

Review

Progress on Modified Calcium Oxide Derived Waste-Shell Catalysts for Biodiesel Production

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Abstract: The dwindling of global petroleum deposits and worsening environmental issues have triggered researchers to find an alternative energy such as biodiesel. Biodiesel can be produced via transesterification of vegetable oil or animal fat with alcohol in the presence of a catalyst. A heterogeneous catalyst at an economical price has been studied widely for biodiesel production. It was noted that various types of natural waste shell are a potential calcium resource for generation of bio-based CaO, with comparable chemical characteristics, that greatly enhance the transesterification activity. However, CaO catalyzed transesterification is limited in its stability and studies have shown deterioration of catalytic reactivity when the catalyst is reused for several cycles. For this reason, different approaches are reviewed in the present study, which focuses on modification of waste-shell derived CaO based catalyst with the aim of better transesterification reactivity and high reusability of the catalyst for biodiesel production. The catalyst stability and leaching profile of the modified waste shell derived CaO is discussed. In addition, a critical discussion of the structure, composition of the waste shell, mechanism of CaO catalyzed reaction, recent progress in biodiesel reactor systems and challenges in the industrial sector are also included in this review.

Keywords: biodiesel; transesterification; waste-shell; heterogenous catalyst; green catalyst; alternative fuel

1. Introduction

The drastic depletion of fossil fuels and continuous anthropogenic greenhouse gas emissions have prompted the search for alternative renewable and sustainable fuels with efficiency similar to the conventional fuels being used today [1,2]. In this regard, renewable and sustainable biofuels had been seen as an alternative in order to reduce fossil fuel usage [3,4]. Biofuels are generally referred to as liquid or gaseous fuels that are produced from renewable sources [5], which are typically generated from biological material or living organisms, such as plants, animal by-products, or microorganisms [6]. In the past

10 years, the biofuel industry has experienced an enormous growth, and the main regions contributing to this development are Europe, Brazil and the United States [7]. Currently, the main application of biofuels is as a liquid transportation fuel [8]. In general, biofuels can be divided into four generations, which depend on the raw materials used. First-generation biofuels are mostly derived from subsistence crops. Second-generation biofuels come from non-food biomass or lignocellulosic crops [9]. This is sustainable, cost-effective, and highly available, which will be advantageous for the biorefinery industry. Noteworthy, the use of lignocellulosic crops lead to a zero net carbon dioxide emission and environmental friendliness [10]. The third generation of biofuels come from algae-sources [11,12]. The best means of utilizing raw materials for second and third generation biofuel production is to avoid the issue of food competition. Besides, there are many advantages in producing biofuels from algae, where the triglyceride-based oil extracted from microalgae is 15 to 300 times higher than that of conventional crops in terms of area [13,14]. Production of biofuels from genetically modified algae is considered as the fourth-generation of biofuels [15]. The growing interest in fourth-generation biofuel usage strives to lower environmental impact, especially on land usage for crop plantation [16].

Typically, the liquid-based biofuels that widely apply to transportation purposes are biodiesel and bioethanol [17,18]. Bioethanol is produced through starch or sugar fermentation, while biodiesel is obtained via the transesterification reaction of oil crops [9]. Biodiesel is used to replace diesel, while bioethanol is used to substitute for petrol [19]. It is noteworthy that the majority of biofuel usage is from biodiesel (76%) (Figure 1a), followed by bioethanol (~20%). Malaysia is one of the most important palm oil producers in the world. The country is experiencing a robust development in new oil palm plantations and palm oil mills. According to a Malaysian Palm Oil Board (MPOB) report [20], the total biodiesel production projected to 2019 in Malaysia shows an increasing trend (Figure 1b), which suggests that Malaysia has an important role to play in fulfilling the growing global need for palm oil-derived biofuels. Biodiesel is generated by esterification of fatty acids (FAs) or transesterification of triacylglycerol (TAG) with alcohol in the presence of a catalyst. Water is co-generated in the esterification reaction of fatty acid, and glycerol is transesterified from TAG (Figure 1c) [21]. Commonly, biodiesel is used in engines with compression ignition with little or no modification [22]. The characteristics of biodiesel are similar but not the same as petroleum diesel. Biodiesel has a high flash point, thus making it safe to store and handle [23]. Biodiesel can be used directly as engine fuel (B100) or blended with diesel in a certain proportion (B20, B50, etc.) [24,25]. Noteworthy, biodiesel has a higher cetane number compared to bioethanol, efficient for engine ignition, while bioethanol has a high-octane number with anti-knocking properties in engines. Earlier literature has discovered that biodiesel exhibited better engine performance than bioethanol, because bioethanol has higher miscibility to water and organic solvent that will contaminate the automotive lubricant parts with resulting corrosion to the engine [26–28].

Generally, there are differences between the esterification and transesterification process. Esterification occurs when a carboxylic acid reacts with alcohol by adding an acid catalyst and produces water as a by-product. Transesterification is the reaction between the vegetable oil or animal fat and alcohol in the presence of a basic catalyst to form ester and glycerol as a by-product [29,30].

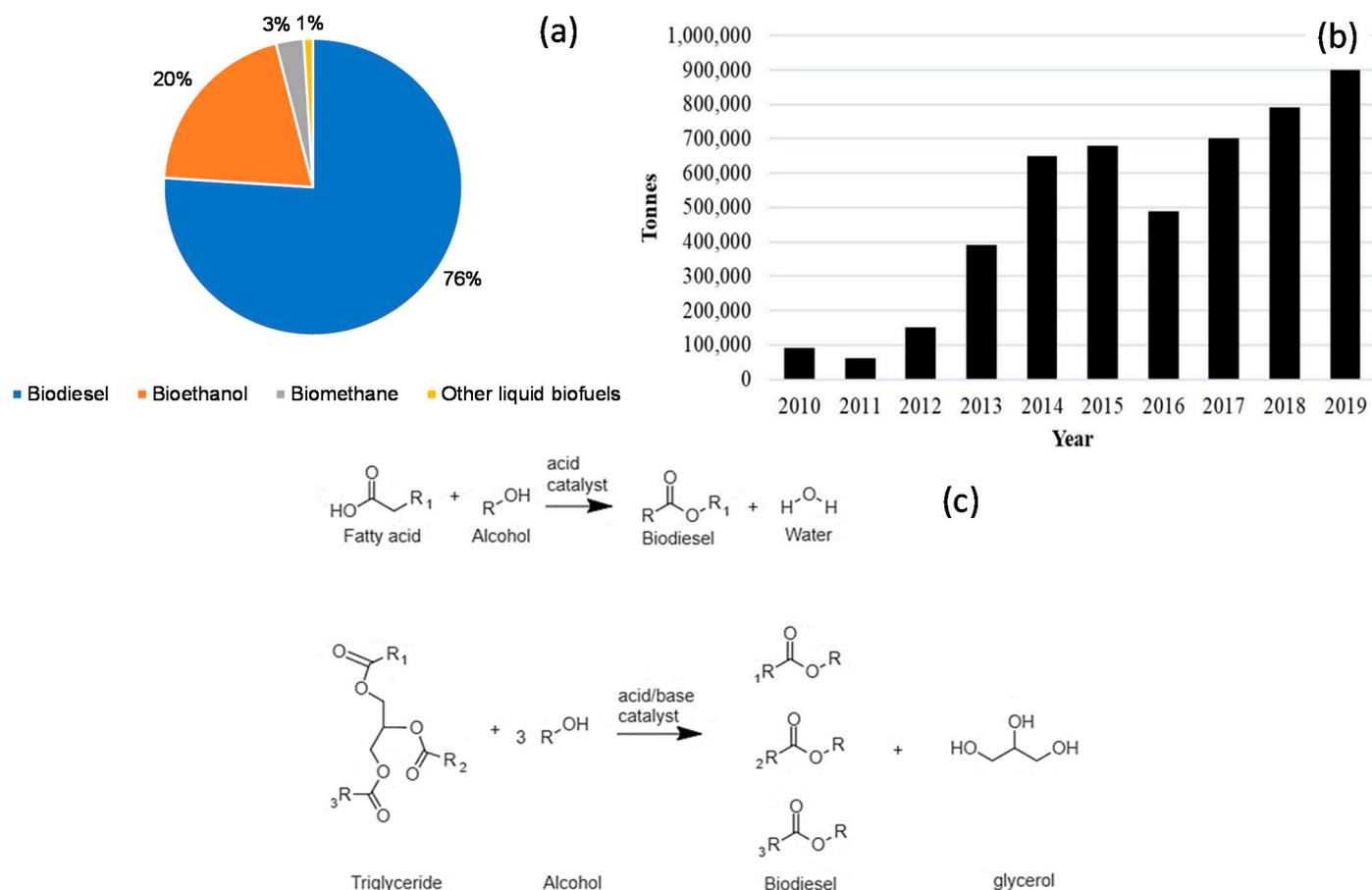


Figure 1. (a) Share of each type of biofuel consumed in the EU transport sector in 2011 (adapted from [31]) (b) Biodiesel production from palm oil from 2010 to 2019 in Malaysia [20] (c) Esterification of fatty acid and transesterification of vegetable oils/ animal fats.

