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Review

A Review on the Efficient Catalysts for Algae Transesterification to Biodiesel

Elena Ghedini, Somayeh Taghavi, Federica Menegazzo and Michela Signoretto *

CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice and INSTM RUVe, Via Torino 155, Mestre, 30172 Venezia, Italy; gelena@unive.it (E.G.); somayeh.taghavi@unive.it (S.T.); fmenegaz@unive.it (F.M.)
* Correspondence: miky@unive.it

Abstract: The depletion of fossil fuel resources and increasing environmental pollution led to a trend for using alternative, clean, green, and sustainable fuel and energy resources. To attain this aim, using biomass as an alternative resource for diesel production has been a hotspot among researchers. Biodiesel has several advantages, such as being lower toxic and more renewable, and eco-friendlier than diesel from fossil fuel resources. Several edible and non-edible bio-sources were used for the production of biodiesel from the transesterification process. Algal oil as a non-edible source is considered an abundant, low cost and green substrate for biodiesel production. Various factors such as reaction conditions and the type of catalyst affect the biodiesel production process. Different catalytic systems such as basic and acidic homogeneous and heterogeneous catalysts and biocatalysts were introduced for the process in the literature, and each proposed catalyst has its own advantages and disadvantages. For instance, in spite of the lower cost and better mass transfer of base and acid homogeneous catalysts, reaction system corrosion, non-reusability, and soap formation are serious challenges of these catalysts at an industrial scale. On the other hand, acid and base heterogenous catalysts overcame the issues of corrosion and recovery, but some matters such as mass transfer limitation, high cost, and weak performance in catalyzing both esterification of FFAs and transesterification of lipids must be taken into account. In addition, bio-catalysis as a high-cost process led to a purer product formation with less side reaction. Therefore, several significant factors should be considered for transesterification catalysts such as availability, cost, reusability, stability, mass transfer, and the possibility to manage both the transesterification of triglycerides and the esterification of FFAs, selecting a catalyst with predominant pros is viable. Here, a review of the biodiesel production from algal biomass focusing on the efficient catalyst of the process is presented.

Keywords: algae to biodiesel; transesterification; efficient catalyst

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1. Introduction

For a long time, fossil resources have supplied fuels and petrochemicals for human requirements, such as household, industrial, and transportation applications. Evidence shows that more than 90% of global energy is provided by fossil fuels [1,2]. However, several challenges such as being non-renewable, oil prices enhancement, and environmental pollution have led scientists to consider sustainable alternatives [3]. Using biomass as a substitute resource and its derived biofuels have in recent years has attracted much attention across the world [4]. Several benefits, including plenteousness, being environmentally friendly, mitigating greenhouse gas emissions, and feasible processing, prove the strong potential of biofuels for future prospects [5]. It is significant to mention that biofuels have several applications in transportation engines, household and industrial needs and are used in all three forms of solid, liquid, and gaseous [6]. Biofuels are classified into three groups of first-generation (formed from food crops), second-generation (formed from food wastes) and third generation (formed from marine biomass like algae) [7]. Since first and second generations of biofuels have some limitations, such as the competition with the human food industry and dependence on landing availability, third-generation biofuels have turned up as an applicable bioresource without mentioned limitations. The idea of energy generation from algae has been given for over 60 years, and it was suggested to use the lipids in algae structure for liquid fuels formation [7]. However, algal biofuels have not been a complete alternative to fossil fuels and need to overcome some obstacles in order to enter the fuel market. The obstacles and challenges are nutrient and resource availability, tough identification, oil productivity besides co-product, and economic boost of the system. Thus, more efforts and work are needed to transfer algal biofuels from promise to reality [8,9].

Several factors in algal biomasses made them promising sources of renewable energy, such as their high growth rate, high photosynthetic activity, considerable sea farming scale for mass cultivation, reduced land requirements, high biomass conversion rate and ease of handling, and reduced, potentially net-zero, CO_2 emissions [10–12]. In Particular, the algae contribution to sustainable development can be provided by several influences. One of the roles is the effect of algae photosynthesis on atmospheric CO_2 depletion. Algal systems need carbon resources from 10 to 50 times more than other plants for photosynthesis and growth and have a very significant effect on the reduction in greenhouse gas emission, global warming, and improvement of urban areas compared to fossil fuels and other biofuel sources [13,14]. The second role is the effect of microalgae cultivation on wastewater treatment. This class of technology can both help on sustainability, feasibility, and lower cost of algae cultivation and boost the health and cleanliness of water [15]. The third role is the impact of using an algal resource on the decrease on fossil fuel dependance and using food crops and food waste as the first and second generations of the biomass, respectively. Therefore, algal biodiesel production can have a positive effect on the reduction of competition with human food, hunger around the world, and land requirements [16].

Among biofuel crops, algae are richer in oil with around 20%–50% extractable oil, which is appropriate for biodiesel production. Some algae are comprised more than 50% of hydrocarbons, being suitable for jet fuels, gasoline, and diesel formation [8,17,18]. Besides, algae can be used for the production of bio-gas, particularly CH_4 and H_2, has a precious energy resource. There is a significant difference between biofuels and fossil-derived fuels. Biofuels are more polar and have oxygen content around 10% to 40%, which makes their chemical properties very different compared to fossil-derived fuels [19].

