure 5. Schematic of packed bed membrane reactor.

7. Ultrasonic-Assisted and Microwave-Assisted Transesterification

7.1. Ultrasonic-Assisted Transesterification

The ultrasonic process implementing sound wave energy was introduced as an effective method for heterogeneous catalyzed transesterification. This method influences the reaction by making and collapsing micro-bubbles. Reduced reaction time, increased reaction rate, low catalyst consumption rate and less methanol demand and improved yield are unique features of this technology, which makes it more applicable. This method leads to a high yield of biodiesel as a result of a natural mixing of oil and alcohol compared to the conventional methods. Moreover, ultrasonic irradiation can break the catalyst into

smaller parts [25,38]. The yield of ultrasonic-assisted transesterification (20 kHz ultrasonic cavitation) at the presence of CaO, SrO and BaO catalysts and palm oil in 60 min increased from 5.5% to 77.3% (CaO), 48.2% to 95.2% (SrO), and 67.3% to 95.2% for BaO [136]. Further, calcium methoxide catalyst catalyzed the transesterification of soybean oil at 65 °C with 9:1 alcohol-to-oil molar ratio, and the biodiesel yield of more than 90.0% was achieved [41].

7.2. Microwave-Assisted Transesterification

Microwave-assisted technology is based upon the application of electromagnetic waves between infrared radiation and radio frequencies of 30 GHz to 300 MHz. Shorter reaction-time as a result of rapid heating and increased biodiesel yield are the main features of this method. The radiation affects the molecular movement but not the molecular structure. Therefore, biodiesel obtained through this technique has the same characteristic as the biodiesel obtained with the aid of conventional methods [25,38]. Microwave-assisted transesterification was carried out in a short reaction time of 10 min and palm oil with the methanol to oil molar ratio of 5:1 was successfully converted to biodiesel (yield of 96.0%) [103].

8. Challenges and Prospects

Despite the benefits of the heterogeneous catalyst over the homogeneous catalyst, there are still some limitations to applying these catalysts. The main limitation is that these catalysts can only be used with triglycerides having less than 0.5% of FFA as they make the catalyst neutral. Leaching of the active phase is another challenge with these catalysts, which reduces the efficiency of the catalyst after several cycles. Further, the product is contaminated due to catalyst leaching. Catalyst deactivation due to water and CaO adsorption in intact contact with air is another challenge. Another challenge with CaO derived catalysts is their tendency to bind to glycerol during the reaction and the formed complex of Ca-Gly is less active in terms of catalysis than the CaO [137].

Calcium-rich catalysts have a significant disadvantage of mass transfer resistance between reactants and products, which leads to a costly production process and prolonged reaction time [138]. Methods, such as ultrasound-assisted and microwave-assisted transesterification are conducted to reduce the mass transfer resistance, which results in less energy consumption and shorter reaction-times [139,140]. Further, to commercialize these heterogeneous alkali catalysts in the future, more fortifying systems need to be generated.

The elimination of CaO from reaction requires more purification steps, which results in a large amount of wastewater. Additionally, CaO exposure to air may cause a problem in its catalytic activity due to the chemisorption of CO₂ and H₂O. It is recommended to store the catalyst in a desiccator to reduce the catalyst exposure to air during the experiment is inevitable. Therefore, measures need to be taken to avoid catalyst air exposure or at least minimize it. Moreover, CaO-based catalysts can only be used with triglycerides having less than 0.5% FFA that increase the cost of biodiesel production. Hence, the pretreatment step is required before applying a CaO-based catalyst to remove the FFA, since high FFA inactivates the CaO-based catalyst.

Therefore, as CaO-based catalysts require specific considerations, in terms of leaching, exposure to air and mass transfer resistance, efficient design of these catalysts are very important to improve the biodiesel yield. There are some methods to make these catalysts more efficient; to mix them with other materials, such as MgO-CaO, CaO-SiO₂, CaO-ZnO to overcome the leaching problems. Further, using supports such as zeolite can minimize the leaching. Therefore, future work is essential to find more compounds to make CaO derived catalysts more applicable for use at an industrial scale.

9. Conclusions

Biodiesel has been categorized within sustainable fuels due to its distinctive benefits such as being non-toxic, biodegradable, renewable, and eco-friendly. Heterogeneous catalysts have become a focus of attention recently as they are able to avoid the problems

caused by the use of homogeneous catalysts, such as elongated separation and purification stages, and thus, avoids the longer reaction time and generation of wastewater. Among heterogeneous catalysts, calcium oxide has gained much attention due to its reasonable price, low solubility in methanol, low toxicity, and high availability from natural resources. Among these aforementioned catalysts (such as pure, supported, mixed oxides), seashell derived calcium oxide catalysts are environmentally friendly and have no detrimental effect on the ecosystem. The large-scale application of those wastes will bring economic advantages to the calcium oxide waste materials and make promising catalysts. However, the obtained catalysts are not stable and suffer from leaching problems during the reaction. The preparation of effective and catalytically stable calcium oxide catalysts is still a significant difficulty. Therefore, a continuous attempt is required to modify the technology in order to improve the sustainable biodiesel production and reduce the costs.

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