Based on various physicochemical properties of the catalysts, both acid and base catalysts can be classified as homogeneous, heterogeneous or enzymatic catalysts [32–34]. Homogeneous acid and base catalysts such as H_2SO_4 , HCl , NaOH and KOH are the most common homogeneous catalysts used in esterification and transesterification reactions [35]. Compared with homogeneous type catalytic transesterification and esterification, heterogeneous catalytic systems have several advantages, including the ease of the biodiesel separation process, catalyst recycling or reuse, lower energy requirements and minimal water consumption. Due to these advantages, processing costs can be reduced significantly [18]. In addition, the use of heterogeneous acid catalysts is the most suitable when the feedstock contains high free fatty acid (FFA) and high water content, as the catalyst has a high tolerance for both of the compounds [36]. Solid acid catalysts such as $\text{SO}_4^{2-}/\text{SnO}^{2-}-\text{SiO}_2$, carbon-supported solid acid catalyst, sulfated zirconia, etc., have been extensively studied for transesterification of high FFA feedstock with high biodiesel yield of 94.8–97.0% [18]. However, a longer reaction time makes this unattractive compared to the short reaction time from the base-catalysed transesterification process [37,38]. Several types of solid base catalysts have been utilized for biodiesel production such as alkaline metal oxide, alkaline metal carbonates or hydro-carbonates, anionic resins and basic zeolites [39]. Among these catalysts, alkaline metal oxides (AMOs) are the most well-known and effective metal group for base-catalysed transesterification reaction [40]. Many reports have been published on AMO catalysts (e.g., CaO) for transesterification in various types of feedstock-based biodiesel production, due to the high basicity of active sites that enhance kinetic reactivity during the transesterification process. Currently, CaO can be generated

directly from natural waste shell/limestone/chemical Ca salt, which reported comparable characteristics to conventional CaO [41–43]. The high availability of calcium resources makes it a cheap material for various applications.

It was discovered that the waste shells are beneficial for the production of a wide range of value-added chemicals and products, such as 1,2,3-triazoles [44], cyclopentanone [45], 7,8-dihydro-4H-chromen-5(6H)-one [46], dimethyl carbonate [47], steam gasification [48], wastewater treatment [49], soil improvement [50], Portland cement replacement [51] and artificial stone [52]. Xiong et al. [44] studied the synthesis of 1,2,3-triazoles catalyzed by waste oyster shell powders (OSPs)-supported CuBr catalyst (OSPs-CuBr). The copper(I) content of the OSPs-CuBr catalyst was found to have the ability to be reused consistently for eight runs. The authors reported that the prepared OSPs-CuBr catalysts showed high catalytic activity with cost-effectiveness for the larger-scale synthesis of 1,4-disubstituted 1,2,3-triazoles. Sheng et al. [45] investigated the multiple characteristics of the *Scapharca Broughtonii* shell, conch shell and oyster shell derived catalyst for cyclopentanone self-aldol condensation. Dimer obtained from the self-aldol condensation pathway of cyclopentanone can be used as a high-density fuel or perfume precursor.

The synthesis of 7,8-dihydro-4H-chromen-5(6H)-one using a one-pot three-component condensation catalysed by eggshell at ambient temperature was reported by Mosaddegh & Hassankhani [46]. Synthesis of 7,8-dihydro-4H-chromen-5(6H)-one and its derivatives contributed to the potential pharmacological activity and as cognitive enhancers for the treatment of neurodegenerative diseases. Based on the high catalytic activity and reusability, the synthesis was completed in a short time with a high yield. The optimum catalyst loading amount to produce the maximum yield was only 0.1 g of eggshell powder. The catalyst was able to be reused in five runs without losing its catalytic activity. In addition, the authors found that benzylidene malononitrile intermediate was generated instead of 7,8-dihydro-4H-chromen-5(6H)-one when condensation occurred without the utilisation of the catalyst.

Gao & Xu [47] examined the viability of eggshell-derived catalyst for the synthesis of dimethyl carbonate (DMC) from the transesterification between methanol and propylene carbonate (PC). DMC is an important methylation and carbonylation agent, which is substituted for dimethyl sulphate and methyl halide in methylation reactions and for harmful phosgene in polycarbonate and isocyanate synthesis. In “green chemistry” and “sustainable societies”, the production and chemical applications of DMC are remarkable for its negligible ecotoxicity, low bioaccumulation and persistency. The maximum value of PC conversion and DMC yield were shown after 1 h under the optimum reaction conditions of 0.8 wt.% catalyst amount, with methanol to PC molar ratio 10:1 in 25 °C and 1 atm, which are 80% and 75%, respectively. The eggshell catalyst was able to be reused at least four times with a minimal deactivation.

Note that waste shell is also widely utilized in the steam gasification process [53,54]. Fan et al. [48] studied steam gasification of Indonesian sub-bituminous KPU coal (KPU) using an innovative composite K_2CO_3 -eggshell catalyst in a fixed bed reactor. In this study, eggshells were calcined at a temperature range of 700–900 °C under N_2 atmosphere. The mixture of pure K_2CO_3 and calcined eggshells were impregnated with the KPU. The introduction of H_2O and N_2 gasified the resultant char after completion of the pyrolysis process. The primary product gases were H_2 , CO, CO_2 and CH_4 . The experiment resulted in improved yields of H_2 and CO in the presence of the composite catalyst with a composition of 15% K_2CO_3 and 5% eggshell. H_2 yield with this composite catalyst was increased by 6% and 123%, respectively, compared to that obtained by utilizing pure K_2CO_3 and no-catalyst. Besides, an increase in carbon conversion rate constant of more than three times in the range of 700–900 °C was also achieved by this composite catalyst, as it reduces the activation energy of gasification by about 38% compared to the no-catalyst reaction.

In addition, waste shells can be used for wastewater treatment. Evidently, Luo et al. [49] utilised waste oyster shell in a bio-contact oxidation tank to treat tidal combined river wastewater. Wastewater quality including chemical oxygen demand (COD), five days' biochemical oxygen demand (BOD_5), salinity and ammonia-nitrogen (NH_3-N), total phos-

phorus (TP) and total suspended solids (TSS) was analysed. According to the average removal percentage of these chemicals (80.05%, 85.02%, 86.59%, 50.58% and 85.32%, respectively), it was confirmed the waste oyster shell bio-filler was efficient in pollutant removal. The oyster shell as active filler indirectly improved the recovery ability of the system in the bio-contact oxidation tank by allowing the microbes from the biofilm that decompose pollutants to attach and grow on it. The growth of microbes and the high porosity of oyster shell reduced the sludge amount form in the bio-contact oxidation tank, thereby ensuring accessibility in the one-year experiment.

Soil contamination has impacted on agricultural toxicity, and thereby threatened human and animal health. Noteworthy, agricultural soil improvement was also achieved by mixing the soil with calcined waste oyster shell. This has been successfully implemented by Bi et al. [50]. Moreover, it was discovered that the amount of heavy metal cadmium (Cd) and arsenic (As) in the soil was remarkably reduced. The oyster shells were calcined at various temperatures between 400–800 °C and it was discovered that higher calcination temperature (800 °C) rendered excellent removal of Cd and As. It is noteworthy to state that the vegetables grown in this improved soil are within the C and A categories regarding food safety standards.

In the case of the construction sector, waste shell partially replaced expensive Portland cement and it was discovered that it has the ability to reduce CO₂ emissions. The mixture of cement, sand, water and eggshell powder for mortar production was investigated by Pliya & Cree [51]. The strength, compression and flexural of the mortar decreased as the replacement percentage of eggshells increased. Hence, the authors suggest that eggshells could act as a filler to enhance these properties. Waste shells were also utilised in the production of artificial stone with high mechanical properties artificial. Silva et al. [52] created artificial stone by mixing oyster shell powder with unsaturated polyester resin. The authors reported that flexural strength of oyster shell stone (20 ± 2 MPa) was higher than marble (natural stone) and even than Aglostone (marble powder plus polyester resin). The authors also inferred that the flexural strength of oyster shell stone might be improved to 50MPa by adding glass microcrystals which are higher than Marmoglass (>32 MPa). Its hardness was also tested an 1216 ± 120 MPa was obtained which is comparable with marble (1471 MPa). This shell stone is currently is available for countertops and worktops, laboratory benches, etc. Based on the above findings, it can be summarized that waste shells are beneficial for a variety of applications. Since the waste shell is a renewable and cheap alternative, its implementation in a variety of applications will not only simultaneously decrease manufacturing cost, but also reduce the burden on the environment and ecological system.

Based on the above applications of waste shell, obviously it is very promising to be used as catalyst for effective production of biodiesel; hence, this paper focused on a detailed review of natural waste shell as catalyst for biodiesel production [55]. To date, many studies have reported that Ca²⁺ ion from CaO catalyst was easily leached out during the reaction, and hence the CaO-catalysed reaction is still far from using an ideal catalyst. Indeed, the limitation of CaO has been solved chemical modification, such as incorporation of AMO, transition metal oxide (TMO) or metal functionalization approaches. Several reviews focused on commercial CaO and eggshell-derived CaO for biodiesel production [56,57]. In the present study, we aim to discuss the remarkable progress of waste shell-derived CaO for biodiesel production from 2011–2020, besides a comparative study of transesterification activity summarized for conventional CaO, waste shell-derived CaO and modified waste-shell-derived CaO catalysts. The review will highlight the reaction mechanism of both CaO and modified CaO derived from waste shells for biodiesel production. Lastly, the review summarizes the existing technology of reactor systems for advance biodiesel production.

1.1. Solid Base Catalysts

Solid based catalysts are principally referred to as a heterogeneous system in the reaction medium, where the solid surface consists of active sites that act as a Bronsted base

(proton acceptor) or Lewis base (electron-pair donor) [58]. There are a few characteristics for a catalyst to be recognised as a solid base catalyst. First, when the surface is characterised, it shows that the basic sites exist. Secondly, the catalyst shows a correlation effect between catalytic activity and the basicity density as well as the distribution strength of basicity. Thirdly, the reaction pathways are similar to the base-catalysed reactions in a homogeneous system. Lastly, the generation of anionic intermediates during the reaction indicates the presence of a base-catalysed pathway [59]. AMOs including MgO, CaO, SrO, and BaO, have been intensively studied as heterogeneous basic catalysts for transesterification of triglycerides with methanol [60]. The basic strength increased in the order of MgO < CaO < SrO < BaO, which was attributed to the decrease in electro-negativity of the conjugated metal cation of AMO. Note that the catalytic activities of transesterification exhibited in the same sequence. Among these AMOs, CaO exhibited promise as a heterogeneous catalyst for biodiesel production [58,61,62]. It is noteworthy to mention that CaO is less soluble in methanol, stable at high temperature, possesses high reaction activity, is non-toxic, naturally abundant and cheap [63,64]. Faruque et al. (2020) [18] reported that CaO showed high stability and long life span especially for moderate reaction conditions. Similar findings were observed [65–67], where the majority of the CaO catalysts exhibited greater reusable capability (>5 cycles) without undergoing any regeneration process.