2. Energy Conversion Processes from Algae

Biomasses are sustainable and renewable sources of energy because they store energy from the sun. Particularly, algae consist around 50% of the photosynthesis that takes place on earth in which they absorb plenty of the sun's energy [20]. The chemical energy stored in algae can be released as heat through a direct burning process. Algae can also be transferred into liquid biofuels such as biodiesel, gasoline, jet fuels, and bioethanol and into biogas such as methane, hydrogen, and syngas that can then be burned for energy generation.

Figure 1 demonstrates a schematic representation of several routes in algae valorization. Thus, the types of products mostly depend on the structure of algae and the routes of algae valorization:

1. Biochemical conversion: a bioenergy resource is a bioethanol formed by the fermentation method. This method is a biochemical route in which sugars in algae are converted into bioethanol normally by yeast action. Hence, the presence and accessibility of sugars in algae are of crucial importance in bioethanol production. A mixture of methane and carbon dioxide as biogas besides ammonia is normally produced through the anaerobic digestion of algae. Methane is significant biogas in the aspect of being a bioenergy source. However, this method is considered an uneconomic and unsatisfactory process [21]. Hydrogen is one of the most important energy vectors which is used in various applications such as electricity and fuel cells. Moreover, hydrogen can be formed by photobiological and anaerobic digestion methods.

2. Thermochemical conversion: thermochemical conversion is a process for the production of three different fuels, including bio-oil (gasoline, jet fuel, biodiesel), biogas, and biochar, and it normally happens at high temperatures with the absence of oxygen [22]. Upon pyrolysis process, two significant sources of energy, including hydrogen and bio-oil, are produced [23]. Furthermore, hydrogen can be produced by the gasification method. In the liquefaction process, wet biomass can be decomposed into smaller components and then repolymerized into large oily components or liquid biofuels [24].
3. Direct combustion: In biopower plants, biomass is directly burned in excess air to heat the water in a boiler and produce high-pressure steam. The steam turns a turbine generator, and hence the electricity is generated.
4. Chemical reaction: among several bioenergy sources, biodiesel is considered as the transportation fuel especially suitable in diesel engines without modification. The presence of oils and lipids in the algae structure could be a renewed interest for making biodiesel with less polluting and more renewable nature. The transesterification process is the desired route in which algal extracted oil could be converted to biodiesel in the presence of alcohol and an acid or a base catalyst [14].

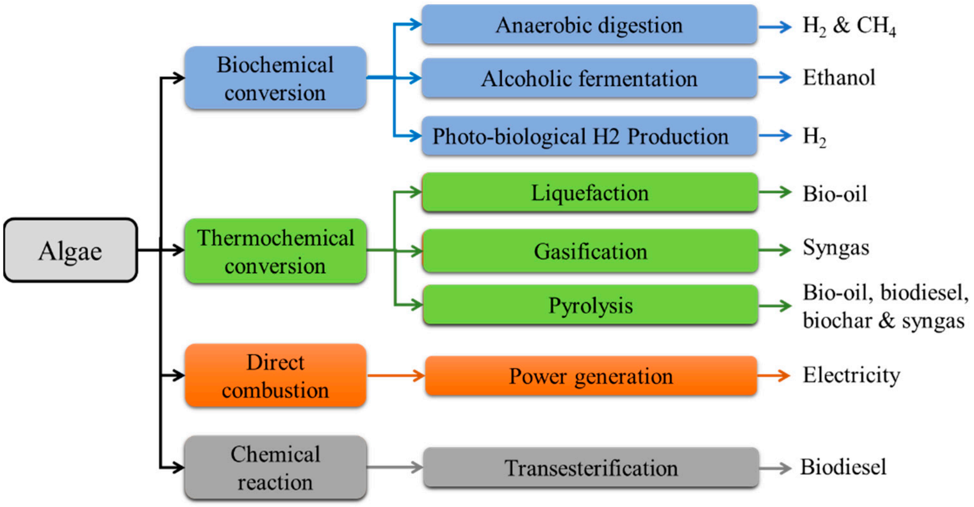

Figure 1. Different routes for algae conversion into energy content.

Therefore, algal biomass can be the source of energy (biodiesel, jet fuels, gasoline, biogases, electricity, and so on) produced upon various reaction routes and processes. Biodiesel can be formed from microemulsification, pyrolysis, thermal cracking, and transesterification processes. Among them, transesterification is the most efficient method for producing cost-effective and high-quality biodiesel. Recently, global researchers have attempted to enhance the lipid accumulation in microalgae through genetic engineering. In particular, increasing the quantity and quality of lipid has been performed by controlling the lipid metabolism in order to improve the microalgae properties as a biodiesel feedstock. Different strategies were used to achieve this aim. For instance, overexpression of lipid synthesis genes could positively improve microalgal proliferation [25,26]. Moreover, the chain length and unsaturation degree of fatty acids in microalgae can influence the oxidative stability of the obtained biodiesel, which were controlled and changed by transgenic overexpression of thioesterases [27,28]. Hence, these modern metabolic engineering tools in the photosynthesis of microalgae have opened new opportunities for renewable diesel production without competing with the food industry and land requeuing. Consequently, in this review, transesterification of algal biomass and particularly its catalytic aspect will be more discussed. Different types of micro and macro algae biomasses as the feedstock for biodiesel (fatty acid methyl esters) production using different homogeneous and heterogeneous catalysts in different reaction conditions will be reviewed. The required properties of efficient acidic and basic catalysts for the process will be discussed in detail.