1.2. Waste Shell-Derived Catalyst

World aquaculture production is increasing rapidly as seafood demand grows and marine capture production stalls. Commercial mollusk shells (referred to as mollusks or shellfish) are an important food component for the global economy, where the commercialisation of mollusks is in second place at a worldwide level. Annually, about 23% (~16.1 million tons) of mollusks are produced, which is equivalent to 19 billion USD [52,57]. According to the FAO global Fishery and Aquaculture statistics database, there are 79 mollusk species listed as cultured and 93 species considered as captured species. They can be classified into four major groups: clams, oysters, mussels and cockles. The clam and oyster are the most prevalent that contribute, 38% and 33%, respectively, to global production [68]. Based on the overview of mollusk farming, Asia has been the main producer of mollusks, followed by Europe and the Americas. China is the leading producer for mollusks (83.4%) followed by Japan (2.2%), South Korea (1.9%), Thailand (1.4%) and Vietnam (1.2%) [57,69]. In 2016, Asia yielded 158.35 million tonnes out of 171.39 million tonnes for total global production [70]. When considering the mollusks' role as a global food source, one of the most worrying factors is the huge amount of residue generated. Most of the waste shells are deposited in landfills, abandoned on land, or returned to the sea, thus causing incalculable environmental impacts. When the aquaculture wastes are deposited in the soil, it will contaminate the environment and create an unfavorable strong odor [52]. Apart from mollusk shells, eggshells are also widely generated during food processing and manufacturing plants as by-products [71]. Eggs represent the main ingredient in a variety of food products such as cakes, salad dressings and fast foods, whose production results in several daily tons of eggshell waste, and incurs considerable global disposal costs. About 250,000 tons of eggshell waste is produced annually worldwide [72]. Similar to the scenario of mollusk waste shell, improper disposal of waste eggshell will result in environmental odor from biodegradation. Thus, it is strongly suggested that all of the waste shells should be recycled, reused and channeled as a valuable product for different applications. Indeed, utilization of waste shell is a priority for sustainable development achievement. Nowadays, waste shells are reused and refined in various fields, such as water treatments, cosmetics, toiletries, food, agrochemicals, bioenergy and pharmaceuticals [70]. Interestingly, waste shell can be potentially used as a bio-based calcium source of catalyst for biodiesel production. Notably, the use of waste shell in biodiesel production is in line with the purpose of the biodiesel development, which is a greener and environmentally friendly product.

1.3. Composition of Waste Shell

Many invertebrates have produced hard-shells composed of crystallized biogenic minerals to protect and support their soft bodies [73]. The major component in the shells is calcium carbonate (calcite) with a composition of approximately 95–99% [54,57,74]. Other than calcium carbonate, mollusk shells also contain organic matrix proteins as secondary compositions, which are known to be important for the nacreous layer and critical in calcification [73]. Mollusk shells are divided into three main layers which are the periostracum, prismatic and nacreous layers. The periostracum layer is the external layer that is composed mainly of conchiolins. The middle layer is called the prismatic layer, which is mainly made up by oriented calcite crystals. The inner pearl layer is mainly composed of orientated aragonite crystals [75].

In the case of eggshell, it can be classified as membranous for snakes and lizards; pliable for most turtles; and rigid for certain turtles and geckos and all species of crocodiles, birds and dinosaurs. The eggs of the avian species are the highest grade of amniotic eggs among oviparous vertebrates. Eggshell is a complex bio-ceramic that allows the regulation of metabolic gas and water exchange, and its properties can be finely tuned according to the environmental conditions of a given species. Calcium carbonate (calcite) is the main component in eggshell, and is the major inorganic substance found in an egg that makes up about 98% of the chemical composition [76]. Other minor components in eggshell are Mg (0.9%) and P (0.9%) [77].

There are four main polymorphs of calcium carbonate, which are calcite (b-CaCO₃), vaterite (m-CaCO₃), aragonite (l-CaCO₃) and amorphous calcium carbonate. Calcite, aragonite and vaterite are polymorphs in nature in order of increasing stability and can co-exist in numerous marine organisms [78,79]. Noteworthy, calcite with rhombohedral structures is the most stable polymorph of calcium carbonate followed by orthorhombic Aragonite. It forms elongated structures called columns, palisades or crystallite. The presence of magnesium (Mg) in aragonite creates weaker bonds in the crystal structure; thus, it is more soluble. Vaterite with a hexagonal structure, which is the most unstable polymorph, readily transforms into aragonite or calcite at room temperature. Therefore, only a small amount of vaterite can be found in nature [80–82]. Other than calcium carbonate, some shells are also composed of chitin. For example, the major composition of oyster shells is calcium carbonate with a chitin outer layer, and an inner layer consisting of calcite (90%) and aragonite (10%) [83]. Chitin is one of the most widely abundant biopolymers in the waste shell, next to cellulose. Chitin is made up of α -(1-4)-linked 2-acetamido-2-deoxy-D-glucose with β -(1→4) linkage, known as oligomer. Commercial chitin is mostly extracted from crustacean shells. About 40 wt.% of waste shells is composed mainly of chitin, lipid, meat offcuts, calcium carbonate and pigments [78]. Depending on the species and cultivation condition of the aquaculture, the composition of chitin in shells will differ from 15–40%. Despite this, the highest composition chitin is tightly bound with calcium (20–50%) and proteins (20–40%) that give a structural stiffness to the shell. Hence, multiple steps of pretreatment are required to recover each component [84].

2. Recent Trend in Waste Shell-Derived Catalyst for Biodiesel Production

Valorisation of waste shell rich calcium as natural material for catalyst synthesis is an outstanding topic. It is considered to be environmentally friendly and provides various beneficial impacts on the biodiesel industry. Figure 2a shows that the scientific investigation of biodiesel production in the presence of a catalyst is widely available; here the statistics indicate an increment from 579 publications in 2010 to 950 publications in 2020. The report indicates that within 10 years (2010–2020), China was the country with the highest number of publications in this field, with 1415 out of 8409 publications from around the world, followed by India (1383) and Malaysia (816) (Figure 2b). However, there are only about 205 publications related to waste shell-derived catalyst (Figure 2c). Figure 2d reveals the trend of countries with publications related to waste shell-derived catalyst for biodiesel production from 2010 to 2020. It can be seen that India has published 55 studies

on the subject, which accounts for 3.98% of total publications. Malaysia comes in second with 39 publications, 4.78% of the total. Publications from Thailand (23), China (19) and Indonesia (19) are also relatively high in number when compared to other countries.

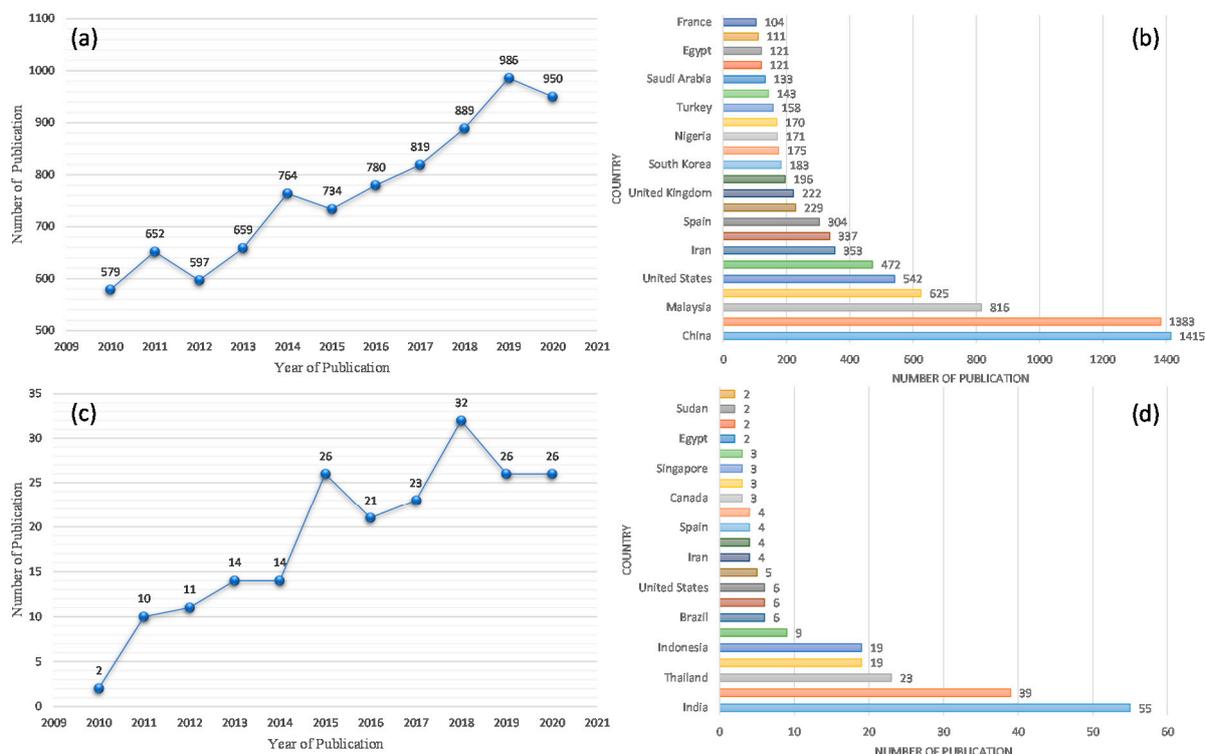


Figure 2. (a) Publication trends on biodiesel production in the presence of catalyst from 2010–2020, (b) Publications on biodiesel production in the presence of a catalyst based on country from 2010–2020, (c) Publication trends on waste shell catalyst in biodiesel production from 2010 to 2020, (d) Publications on waste shell catalyst in biodiesel production based on country from 2010–2020 (data collected from SciFinder Database).

3. Waste Shells vs. Modified Waste Shells Catalyst

3.1. Waste Shells-Derived Catalyst for Biodiesel Production

Table 1 presents various types of waste shell-derived catalysts for transesterification of vegetable oil. The majority of the waste shells can be transformed into active CaO after calcination at a temperature within the range of 800–1000 °C. It can be seen that the majority of the pure CaO derived from waste shells successfully converted the low FFA feedstock (palm oil, Camelina Sativa oil, soybean oil and some low FFA waste cooking oil) into biodiesel [74,85–92]. High biodiesel yield (90–97%) was achieved by Hangun-Balkir [74] from transesterification of Camelina sativa oil (FFA: 1.6%) over waste eggshell and lobster shell-derived catalysts. Both waste shells were prepared by calcination at 900 °C. The transesterification was catalysed by 1% (*w/w*) catalyst loading with 12:1 MeOH:oil molar ratio at 65 °C for 3 h. The authors compared the biodiesel yield that was catalysed by commercial CaO, waste eggshell and lobster shell. The maximum biodiesel produced was 99%, 97% and 90%, respectively. Buasri et al. (2013) [86] used waste mussel, cockle and scallop shell as a catalyst for transesterification of palm oil (FFA: 0.1%) at 65 °C with MeOH:oil molar ratio of 9:1 within 3 h and 10 wt.% catalyst loading under 1 atm pressure in a glass reactor. The waste mussel shell-derived catalyst with a large surface area of 89.91 m²/g and pore volume of 0.130 cm³/g produced 97.23% of biodiesel. However, scallop (74.96 m²/g, 0.097 cm³/g) and cockle (59.87 m²/g, 0.087 cm³/g) shell-derived catalysts produced 96.68% and 94.47%, respectively. Reusability is the most important feature of heterogeneous catalysts in industrial applications. Based on former literature,

the majority of waste shell-derived CaO catalysts can be reused up to five times without further undergoing regeneration treatment [74,88,93,94]. Notably, Laskar et al. successfully regenerated the CaO derived from snail shell [92]. After being washed with water and dried, the spent catalyst was reactivated at 900 °C for 4 h. The experimental results showed that 91% of biodiesel yields were obtained consistently within the eighth run but dropped to 77% sharply in the ninth cycle over the regenerated catalyst, suggesting that the active sites of pure CaO catalyst could be recovered after undergoing the regeneration process. It is worth mentioning that, based on Table 1, the majority of pure CaO derived from shell still exhibited lower catalyst stability.

When comparing the conventional reflux system with microwave-assisted transesterification, it was observed that the use of a microwave system successfully converts the biodiesel within a shorter reaction time [95]. This fact was in agreement with Khemthong et al. [87], whereby an effective transesterification activity on palm oil (FFA: 0.55%) using CaO derived from waste eggshells using the microwave at 900 W has been achieved within 4 min. This method improved the transesterification rate as compared to the traditional heating method for biodiesel production. Various conditions were tested to obtain the optimum condition in order to carry out transesterification reaction. Overall, the authors produced a maximum biodiesel yield of 96.7% using 15 wt% of catalyst loading amount and MeOH:oil molar ratio of 18:1 at 122 °C. The effectiveness of microwave technology is due to the presence of electromagnetic radiation that transmits energy directly to the molecule of reactants, thus resulting in intense local heating able to accelerate molecular restructuring. Some studies [87,90,93] reported on microwave-assisted biodiesel production and noted that high microwave power could accelerate the reaction and improve product yield in a short time (4–5 min).

Waste cooking oil (WCO) refers mainly to frying oil used at high temperatures, edible fat mixed in kitchen waste and oily wastewater [96] and has been shown to have a high content of acidic compounds (FFA: >3%) [97]. The amount of FFA from feedstock is an important criterion for catalyst selection. WCO with high FFA concentration will result in increased soap formation with an alkaline catalyst, so it needs to be pretreated with an acid catalyst to reduce FFA concentration [98]. Due to this reason, it can be suggested that the WCO with low FFA value will easily transesterify to biodiesel. Evidently, Aitlaalim et al. [88], Lin et al. [90] and Sirisomboonchai et al. [91] successfully transesterified the WCO with FFA value within the range of 0.30–0.61%. It was found that the biodiesel yield was within the range of 86–94%. Since the FFA for these WCO is lower than 3%, an undesired saponification reaction would not occur during the transesterification reaction.

Although waste shell-derived CaO are effective catalysts for transesterification of low FFA feedstock with high biodiesel yield (90–99%) and high reusability (3–6 cycles), waste shell-derived CaO shows poor performance in the presence of feedstock with high FFA and moisture. The presence of moisture favors hydrolysis of triglyceride to diglycerides and more FFAs, while the presence of FFA with high acidity favors the reaction with the basic CaO catalyst. Generally, CaO-catalyzed transesterification process renders two plausible pathways; the first preferable step is a partial heterogeneous reaction attributed to basic sites of the Ca-O surface; while the second unfavorable step is a homogeneous reaction that contributes to the Ca²⁺ liquid species that leach into methanol, which causes the loss of active sites. The leached Ca²⁺ further reacts with FFA in oil via a saponification process that forms soap as by-product. The formation of soap during reactions resulted in the poisoning of the catalyst surface, which resulted in the reduction of both transesterification reactivity and reusability. Besides, the presence of catalyst-soap suspension in the reaction medium makes the separation between glycerol and biodiesel product difficult and thus reduces the biodiesel yield [99].

Therefore, further modification of CaO derived from the waste shell is needed as this may enhance the hydrophobicity of the catalyst as well as the generation of new acid sites (Lewis or Bronsted acid sites) in CaO system. The presence of both acid-based properties of the catalyst are crucial for the process of biodiesel production, especially highly adapted to a

wide-range of low-cost and high acid oil feedstock. It was noted that Lewis/Bronsted bases sites (attributed to lattice oxide & OH^- phases) favor transesterification of triglyceride oil to ester, while Lewis/Bronsted acid sites (attributed from metal and H^+ phases) favor the esterification process of FFA in oil into ester. Thus, the presence of acid sites from modified CaO appeared to be insensitive to FFAs and moisture and hindered the saponification reaction, which increased yield [100]. Generally, the basic nature and acid active sites of catalysts can be determined by several types of analysis, such as Hammett's indicators (references), and CO_2/NH_3 desorption from thermal programmed desorption (TPD), or a microcalorimetry instrument that provides the basic/acid density as well as the different strength (weak, medium, and strong) of the adsorption profile. On the other hand, in-depth information of Lewis and Bronsted sites for acid-based profile, usage of model catalytic reactions, and theoretical/modeling approaches to determine acid-base active site can be obtained from other techniques such as Fourier-transform infrared spectroscopy (FTIR), Electron Spin Resonance Spectroscopy (ESR), Nuclear magnetic resonance (NMR), photoluminescence, Raman, UV-Visible Spectroscopy (UV-Vis), and X-Ray Photoelectron Spectroscopy (XPS) [101].

3.2. Modified Waste Shells-Derived Catalyst for Biodiesel Production

As mentioned above, waste shells are natural and renewable resources that can be used for the preparation of CaO-based catalyst. Calcium carbonate in the waste shells can be decomposed to CaO through calcination, which can be used as bio-based material for biodiesel production [74]. Although CaO is highly active for the transesterification process, the CaO is limited in stability and sensitive to FFA content and frequent dissolution and leaching of Ca^{2+} ions. This phenomenon resulted in reduction of catalytic activity during a reusability study, where the leached Ca^{2+} contaminated the biodiesel product at the end of the process [61,102]. Indeed, CaO catalysts have been extensively modified by adding a second or more chemical components to improve its catalytic activity and the stability of the system. Generally, these modified CaO catalysts were prepared via incorporation of AMO, TMO, mesoporous material, and through functionalization approaches.

Based on the previous section, other AMOs including MgO, SrO, and BaO have been intensively studied as heterogeneous basic catalysts for transesterification of triglycerides [60]. Taking into account the superior basicity characteristic for these AMOs [103–105], combining these with CaO derived from waste shell has been focused on. Boro et al. [104] investigated biodiesel production from WCO by using a series concentration of Ba (0.5%, 1.0% 1.5%) doped waste *Turbonilla striatula* shell-derived CaO catalyst. It was found that, as the Ba concentration increased from 0.5% to 1.0%, the basicity properties increased, and reduced when the Ba concentration increased to 1.5%. This author suggested that reduction of basicity is due to reduction in the CaO species. The study revealed that Ba1.0/CaO showed higher biodiesel yield (98%) and the capability to be reused four times. Similarly, Boro's study in transforming Nahor oil (FFA: ~8%) [106] and WCO (FFA: 11%) [104] into biodiesel rich fuel over Ba modified waste shell-derived CaO catalyst and Ba/CaO catalysts, yielded biodiesel of 98%. Mg/CaO synthesized from waste eggshell was also found effective in transesterification of edible waste oil. EDX analyses showed MgO/CaO catalyst consisting of 26.03% calcium, 41.93% oxygen, and 32.04% magnesium. The highest biodiesel yield of 98.37% was produced at the optimum condition of 4.5 wt% catalyst loading amount, 16.7:1 MeOH:oil molar ratio at 69 °C for 7 h with reusability up to six times [105]. Tomano et al. [103] investigated the properties of Sr substituted cuttlebone-derived CaO for the conversion of biodiesel from palm olein. The Sr species were loaded within a range of 1–10 wt.%. Different content of Sr dispersion on CaO surface was indicated by the mapping analysis. However, the rich Sr species on the CaO surface could result in a reduction of BET surface area of the Sr/CaO catalyst. Overall, Sr/CaO with 1 wt.% of Sr loading has the highest BET surface area. The transesterification was carried out in 60 °C with 9:1 methanol/oil ratio and 5 wt.% catalyst loading for 3 h. The 1 wt.% Sr/CaO rendered highest conversion of biodiesel at 95%. Not that the biodiesel

yield produced by AMO doped CaO was mostly >95% and the catalyst can be reused up to >5 times after regeneration treatment.