3. Transesterification Process

As was mentioned in the last part, biodiesel production from algae can be adapted from its lipid fraction. Biodiesel can be produced from the transesterification of mono-, di-, and tri-acylglycerides and the esterification of free fatty acids (FFAs) that are present naturally in biological lipids, such as plant oils and animal fats. The process of biodiesel production from algae is shown in Figure 2. The first initial viable step is the extraction of oil from the cell walls of algae. Several methods were reported for this step. Many mechanical methods have been used for lipid extraction from algae both at pilot-scale and commercial levels. There are several mechanical approaches consisting of microwave-assisted pyrolysis extraction [29], ultrasonic-assisted extraction, the expeller press method [30], bead beating [31], pulsed electric field, and hydrothermal liquefaction [32]. Second, chemical methods by using organic solvents such as chloroform, petroleum ether, acetone, methanol, and hexane, and also soxhlet and supercritical fluid extractions have been available for algal lipids extraction [33]. In addition, some non-mechanical methods and non-solvent extraction, such as enzyme-assisted extraction, osmotic pressure, and isotonic solution methods, were reported recently. It seems that these new methods are more reliable in economic, technical sustainability, eco-friendly, and scalability aspects [34–37]. However, an attractive and reliable procedure is one that certifies reduced extraction cost involved, lower energy requirements, less hazardous, and high oil yield [38,39].

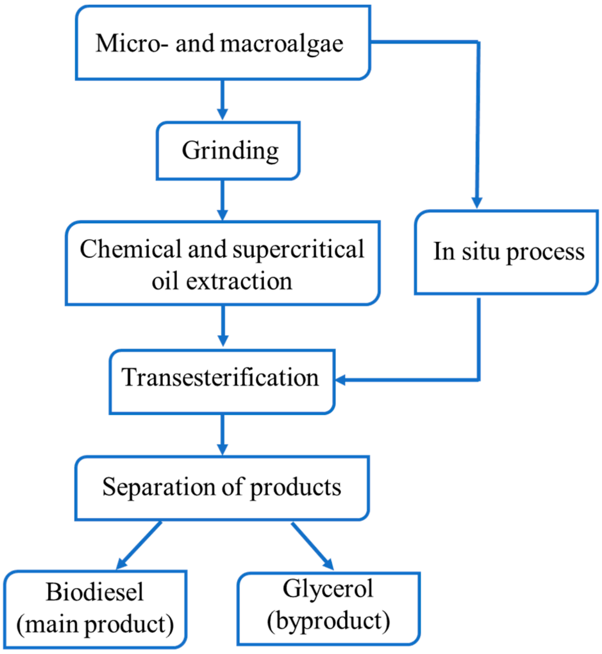

Figure 2. Biodiesel production process from algal biomass.

After algal lipids extraction, the step of transesterification of lipids to biodiesel has to be performed. Transesterification is an equilibrium reaction in which one-mole ester molecule (triglyceride ester or algal extracted oil) and three moles monohydric-alcohol ($C_nH_{2n+1}OH$) react to produce a new ester (mono-alkyl esters or biodiesel) and the byproduct of glycerol (glycerin) (Figure 3). Base or acid catalysts can be efficient for this process. Besides, algal biomasses are rich in free fatty acids (FFAs), which can be converted to biodiesel only in the presence of an acid catalyst (Figure 3). Since the transesterification reaction is an equilibrium, there are several factors that could be significant in keeping forward reactions. The best stochiometric monohydric-alcohol/ algal extracted oil ratio is suggested to be between 4:1 to 12:1. The ratio must be precisely controlled because the lower ratio causes a lower biodiesel yield and the higher one leads to the presence of a high amount of alcohol and the issue of its removal. In addition, other reaction conditions factors such as temperature, rate of stirring, purity of feedstock, and time are viable in the improvement of biodiesel yield [40–45]. However, the presence of a promising catalyst could help to increase the reaction rate, transesterification reaction conversion, and biodiesel yield.

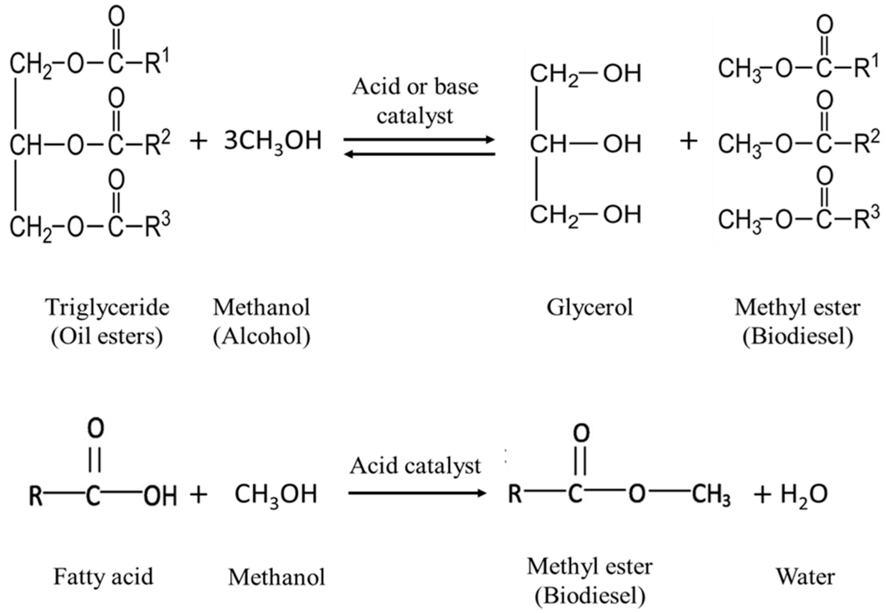

Figure 3. Chemical equations of biodiesel production from triglyceride.

Recently, direct and in-situ transesterification of wet microalgae has attracted great attention (Figure 2). In the in-situ process, near- or supercritical conditions (such as supercritical methanol and carbon dioxide) can directly convert the presented triglycerides in algae to biodiesel. Direct transesterification led to several advantages in the aspect of time, energy, and the cost of the process. The presence of the catalyst in in-situ transesterification can also improve the efficiency of the process [46,47].

4. Efficient Transesterification Catalyst

The classification and sub-classifications of catalysts that have been used for all algal and non-algal lipids transesterification by now is shown in Figure 4. The transesterification catalysts are mainly classified into two groups: homogeneous and heterogeneous. There are some sub-classifications of catalysts, particularly acid and base catalysts. Recently, biocatalysts were introduced as the third classification group.

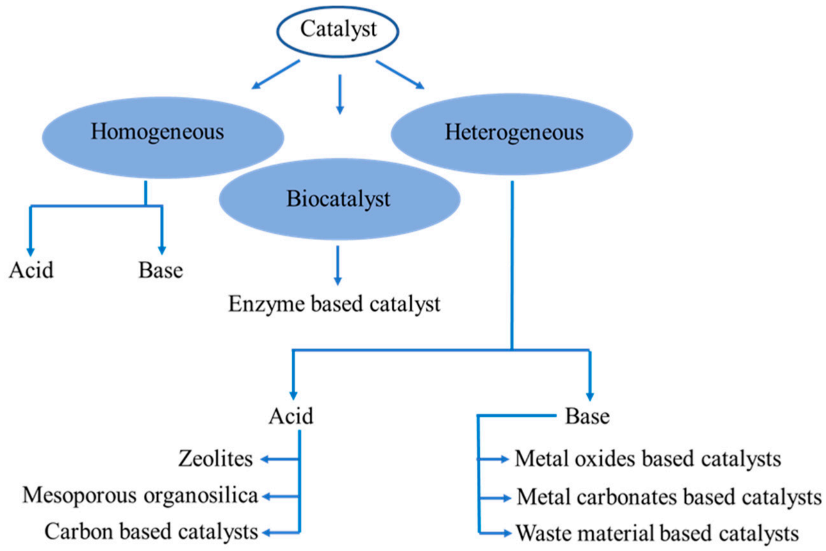

Figure 4. Algal transesterification catalysts classification.

4.1. Homogeneous Transesterification Catalysts

Using homogeneous catalysts has led to several challenges. Since they are the same liquid phase as the reaction mixture, the separation process could be an expensive issue. Besides, soap and water generations with consuming more homogeneous catalysts and production of byproducts from high FFA biomasses in homogeneous catalysis decrease the biodiesel yield [48].

As a larger number of researches have been found using base catalysts for the transesterification of algal lipids to biodiesel, it can be evolved that the alkaline catalysts have been more active with higher conversion rates and accordingly being more efficient for this process. Some researchers used homogeneous base catalysts for algal lipids transesterification. Among them, NaOH and KOH have been the cheap and available catalysts and hence are widely used for transesterification of different classes of lipids [49].