Transition Metals (TM) such as Zn, Fe, Mn, Al, Mo, Cu, etc., are important materials that have been used in many catalytic reactions. Indeed, TMOs are commonly used in the process of oxidation, dehydrogenation, selective oxidation/reduction, ammoxidation, metathesis, water–gas shift, etc. The unique physicochemical properties of TMOs favour the selective reaction pathways such as surface acidity and basicity, cationic and anionic vacancies, high mobility of lattice oxygen, etc. [107]. Due to the excellent chemical properties of TMOs, the chemical properties of CaO could be tailored through TMO addition. Hence, TMO modified CaO will have both acidic-basic sites, which actively convert high FFA feedstock to biodiesel via both esterification and transesterification processes [108]. Evidently, Joshi et al. [109] successfully converted high FFA feedstocks (Jatropha (6.25%) and Karanja oils (8.75%)) over Zn, Fe, Mn and Al-doped CaO derived from eggshell to biodiesel. Interestingly, the specific surface area and basicity character of TMO doped CaO catalyst are greater than for pure CaO. The high basicity character of TMO modified CaO is possibly due to the existence of synergistic interaction between the multi-metal ions. The authors also stated that the electron-donating property of oxygen anion in the TMO makes the combined metal ions more electropositive, which may lead to the formation of more Lewis base sites on the surface of CaO. As expected, the TMO doped CaO effectively transesterified and esterified the high FFA feedstocks with yield within a range of 76–98% and have the ability to be reused for four cycles with a biodiesel yield within the range 92–95%. Similarly, Rahman et al. reported on the transesterification of eucalyptus oil by using Cu and Zn doped CaO derived from eggshell [110]. Zn doped CaO exhibited excellent basic sites, a larger surface area and pore volume than Cu doped CaO and CaO itself. The transesterification of eucalyptus oil was performed at the optimum condition: 5 wt.% catalyst loading, 6:1 MeOH:oil molar ratio, 65 °C for 2.5 h. The biodiesel yield for catalyzed transesterification of eucalyptus oil was in the sequence of Zn/CaO > Cu/CaO > CaO. The authors reported the reusability of the Zn/CaO up to seven times with the yield of the biodiesel maintained > 85% to the sixth run. The effectiveness of TMO modified CaO was agreed by Kaur and Ali's study, in which the transesterification of jatropha oil occurred over Mo doped CaO at reaction parameter: 12:1 ethanol to oil molar ratio, 65 °C using 5 wt.% of catalyst loading within 4.5 h of reaction time. The results showed that 99% of biodiesel was achieved and the catalyst can be reused up to five times [111]. Das et al. [112] utilised cobalt-doped waste eggshell derived CaO catalyst, in the conversion of lipid extracted from *Scenedesmus quadricauda* species algae to biodiesel. In this work, about 98% of algae oil was successfully converted into biodiesel over Co/CaO catalyst. Note, the Co/CaO exhibited stable activity for at least three reaction runs. The authors remarked that partial leaching of the Co and deposition of reaction products to the catalyst active sites were the possible reasons for lower catalyst stability. More recent studies for biodiesel production using TMO doped CaO derived from waste shell (W-Mo/CaO, Zn/CaO and Fe₃O₄/CaO) have been reported by Mansir et al. [113], Borah et al. [114] and Helwani et al. [115]. In general, the TMO doped catalyst produced high biodiesel yield within the range 90–97% and reported that these catalysts can be reused in up to five consecutive runs. The above findings suggest that TMO modified CaO catalyst has been found to be the most promising technique in overcoming the dissolution of active Ca²⁺ and improving the catalyst stability.

Functionalization is a treatment incorporating other chemical elements or compounds such as alkaline (KOH, NaOH, KF) and acid (H₂SO₄, HCl, HSO₃Cl) to tune desirable characteristics in the catalyst [116]. Alkaline functionalisation is an approach to improving the surface area and pore volume of the catalyst [117], while acid functionalisation will improve the acidic properties of the catalyst. Thereby, the acid functionalised CaO catalyst is capable of converting high FFA feed to biodiesel via esterification [118]. This is evinced by Nurhayati et al. finding [118], with sulfonated blood clam shell catalyst (CaO treated by 3M H₂SO₄) effectively converting both FFA and TAG to a high yield of biodiesel

(~97%) under reaction conditions: 12:1 MeOH:oil molar ratio, 60 °C for 3 h using 1 wt.% catalyst loading. Cho and Seo [119] also treated quail eggshell with 0.005 M HCl for 2 h and maximum biodiesel conversion of 89% was obtained by transesterification of palm oil at 65 °C within 2 h using 1 wt.% of catalyst and 12:1 methanol:oil molar ratio. Other cases of high FFA microalgae oil were studied by Syazwani et al. [120] with the utilisation of CaO derived from Angel Wing shell catalyst. The CaO catalyst was modified via sulfuric acid treatment and the result indicated that the CAWS_(x)SO₄ catalysts were capable of converting the palm fatty acid distillate (PFAD) (FFA: 92%) to biodiesel rich fuel. The optimal biodiesel conversion (98%) from the PFAD was acquired at the reaction temperature of 80 °C, 15:1 MeOH:PFAD molar ratio and 5wt.% catalyst loading for a 3h reaction time [121].

As discussed previously, the alkaline functionalisation approach has been extensively investigated to improve the textural properties of the CaO [117]. This was confirmed by Nurdin et al. [122] in the transesterification of castor oil. Obviously, KOH/CaO derived from mussel shell shows high surface area and pore volume properties. The authors reported the catalyst's reactivity, capable of maintaining biodiesel yield to ~80% for four reaction runs under optimal condition: 6:1 MeOH:oil molar ratio, 2 wt.% catalyst loading, 60 °C for 3 h. Other than KOH, CaO was also modified by alkaline potassium fluoride (KF). Thi & Myat [123] treated the waste eggshell derived CaO with KF in order to promote stronger active sites formation. KF was functionalized with CaO via a wet-incipient method under microwave irradiation. The authors remarked that the composition of Ca and KF in KF/CaO catalyst influenced the catalytic transesterification activity. The study indicated that the maximum yield of biodiesel was not achieved with the high amount of KF, due to over-coating of the catalyst surface by potassium and fluoride components. Biodiesel production was performed at the optimum condition with 8:1 MeOH:oil molar ratio, 5 wt.% catalyst loading at 65 °C for 2.5 h with maximum biodiesel yield of ~95%, while a reusability study showed that KF/CaO only can be reused for up to four runs with biodiesel yield > 80%. The stability of KF/CaO was further compared with pure CaO, when KF/CaO rendered better stability with less Ca leaching. Beyond that, Komintarachat & Chuepeng functionalised KCl on green mussel-derived CaO (CaO_{waste}) for transesterification of WCO under optimum conditions of 4 wt.% catalyst loading, EtOH:oil molar ratio of 10:1, 80 °C within 3 h [124]. The optimum biodiesel yield obtained was 97%. A comparison study was performed between CaO_{com}, synthesised CaO calcined from green mussel shell (CaO_{waste}) and KCl-impregnated CaO waste (KCl/CaO_{waste}), when KCl/CaO_{waste} catalyst was shown as most effective in facilitating the transesterification reaction.

Instead of metal oxide dopant and acid-alkaline functionalization approaches, the CaO can be modified via a hydration–dehydration technique. The hydration-dehydration of CaO catalyst involves the replacement of CO₃²⁻ with OH⁻ form Brønsted basic sites [125]. Ahmad et al. [126] treated waste eggshell-derived CaO with the hydration-dehydration method for the transesterification of algal biomass. With this method, the calcined eggshells were refluxed in the water at 60 °C for 6 h, followed by partial thermal treatment. Noteworthy, hydroxylation reaction occurred during water treatment, which simultaneously promoted the hydroxide surface on CaO. When the water-treated samples were sent for partial dehydration process, the attached water molecules were removed from the catalyst lattice, which led to the fractionation of crystallites to smaller sizes (higher surface area) and generation of higher porosity [100]. Ahmed further reported that the yield of biodiesel obtained was 93% under condition of 2 wt.% catalyst loading, 30:1 MeOH:Algal biomass at 60 °C for 3 h [126]. The authors reported that this catalyst was stable for six cycles with an average yield of >85%. A series of Zn doped CaO derived from eggshell (0.5–2 wt.% Zn²⁺ concentration in CaO) nano-catalysts was prepared and employed in the transesterification of WCO [114]. Maximum biodiesel conversion of 97% was recorded under the reaction conditions of 20:1 MeOH:oil molar ratio, 5 wt.% catalyst loading, 65 °C reaction temperature and 4 h of reaction time. Recently, Niju et al. utilized modified CaO derived from eggshell for transesterification of WCO and the result showed that biodiesel