Recently, Sivaramakrishnan et al. [50] performed two-step and direct transesterification of *Chlorella* sp. and *Scenedesmus* sp. microalgae to biodiesel. NaOH as an alkaline catalyst was used in both methods. In a two-step process, the oil extraction is considered as the first step in which they have performed several methods such as ultrasonic, autoclave, microwave, and lyophilization for cell disruption. The cell disruption caused the break of the cell wall and releasing intracellular lipids. Ultrasonic showed a higher yield of extracted oil because ultrasound waves establish stable cavitation owing to the rapid compression/decompression cycles, which create heat shock waves and break the microalgal cells. Then, a wide variety of organic solvents were tested for the extraction of oil. They have shown different parameters are important in the first step, such as the solvent to algae ratio, stirring speed, temperature, and extraction time what have been optimized. On the other hand, direct transesterification was carried out with ultrasound disrupted dry algal biomass. In both two-step and direct transesterification, low-cost methanol produced higher biodiesel yield among several alcohols. The concentration of NaOH catalyst was the most important parameter for increasing biodiesel yield, and it was proved to be an optimum concentration because an excessive amount of NaOH leads to soap formation and thus decreases the yield. In addition, other reaction condition parameters such as the methanol:oil molar ratio and temperature have to be optimized for improving biodiesel yield in this kind of reaction. The two-step transesterification and direct transesterification have shown similar biodiesel yields and almost similar net energy requirements for both microalgae. Venkatesan et al. [51] used brown seaweed "*Stoechospermum marginatum*" as the feedstock and first performed the extraction of the lipid by the Soxhlet extraction technique following by transesterification of extracted lipid in the presence of NaOH catalyst. Plata et al. [52] also used a synthetic algae oil based on the composition of the fatty acid in *Chorella vulgaris* for a homogeneous transesterification with NaOH catalyst. In all researches discussed above, the optimization of reaction conditions and the concentration of NaOH catalysts were focused on as significant factors. It was shown that, in the presence of NaOH, the temperature range of 40–65 °C could be the best to achieve highest biodiesel yield.

KOH, as an alkaline catalyst, has shown almost the same trend of NaOH in which the reaction conditions and the optimum concentration of KOH were essential parameters in increasing biodiesel yield. However, a higher yield of biodiesel (81.98%) was produced in almost similar reaction conditions from transesterification of a blend of algae oil and *Jatropha carcus* oil by using KOH catalyst in comparison to those reported in the literature [53]. Besides, Dong et al. [54] introduced an interesting two-step process using microalgae biomass as the feedstock. They started the process by in situ pre-esterification of microalgae in the presence of Amberlyst-15 heterogeneous catalyst followed by KOH base-transesterification. They have shown that in addition to optimization of reaction condition and catalyst concentration, the first step esterification was very beneficial in reducing FFAs and caused to an increase in the yield of fatty acid methyl ester or biodiesel (up to 94.87% ± 0.86%,) by using less catalyst compared to that obtained by a one-step acid or base catalytic in situ process.

Therefore, as can be derived from the literature, microalgal biomasses have a very high amount of FFAs, which should be precisely taken into account in algal biodiesel production. It seems that transesterification of algal biomass by homogeneous catalyzed traditional method is strongly dependent on the amount of water and FFA in algal lipid [55,56]. In particular, when homogeneous base-catalysts have been used in the traditional transesterification, FFAs led to the production of byproducts and the reduction in conversion efficiency. This issue has been a big challenge, especially at an industrial scale [57], because the FFA purification or stepwise conversion of the lipids cannot be a desirable economical solution.

Acid catalysts in biomass transesterification have several advantages. Among those, the possibility to carry out both esterification and transesterification reactions simultaneously is significant. H_2SO_4 was widely used as a homogeneous acid catalyst of esterification and transesterification processes in several pieces of research [58–61]. Recently, research was reported for direct biodiesel production from wet *Chlorella vulgaris* microalgae assisted by radiofrequency heating for algal cell wall destruction and reaction acceleration. After wet algae cell destruction, esterification with alkali (NaOH) or acid (HCl) homogeneous catalysts and the transesterification with alkali (NaOH) homogeneous catalyst were carried out simultaneously. Using a radiofrequency heating system helped in developing the direct biodiesel production from algae with less reaction temperature, pressure, solvent compared to other researches [62]. In addition, another group performed direct transesterification of wet *Nannochloropsis* sp. microalgae to biodiesel assisted by microwave heating approach for both lipids' extraction and their transesterification, simultaneously. The presence of the small amount of 1-ethyl-3-methylimmidazolium methyl sulphate (EMIM $MeSO_4$) as ionic liquid with acidic property catalyzed direct transesterification reaction [63]. Another group also used ionic liquid of tetrabutylphosphonium formate (P4444 For) as the catalyst for one-pot transesterification of wet *Chlorella vulgaris* (*C. vulgaris*) microalgae into biodiesel, and the catalyst showed a good result being capable of leading cell disruption and transesterification in a single step [64]. On the other hand, research was reported in performing two-step catalytic conversion of high FFA-containing "*Scenedesmus* sp." microalgae in which H_2SO_4 acid catalyst was used for the first step of FFAs esterification and NaOH, KOH, and $KOCH_3$ base catalysts were used for the second step pretreated biomass lipid transesterification [65]. In addition, Jesus et al. worked on the formation of biodiesel from the microalgae *Chlorella pyrenoidosa* by acid-catalyzed transesterification process using HCl as the catalyst. They optimized the process using 2-methyltetrahydrofuran or cyclopentyl methyl ether co-solvents and obtained higher biodiesel compared to the non-green chloroform solvent [66]. Good catalytic performance of homogeneous acid catalysts was due to high mass transfer between reactant and catalyst. However, some limitations in commercializing these catalysts, such as reaction system corrosion, waste generation, and recyclability limitation, motivated researchers to develop solid acid catalysts.

4.2. Heterogeneous Transesterification Catalysts

Heterogeneous catalysts have a different phase compared to the reaction mixture and lead to a simpler separation and purification. Moreover, they do not have the problem of equipment corrosion and are easier to be recycled [48]. When heterogeneous basic catalysts are used in transesterification, unlike Lewis or Brønsted basicity factor, the strength and density of basic sites have a significant effect on the rate of the reaction. Basic polymers, different compounds of the group IIA elements such as oxides (CaO, MgO, SrO, and BaO) and carbonates ($CaCO_3$, $MgCO_3$, and $Ca(OCH_3)_2$), basic zeolites, and oxides of first-row transition metals have been used for transesterification of several biomasses derived lipids. In particular, CaO as a group IIA element oxide has been widely used in algal lipid transesterification because of availability, reasonable cost, high basicity property, and low corrosion effect. Al_2O_3 has also shown a very good support performance due to excellent stability and leading to excellent active phase dispersion [43,44,67].

A group of researchers [68] investigated biodiesel formation from different types of algal and non-algal biomasses using a new method. They performed the simultaneous esterification and transesterification of FFAs and triacylglycerides with supercritical methanol in a fixed bed reactor using acid and basic pristine and modified heterogeneous catalysts based on zirconia (25 mm, 300 Å), anatase titania (80 mm, 60 Å) particles, and α-alumina particles (300 mm). The modified version of catalysts were phosphate zirconia and alumina, hydroxide-modified zirconia, titania, and alumina particles. This kind of process is known as the Mcgyan-process, in which normally ultra-stable porous metal oxide microspheres are used as the catalyst for performing both esterification and transesterification reactions under supercritical conditions.

They found that the modification of metal oxide catalysts is not necessary. In particular, a high yield of biodiesel (90%) was produced while using algal biomass as the feedstock and titania particles as the catalyst. The quality of biodiesel was very high without loss of efficiency. Some years later, the same group typically focused on algal biomass, including *Dunaliella tertiolecta*, *Nannochloropsis oculata*, wild freshwater microalgae, and macroalgae lipids using an improved Mcgyan-process. They designed the modified system using a single-reactant (methanol and lipids) stream and hexane as the carrier solvent in order to have a single homogeneous feedstock solution. Titania microspheres were used as the catalyst of reaction, which has shown great recyclability properties. They demonstrated that Mcgyan-process with a heterogeneous catalyst has a variety of advantages compared to the conventional homogeneously base-catalyzed batch system. The catalyst consumption, amount of H_2O as the solvent, production of waste, and also by-products such as soap and glycerol were less for the Mcgyan process with heterogeneous catalysts compared to the homogeneous process. In addition, Mcgyan, as a continuous process, has shown a very better conversion rate and was suitable for a variety of feedstocks, and it was not sensitive to H_2O and FFAs. Whereas all these factors were an issue for the homogeneous process. Furthermore, the use of titania microspheres as a heterogeneous catalyst and continues process in a supercritical condition caused a very short reaction time of 30 s, which could be considered as good feedback for time-saving in the industrial process [69].

Umdu et al. [70] selected a yellow-green microalga, *Nannochloropsis oculata*, as the feedstock and extracted the lipid by Soxhlet extractor and hexane solvent. Since the oil extracted had a low amount of FFAs, the basic catalyst has shown good performance in the transesterification process. First of all, the dispersion of basic active sites is prominent. They carried out the reaction by using pure CaO and MgO basic catalysts, but the samples were not active. On the contrary, when Al_2O_3 supported CaO and MgO catalysts were used, the biodiesel yield was raised. Al_2O_3 is not active for transesterification reaction, but when it was mixed with CaO and MgO, great activity was demonstrated owing to the dispersion of CaO and MgO crystallites on Al_2O_3 or the creation of new basic sites.