conversion at 94% with reusability > 90% for six runs [127]. Similarly, Niju's research study also discovered a high biodiesel yield (97%) from transesterification of WCO over calcination–hydration–dehydration modified CaO. The CaO was produced from *Tellina tenuis* shells [128]. Based on Niju's observation, an excellent porous structure of the CaO catalyst was obtained from this method, and the large surface area confirmed the enhancement of the transesterification process [54,129]. Although several studies proved that the CaO synthesized from the hydration–dehydration approach exhibited excellent transesterification activity, this catalyst is chemically unstable as it possesses low reusability. This was in accordance with our former research group finding [100], where the modified CaO catalyst from natural waste clamshell (*Meretrix meretrix*) was used for transesterification of palm oil. The CaO modified via hydration–dehydration treatment showed high biodiesel conversion (98%) under a reaction time of 2 h, 1 wt.% catalyst loading and 9:1 methanol:oil molar ratio. Unfortunately, the catalyst was only capable of maintaining two runs of reaction with 98% biodiesel yield. Instability of the catalyst is due to the presence of active Ca(OH)₂ phases, which partially decomposed during the transesterification reaction. Interestingly, Chen's group [130] replaced the water medium with an alcohol medium during the catalyst's hydration treatment for the purpose of better Ca(OH)₂ stability during transesterification. The modified abalone shell-derived CaO (M-CaO_100) was treated by using ethanol in the hydration–dehydration method. Similarly, the ethanol acted as water that partially hydrated CaO to Ca(OH)₂ species, the results showing high basic density and excellent textural properties. The study further reported that a 7 wt.% catalyst loading, 9:1 MeOH:oil molar ratio and a reaction time of 2.5 h is required to obtain a biodiesel yield of 96%. In detail, after the fifth run, the biodiesel yield of the M-CaO_100 catalysed reaction dropped from 95.0% to 88.5%. The loss in activity during the reusability process was due to formation of calcium diglyceride on the catalyst surface, which resulted in unfavourable reaction between Ca(OH)₂ with the by-product glycerol. Overall, the results suggested that the ethanol treatment did not provide a significant stability effect to reduce Ca²⁺ leaching behaviour for M-CaO_100. Based on the above discussion, it is still a great challenge to identify a highly stable solid CaO derived from waste shell for biodiesel reaction.

It can be noted that not all of the literature studies on modification of CaO showed a significant impact on the stability of the catalyst for transesterification of plant-based oil. However, it has confirmed that the CaO catalysts were ineffective in transforming high FFA feedstock to biodiesel. This is due to the partial homogeneous state of CaO (dissolution of Ca²⁺) and lead to a big challenge for large scale biodiesel production. The high basicity of CaO catalyst is sensitive to the acid characteristics of FFA and the moisture content in low grade feedstock. Therefore, FFA content in oils needs to be kept as low as possible (0.5–1%) to hinder the saponification reaction, because otherwise it will react with the Ca²⁺ to produce soap as by-product. Excessive soap formation inhibits the biodiesel-glycerol phase separation and thus reduces biodiesel yield drastically. Due to this, modification of CaO is necessary to generate the acid sites in the catalyst system. The presence of Lewis/Bronsted acid sites is able to esterify the presence of FFA in low-grade feedstock into ester product without reducing the transesterification reactivity of the catalyst.

Table 1. Summary of various types of waste shell derived catalysts in transesterification of biodiesel production.

Waste Shells	Feedstocks	FFA (%)	Catalyst	Calcination		Transesterification			Conversion/Yield (%)	Reusability (%)	Ref.
				Temperature (°C)	Duration (h)	MeOH:Oil	Catalyst (wt%)	Duration (h)			
Angel Wing Shell	Microalgae Oil	8.03	CaO	805	2	150:1	9	1	84.11	3	[120]
Blood Clam Shells	Crude Palm Oil	<2	H ₂ SO ₄ /CaO	900	5	12:1	3	3	96.69	-	[118]
Capiz Shell	Refined Palm Oil	0.10	CaO	900	2	8:1	3	6	92.83	3	[85]
Chicken Eggshell	Jatropha Oil	6.25	ZnO-CaO	900	4	12:1	5	1	98.20	4	[109]
Cockle Shell	Palm Oil	0.10	CaO	1000	4	9:1	10	4	94.47	4	[86]
Crab Shell	Jatropha Oil	6.25	CaO	900	2	18:1	4	5 (min) (Microwave)	92.11	5	[93]
Cuttle Bone	Palm Oil	0.10	Sr/CaO	1000	5	9:1	1	3	95.47	-	[103]
Eggshell	Palm Oil	0.55	CaO	800	4	18:1	15	4 (min) (Microwave)	96.70	5	[87]
Eggshell	Camelina Sativa Oil	1.60	CaO	900	3	12:1	1	3	97.20	-	[74]
Eggshell	Nahor Oil	<1	Li Doped CaO	800	2	10:1	5	4	95.00	3	[106]
Eggshell	WCO	-	MgO/CaO	900	4	16.7:1	4.5	7	98.30	6	[105]
Eggshell	Eucalyptus Oil	0.56	ZnO/CuO	900	4	6:1	5	2.5	>90	7	[110]
Eggshell	Microalgal Oil	0.37	Co/CaO	900	4	-	1.5	4	98	3	[112]
Eggshell	Palm Oil	0.10	KF/CaO	900	3	8:1	5	2.5	~95	4	[123]
Eggshell	Algal Biomass	-	HD CaO	900	3	30:1	2.1	3	93.44	6	[126]
Grooved Razor Shell	WCO	0.66	CaO	900	-	15:1	5	3	94.00	6	[88]
Lobster Shell	Camelina Sativa Oil	1.60	CaO	900	3	12:1	1	3	90.00	-	[74]
Mussel Shell	Soybean Oil	0.10	KI-CaO	1000	4	6:1	3.5	4	85.00	-	[89]
Mussel Shell	Palm Oil	0.10	CaO	1000	4	9:1	10	4	97.23	4	[86]
Mussel Shell	Castor Oil	1.00	KOH/CaO	1000	1	6:1	2	3	91.17	5	[122]
Oyster Shell	WCO	1.00	CaO	1000	2	9:1	6	3 (Microwave)	87.30	-	[90]
Quail Eggshell	Jatropha Oil	6.25	CaO	900	2	18:1	4	5 (min) (Microwave)	92.78	5	[93]
Quail Eggshell	Palm Oil	0.10	H ₂ SO ₄ /CaO	800	-	12:1	0.01 (g)	2	89	-	[119]
Scallop Shell	Palm Oil	0.10	CaO	1000	4	9:1	10	4	96.68	4	[86]
Scallop Shell	WCO	0.62	CaO	1000	2	6:1	5	2	86.00	4	[91]
Snail Shell	Soybean Oil	0.10	CaO	900	4	6:1	3	7 (28°C)	98.00	9	[92]
Turbonilla Striatula Shell	WCO	<1	Ba Doped CaO	900	3	6:1	1	3	>98%	4	[104]

4. Mechanism of CaO Catalysed Transesterification

The most usual foundations for heterogeneous transesterification mechanisms are Eley-Rideal (ER) and Langmuir-Hinshel (LH) [131]. Both mechanisms are a theoretical model of bimolecular chemical reaction that can take place on a solid surface. In the ER mechanism, an atom or molecule adsorbs onto the surface, followed by direct reaction with another atom or molecule attached to the catalyst's surface. However, in the LH mechanism two atoms or molecules are initially adsorbed on the surface of the catalyst, and diffuse across the surface until they are close enough to interact [132]. The ER mechanism for the transesterification process involves three steps (Figure 3a): (i) methanol (M) is first adsorbed on the active site of the catalyst surface (S); (ii) then the triglyceride (TG) reacts with the methoxide ion to form fatty acid methyl ester (FAME) and glycerol (GL); and (iii) finally the glycerol is desorbed from the surface of the catalyst active site [133]. In the case of the LH mechanism, the reaction involves a five-step process. In the first two steps, the methanol and oil are individually adsorbed on the surface of the catalyst and generate two different active sites for further reaction. Both reactants will further react with each other in the following step, which is known as the determining step. The glycerol and FAME produced from the determining step is then desorbed separately in the last two-step of the transesterification process (Figure 3b) [133].

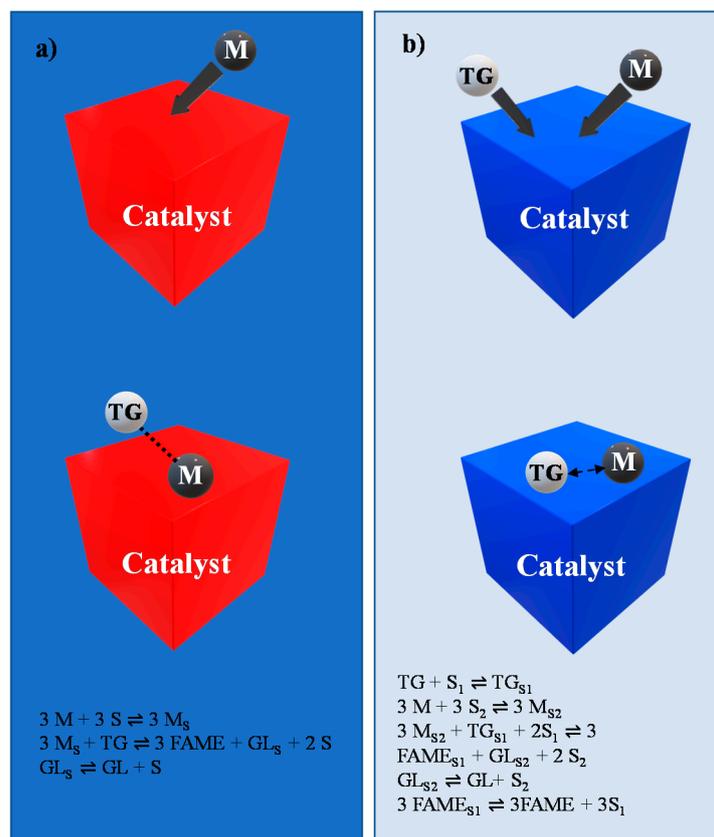


Figure 3. (a) Eley-Rideal (ER) mechanism and (b) Langmuir-Hinshel (LH) mechanism (data adapted from <http://www.chem.ucl.ac.uk/cosmicdust/er-lh.htm>).