However, it was proved by X-ray diffraction that the crystalline size of CaO and MgO does not have a direct effect on biodiesel yield. In addition, the results of CO_2-TPD have shown the dependence of biodiesel yield on both the density and strength of basic sites in both catalysts. In fact, the high basic site density and mild basic strength were appropriate for achieving the high biodiesel yield. Recently Rahman et al. [71] carried out research in which they used the chicken waste (chicken manure, chicken bone, and eggshell) as the catalyst for transesterification of a harmful algae (*E. compressa*) to biodiesel. CaO existed in chicken waste after calcination at different temperatures was considered as the basic active site of the catalysts. As was mentioned earlier, high FFAs in algal crude oil are a challenge, especially in transesterification by alkaline catalysts, which causes excessive saponification, difficulty in separation of glycerol from biodiesel, and high catalyst consumption and also reduces the catalyst efficiency. Thus, first, esterification of algal crude oil was performed by a sulfuric acid catalyst. Then, pretreated algal oil was transferred to the transesterification step, and all needed parameters of reaction conditions were optimized. In the case of chicken waste as the catalyst, calcination temperature was demonstrated a prominent effect on catalyst performance. DTG and XRD results were shown that one of the phenomena happening through calcination is the conversion of $CaCO_3$ into the alkaline active site of CaO by the liberation of CO_2 at a temperature range of 600–900 °C. Increasing the calcination temperature by 800 °C led to a rise in surface area and pore volume in all three different catalysts, which itself caused the enhancement of active site at the external surface and improvement in reagents and products diffusion and activity of catalysts. Chicken bone-derived catalyst with higher surface area and pore volume demonstrated higher activity in the reaction. However, adding 2% water to the methanol eggshell catalyst indicated the highest yield of biodiesel (95%). The catalysts were also recyclable for three runs with excellent catalytic activity. Hwa Teoa et al. [72] used nano $Ca(OCH_3)_2$ (calcium methoxide), which was synthesized from CaO and was another form of alkaline Ca-based catalyst for transesterification of Nannochloropsissp algae to biodiesel. They achieved a very high yield of biodiesel (99.0%) from pre-extracted algal lipid over 3 wt.% of catalyst loading. The thermogravimetry analysis showed that the $Ca(OCH_3)_2$ catalyst can be stable up to 400 °C. N2-physisorption isotherms also indicated that the catalyst is mesoporous, which could be an appropriate property for its activity in transesterification reaction. In SEM images of CaO and $Ca(OCH_3)_2$, it was pointed out that the CaO catalyst has an irregular shape on the surface owing to agglomeration of the bulk particles but $Ca(OCH_3)_2$ has a flower-like cluster structure leading high mass transfer into its interstices. Therefore, the reaction results showed higher activity of $Ca(OCH_3)_2$ compared to CaO. It seems that higher activity of $Ca(OCH_3)_2$ was due to the formation of CH_3O- species from catalyst being a cluster of tiny plate-like architectures and the active site of catalyst. Hence, it helped methanol in joining triglyceride molecules for the production of biodiesel. $Ca(OCH_3)_2$ demonstrated great stability for five runs of the reaction. According to the SEM image, they have demonstrated that the flower-like crystals of catalyst altered to an aggregated cake-like sticky structure of $Ca(OH)_2$ (also demonstrated by XRD of deactivated catalyst), which blocked the interaction between catalyst and reactant. Moreover, $Ca(OCH_3)_2$ nanocatalysts could be promising for this green process.

In heterogeneous acid catalysts, high porosity, presence of stronger and more Brønsted acidity, and an appropriate hydrophilic/hydrophobic balance on the surface are considered as prominent features for higher catalytic activity [73]. It seems that Lewis acidity is very prone to be quickly deactivated by water and glycerol produced during transesterification. Although unlike homogeneous and heterogeneous base catalysts, heterogeneous acid catalysts can effectively catalyze the simultaneous esterification and transesterification of high FFA-containing biomasses, there are some issues regarding this class of catalysts that still need some technological innovations for the transfer to industrial scale [68,74]. Some of the challenges for solid acid catalysts are low reaction rate, possible undesirable side reactions, poor thermal/hydrothermal stability [75,76], and mass transfer limitations for bulky molecules, especially in the case of microporous zeolites [77].

Among heterogeneous acid catalysts, zeolites, mesostructured solids, and ion-exchange resins have demonstrated promising performance in the acid esterification and transesterification of high FFA-containing biomasses to biodiesel [78–81]. Zeolites are microporous aluminosilicate crystals with tunable acidity, molecular sieve, and shape-selective properties. Whereas their microporous property causes harsh limitations for the penetration of bulky molecules. Hence, some valuable researches have been reported for the synthesis of zeolites without mentioned limitation. Hierarchical zeolites with bimodal micro- and meso-porosity can be synthesized with higher surface and almost similar acidity properties as the original conventional ones. There are different approaches for synthesizing hierarchical zeolites [82]. Carrero et al. [33] carried out the biodiesel production from transesterification of *Nannochloropsis gaditana* (one of the most suitable microalgal oil sources), and they compared the activity of different catalysts. They selected ZSM-5 and Beta from two different MFI and BEA classes of zeolites with different porosities and crystalline structures. As was mentioned, the microporous structure of zeolite hinders the penetration of bulky lipid molecules. Furthermore, hierarchical nanozeolites were synthesized by functionalization of the zeolitic seeds with organosilanes. The crystalline structure of both zeolites and also the Si:Al ratios (around 30) were fixed after silanization. According to Ar-adsorption-desorption results, it was demonstrated that external surface area of both zeolites increased, and isotherms and pore size distributions also proved the introduction of secondary porosity in the range of micro-mesopores. This factor could be crucial in improving bulky lipids penetrations and access to acid active sites. However, the surface area and pore volume of H-Beta was higher than H-ZSM-5 after silanization. Moreover, another important property of zeolites for transesterification process is acidity. NH_3-TPD has shown the amount and strength of acid sites decreased in the case of hierarchical H-ZSM-5, while it was almost without alteration for H-Beta zeolite.