As mentioned in the previous section, CaO is the most studied alkaline-earth metal oxide catalyst for transesterification. The presence of conjugated oxygen anions on the surface of CaO generates strong Lewis basicity that greatly affects the catalytic activity during the transesterification reaction [134]. The generation of basic sites on the oxide phase of the Ca-O surface plays role in abstracting the protons from the organic matter, which trigger a basic catalytic reaction [135]. Figure 4a illustrates the mechanism of CaO catalysed transesterification. The presence of basic active sites in the CaO catalyst abstracts

the proton from methanol to form a higher catalytic activity methoxide anion (CH_3O^-). The CH_3O^- then carries out a nucleophilic attack on the carbonyl carbon of triglyceride to form the tetrahedral alkoxy carbonyl intermediate. The rearrangement of this unstable intermediate results in the decomposition of the diglyceride anion and the formation of fatty acid methyl ester (biodiesel). Finally, the proton attracts the diglyceride anion to produce diglyceride and regenerate the active site of the CaO catalyst. This mechanism is then repeated twice for another two-carbonyl carbon and glycerol is yielded as a by-product. Both the first and second steps of the complex process of the transesterification of triglycerides and diglycerides with methanol are always much faster than the reaction of monoglycerides, which ultimately produces biodiesel and glycerol [136].

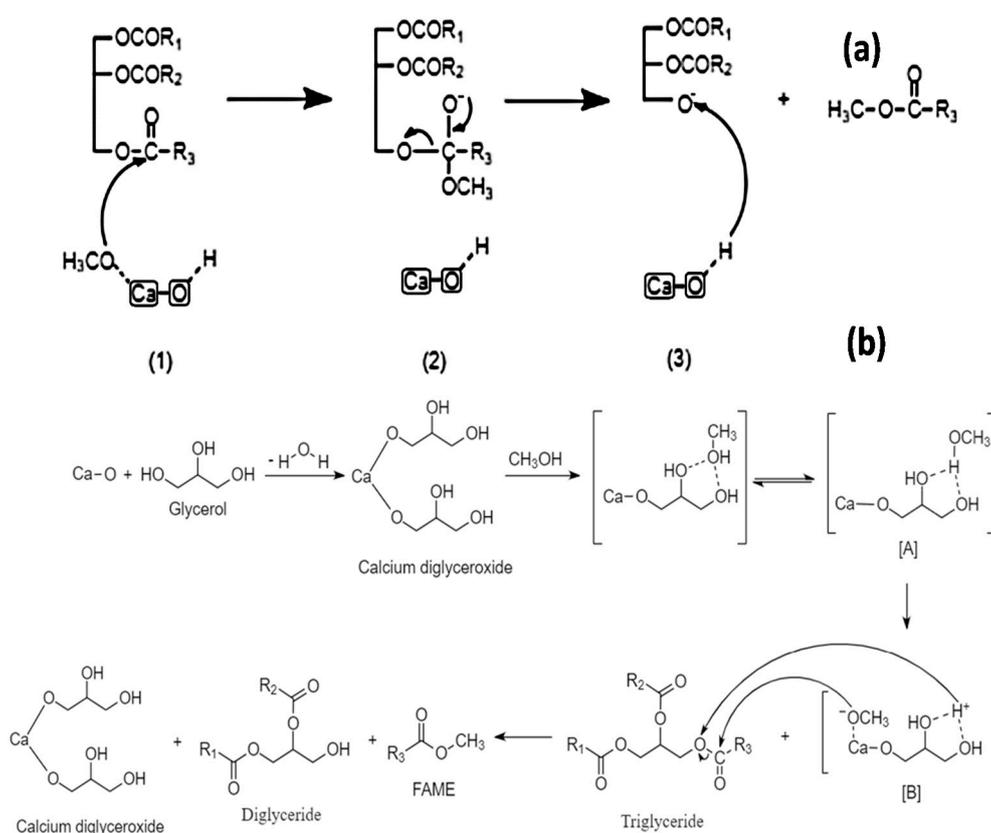


Figure 4. (a) Mechanism of CaO catalyzed transesterification (data adapted from [21]) (b) Mechanism of CaO reacted with by-produced glycerol in production of fatty acid methyl ester (FAME) (adapted from [137]).

The generated by-product glycerol is a trihydric alcohol, which tend to react with CaO via the dihydroxylation process to form CaO -glycerol complexes, known as calcium diglyceroxide ($\text{Ca}[\text{O}(\text{OH})_2\text{C}_3\text{H}_5]_2$). The catalytic activity of these complexes is slightly lower than CaO in transesterification. Figure 4b shows the mechanism of CaO reacted with glycerol. The protons of the methanol are abstracted by two of the $-\text{OH}$ groups located next to each other in calcium diglyceroxide and contribute to the establishment of intermolecular hydrogen bonding to generate species A and B. Species B then reacts with triglycerides to yield biodiesel. Calcium diglyceroxide is finally regenerated and makes the process self-repeating, which further enhances the transesterification reaction [131,135,137].

5. Recent Progress of Reactors Used for CaO and Waste Shell Catalyzed Transesterification

Generally, the lab-based transesterification and esterification process is conducted by using a three-neck round-bottom flask fitted with a reflux condenser, magnetic stirrer and a thermometer with water cooling condenser (Figure 5a) [114,138]. Notably, the ma-

majority of the waste shell catalyzed transesterification focused on the reflux distillation system [129,139]. The conventional heating system for biodiesel production has shown some drawbacks. Limitations typically are the dependence on the thermal conductivity of the material, the heterogenic heating of the surface and specific heat. To date, these reflux distillation techniques are being replaced by more advanced systems.

In biodiesel production, proper mixing is critically important to create sufficient contact between oil and alcohol. In this context, ultrasonication helps by facilitating the liquid–liquid interfacial area through emulsification, which can effectively generate vapour bubbles and cavitation bubbles in viscous liquids (Figure 5b) [140,141]. The ultrasound in the chemical processing enhances both the mass transfer and chemical reactions, offering the potential for shorter reaction times, cheaper reagents and less extreme physical conditions [142,143]. In Teixeira et al. [142] on transesterification of beef tallow, it was reported that using ultrasound irradiation shortens the reaction time (70 s). Obviously, the transesterification of beef tallow using ultrasound irradiation had a biodiesel conversion (92%) that was comparable to the conventional method (reflux distillation system) that needed 1 h (91%). Note that the quality of the biodiesel was like biodiesel produced with the conventional method. These findings suggest that the process involving ultrasonic irradiation could be a feasible and effective method for the production of good quality biodiesel from beef tallow. Recently, Wilayat et al. [144] produced biodiesel from WCO by using CaO assisted by ultrasonic wave. About 1–4.4% of catalyst is used for the biodiesel reaction with the presence of an ultrasonic wave generated from an ultrasonic cleaner at 28 and 42 kHz of frequency. The results have shown a highest methyl ester yield at ~90% using 9:1 MeOH:oil molar ratio and a frequency of 40 kHz. Clearly, the increment frequency of the ultrasonic wave causes an increase in the transesterification rate. The ultrasonic-assisted transesterification of palm oil in the presence of CaO was investigated by Mootabadi [145]. The reaction process was carried out with 20 kHz ultrasonic cavitation, reaction time (10–60 min), MeOH to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3%) and varying of ultrasonic amplitudes (25–100%). At optimum conditions of 60 min, 95% of biodiesel yield was achieved as compared to 2–4 h under the conventional reflux process. A further study on ultrasonic-assisted transesterification of palm oil with the aid of waste ostrich eggshell-derived CaO was reported in the earlier literature [146]. Under ultrasonic conditions, ~93% of biodiesel yield was achieved under the optimal condition: reaction time: 69 min; MeOH:oil to oil ratio of 9:1, catalyst loading of 8 wt.%.

Microwave irradiation provides an alternative energy source suitable for use in heating of the transesterification process. During transesterification of oil-based triglyceride with alcohol, the microwave system is able to activate the smallest variance in degree of polar molecules and ions, such as alcohol (R–OH), with a continuously changing magnetic field. The varying electric field resulted in an interaction between the triglyceride and alcohol ions (R–O⁻), thereby rapid rotation occurs between the reaction medium, which further generates heat attributed to molecular friction. Hereafter, the microwave-assisted system will accelerate the generation of heat and pressure from the reaction medium, which supports further decomposition and re-structuring of the molecular structure, and increases the mass transfer rate. It can be suggested that the high conversion of triglyceride into desired biodiesel will be attained within a shorter reaction period [147,148]. It is noteworthy that the former literature also revealed that the microwave system might enhance reaction rate, purity and yield of product in biodiesel synthesis [149,150]. Figure 5c shows an example of a modified Samsung 1000 W 2450 Hz household microwave oven. Two holes were drilled in the top of the domestic microwave oven, one to position the stirrer and the other to shift the thermocouple inside the microwave. The microwave was fitted with a mechanical stirrer, which was powered by a motor to replace the carousel. The thermocouple was attached to a USB-5104 4-channel thermocouple logger. For this experiment, a one-litre beaker was supplied and a separation funnel was used to isolate the biodiesel from the reaction mixture. The reaction analysis was conducted by varying microwave power input, catalytic loading and methanol to oil molar ratio. Although the application of a modi-

fied household microwave for biodiesel synthesis is an effective and low-budget study, its application is still not considered as ideal for scientific experiments due the lack safety features such as overpressure guard, temperature control regulator and power control, etc. Due to this concern, researchers continue to discover the potential of a microwave-assisted system for biodiesel synthesis [93,151,152]. The efficiency of the microwave reaction system has been further proved by Liou and Chung in the microwave-assisted transesterification of *Jatropha* oil over KOH impregnated CaO catalyst [151]. The optimum condition for producing the highest yield of biodiesel was as follows: 8.42 MeOH:oil molar ratio, 3.17% catalyst loading and total reaction time of 67.9 min. The average conversion for three repeated experimental runs at optimum condition was found to be 97.1%. The biodiesel obtained also had properties satisfying the desired standards. Similarly, Zamberi and his partners reported the utilization of CaO derived from waste cockles on the biodiesel production of WCO via a microwave heating system. Within 4 min, more than 95% yield concentration was recorded through the microwave irradiation method [153]. This was based on Buasri and Loryuenyong's findings on biodiesel production from *jatropha* oil over CaO derived from eggshell via a microwave-assisted reaction system [93]. Apparently, rapid transesterification reaction is observed which yielded a conversion of oil of nearly 94%, reaction time 5 min, microwave power 800 W, MeOH:oil molar ratio 18:1, and catalyst loading 4 wt.%. Overall, based on these studies, it is highly affirmed that the transesterification assisted by the microwave-assisted method improved biodiesel yield, quality and reaction rate. When comparing the technology effectiveness of biodiesel production by using the ultrasound irradiation, ultrasonic wave and microwave reaction systems, it was observed that the transesterification process under ultrasound irradiation is much faster. This is due to a collapse of the cavitation bubbles and ultrasonic jets that impinge feedstock to methanol, disrupting the phase boundary and causing emulsification. Overall, the ultrasound irradiation method is the most promising alternative heating source for the biodiesel industry.

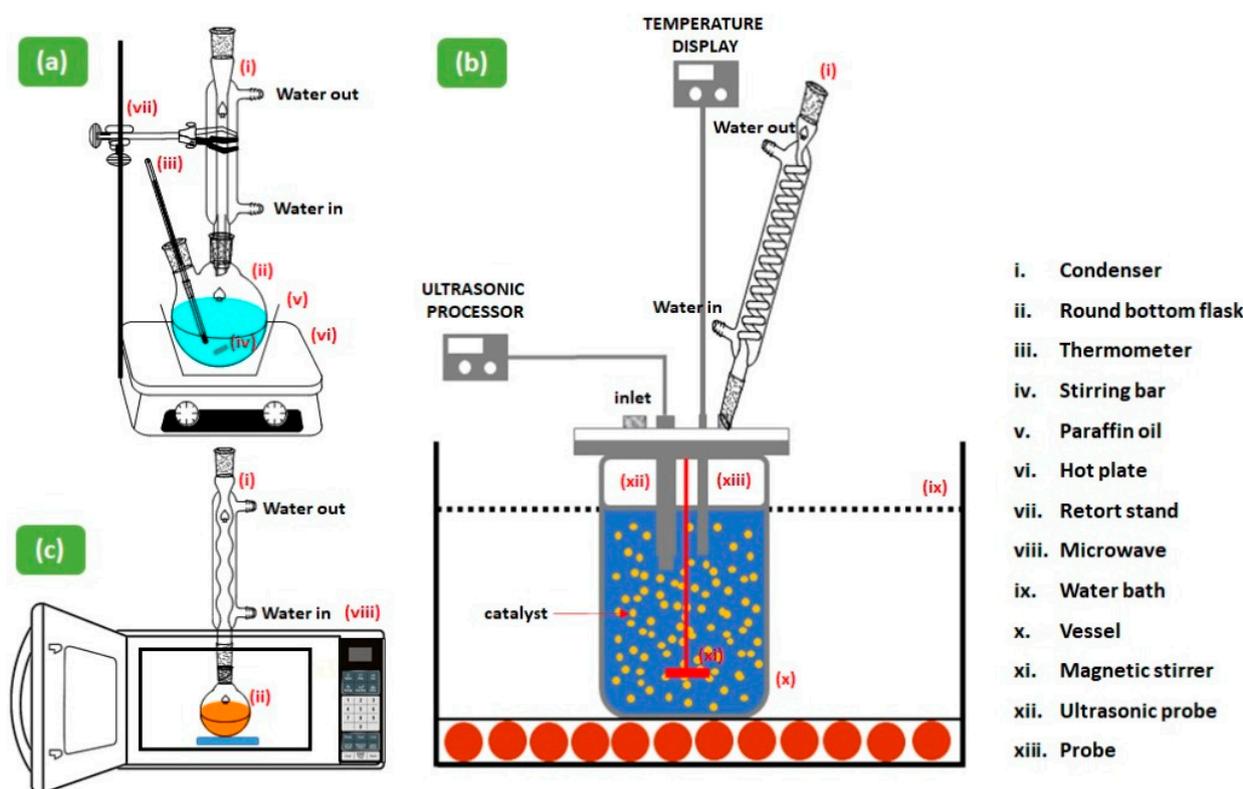


Figure 5. (a) Set up of transesterification reaction, (b) Component part of ultrasonic-assisted transesterification (adapted from [141]) (c) Transesterification by using a batch process within a modified Samsung 1000 W 2450 Hz household microwave oven (adapted from [152]).

6. The Challenge of Waste Shell-Derived Catalyst and Advance Reactors for the Biodiesel Industry

Calcium-rich waste shell materials as a low-cost green resource are readily available around the world. Utilization of the waste shell modified catalyst is a tremendous prospect for the biodiesel industry. Yet, there are still challenges for further improvement on an industrial scale. This is due to the instability of CaO catalyst which commonly suffers from Ca^{2+} leaching problem [135]. Other problems such as low surface area, water sensibility, leaching of active sites by glycerol, and competing with soap-forming side reactions have afflicted the utilization of waste shell-derived CaO catalysts. According to the research work done by Kouzu and Hidaka, the leached Ca^{2+} is increased when there is excess water content in the reaction medium [135]. This is noteworthy to mention, since Ca^{2+} easily dissolves and leaches into the reaction product; hence, additional advance separation and purification are needed to extract Ca^{2+} ions from the biodiesel. Thus, it will produce a significant volume of wastewater during the purification process. Furthermore, the CaO catalyst was often easily deactivated by water or CO_2 [154]. Due to the adsorption of CO_2 and humidity, the CaO surface is readily contaminated by moisture attachments and transforms to CaCO_3 and $\text{Ca}(\text{OH})_2$, respectively. This $\text{Ca}(\text{OH})_2$ phase will apparently act as a partial homogenous catalyst in the transesterification reaction, hence leading to the increment of Ca^{2+} leaching species. Based on the above discussion, the instability of CaO derived from waste shells can be resolved by combining the CaO with other chemical compounds such as AMOs, TMOs and functionalization approaches. Moreover, alkaline metal and transition metal are considered inexpensive materials, which do not significantly contribute to the overall production cost when the catalyst can be reused for many runs under a simple purification process as compared to a homogeneous [154].

In the case of reactor design, although intensification systems such as microwave- and ultrasonication-assisted transesterification offer the opportunity to save operation time as well as improve productivity, one of the limitations of microwave scale-up technology for industrial purposes is the restricted penetration depth of microwave irradiation into absorbing materials. Weissman et al. [155] reported that the penetration depth of microwave irradiation is limited to 2–5 cm and therefore the vessel size cannot be expanded unrestrictedly. High microwave power may also lead to rapid input of energy into the reaction and to overheating. Another issue is related to the homogeneity (inhomogeneity may lead to hot spots and product degradation) and stability of solvents, reagents, and products at temperatures higher than 200 °C. The continuous occurrence of instability and degradation of the reaction mixture will result in safety issues.

As a consequence of microwave input, the system will result in a rise in pressure during the reaction; hence the construction materials for the microwave reactor must be able to withstand high temperatures and high pressure (e.g., 250 °C, 20 bar). Based on this fact, it is believed that the implementation of ultrasonication scale-up technology will face additional issues including the implementation of the ultrasonic homogenization system. This technique is very important in producing chemical and physical effects that arise from the collapse of cavitation bubbles. As reported by Shinde and Kaliaguine, high-frequency ultrasound (~40 kHz) will rapidly increase the rate of transesterification reaction and hence increase biodiesel yield [140]. As a consequence, the ultrasound amplitude and power should be carefully controlled for up-scaling purposes. Noteworthy to mention is that, when comparing microwave- and ultrasonication-assisted method, the ultrasound offers a much cheaper process and less extreme physical conditions. Despite the large number of studies that have investigated ultrasonic-assisted biodiesel production [142,156], it appears that there has been no thorough study conducted on the use of ultrasound for improving biodiesel production for scale-up purposes.

7. Conclusions

Natural waste shells are rich in calcium that is potentially convertible into Ca-based catalyst for biodiesel synthesis via transesterification/esterification pathways. Generally,

the calcium is present in the form of calcium carbonate (95–99%), and further treatment is required in order to expose the calcium active phases (e.g., oxide or hydroxide phases) for further reaction. The waste shell-derived CaO or Ca(OH)₂ shows similar characteristics to the conventional form, such as basicity and surface area. It was noted that both properties, especially the high basicity density and strong basic strength of catalyst, greatly enhance the transesterification rate for biodiesel production. However, the present form of waste shell-derived catalysts is still limited in use for feedstock with high free fatty acid or high moisture content found in non-edible oil and waste cooking oil. Unfavorable side reactions occurred between Ca from waste shell-derived catalysts with FFA or moisture to form unwanted soap product, and the ease of dissolution of catalyst by Ca leaching, respectively. Thus, further modification of waste shell-derived catalysts has been extensively studied by researchers to improve the stability of catalyst, as well as resist FFA/moisture in the feedstock. The modification can be performed via incorporation of alkaline metal oxide, transition metal oxide, and functionalization with chemicals (KOH, NaOH, KF, H₂SO₄, HCl, HSO₃Cl) to tune the acidity-basicity of active sites and textural properties of waste shell-derived catalysts. The findings show that the transesterification reactivity significantly improves with higher biodiesel yield, as well as a better reusability profile. Other than modifying the waste shell-derived catalyst, intensification of transesterification was performed by using microwave- or ultrasonic-assisted technology to replace the conventional reflux heating, with short operation time as well as clean biodiesel product. However, implementation of this technology for scale up biodiesel production must meet the challenge of construction and operating cost. Thus, continuous development of reactor technology for biodiesel production is in progress to strive for better ecological processes.

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