All these factors had obvious effects on the transesterification of *Nannochloropsis gaditana* lipid. Hierarchical zeolites had higher biodiesel production compared to conventional ones because the bimodal porosity improved acid sites accessibility for bulky reactants. In addition, H-Beta has shown a better performance which can be related to different textural properties, porosity, and acidity of zeolites that can be consequently prominent in the acid-catalyzed transesterification process. This trend also was found in another research in which strong acid zeolites such as USY, BEA, and FAU-X were used for transesterification of triglycerides and the biodiesel yield and triglycerides conversion were low because of limitation in triglycerides accessibility to acidic active sites in microporous zeolites [83]. In addition, changing Si:Al ratio can be an aspect of zeolites for improvement of their catalytic performance in the transesterification reaction. Si:Al ratio must be optimized in order to keep the optimal hydrophobic balance for avoiding the deactivation of zeolite by water as a byproduct and also to modulate the acidity of zeolites [78]. A magnetic catalyst was synthesized consisting of $MgO/ZSM\text{-}5@Fe_3O_4$, and by incorporation of 15 wt.% of polyethylene glycol (PEG), the basicity, the surface area, and mesoporosity of the catalyst were increased. The catalyst was used for microwave-assisted transesterification of *Spirulina platensis*. Microwave radiation helped on the oil releasing of microalgae, and the obtained oil reacted with ethanol and produced biodiesel with the assistance of catalyst and microwave energy [84].

On the other hand, mesostructured solid materials do not have the issue of bulky component penetration in the transesterification of lipids. Bala et al. [85] reported the performance of a mesoporous organosilica (KIT-5) in the esterification of algal FFA. KIT-5 has a very high surface area with an ordered cage-type mesoporous structure which is appropriate for bulky FFA as the reactant. However, the acidity of the catalyst also has to be adverted. Hence, KIT-5 was loaded with different concentrations of phosphotungstic acid (PTA) from 5% to 40%. KIT-5 loaded with 35% PTA has shown the best performance in direct esterification of algal FFA to biodiesel at a low temperature due to consisting of three important factors of mesoporosity, amount, and strength of acid sites. The catalyst has shown a very high activity after several cycles. Another work demonstrated the catalytic activity of three carbonaceous materials, including rice husk, moringa, and algae biomass with sulfur-incorporated functional groups (SO_3H-RH, SO_3H-MOR, SO_3H-BM) in algal oil esterification. SEM and N2-physisorption results have shown higher surface area and pore volume for SO_3H-RH catalyst displaying higher capability of this catalyst in attaching with –SO_3H functional groups and hence providing a higher density of acid active site for biodiesel production. This trend also was assigned in the results of the ion-exchange titration technique, which has shown the decreasing order of acid density in the catalysts as SO_3H-RH > SO_3H-MOR > SO_3H-BM, meaning that rice husk was attached with more acid sites through the microwave sulfonation. Thus, all mentioned properties caused a higher response of SO_3H-RH catalyst in the aspects of activity and reusability for the esterification process [86]. TiO_2-ZnO nanocomposite catalyst prepared by co-precipitation method has shown an excellent activity and stability in biodiesel formation from *Ulva lactuca* seaweeds in mild reaction conditions. Generally, these kinds of mixed metal oxide nanoparticles are considered acid catalysts that could be active catalysts for the transesterification process. XRD has indicated the amorphous nature of TiO_2-ZnO nanocomposite and the particle size was 12 nm. The nanocomposite was successful in catalyzing the transesterification with high activity through four cycles of reaction [87].

It was mentioned that using algal feedstock could be more challenging compared to other feedstocks because algal biomass has a high amount of FFAs besides triglycerides. It is already known that FFAs can be both polar and non-polar while triglycerides are non-polar. It seems that the polarity of algal lipids has viable effects on the performance of solid acid catalysts in esterification and transesterification reactions. Hence, all different algal lipids, including palmitic acid, glyceryl tripalmitate, glyceryl dipalmitate, sorbitan monopalmitate, and dipalmitoyl phosphocholine were used as the model components in the several solid acid-catalyzed biodiesel (methyl palmitate) productions. Seven catalysts were used for esterification and transesterification of different model components, including Amberlyst 15 and Amberlyst 46 as sulphonated ion exchange resin [88], Smopex 101 as a polyethylene-based fiber grafted with styrene and sulphonated with chloro-sulphonic acid [89], Nafion NR50 as a perfluorinated resin sulphonic acid [74,76,90], Zeolite CBV8014 as NH_4 type ZSM-5 zeolite with SiO_2/Al_2O_3 ratio of 80 [91], Zeolite CBV600 as H form Y-type zeolite with SiO_2/Al_2O_3 ratio of 5.2 [92] and Montmorillonite K-10 as a clay type catalyst with SiO_2/Al_2O_3 ratio of 4.6 [93]. As can be seen in Table 1, the catalysts have different properties, such as different surface areas and acidities. Reaction results have shown that sulphonated solid acids can be very active in the esterification of FFAs, and some zeolites can be active too. However, it seems that acid sites concentration and also surface area have small or no effect on the FFAs esterification process, while these catalytic properties are more effective in transesterification because tripalmitate is a bulky molecule. For this reason, Nafion NR50 has shown the best performance in transesterification of tripalmitate, and the smaller dipalmitate converted quite better to methyl palmitate with Amberlyst catalysts as well as zeolites with smaller pores. In addition, the sulphonic acid groups on the surface of Nafion NR50 made this catalyst more reactive in the esterification of palmitic acid and transesterification of triglyceride and diglyceride as well as the phosphocholine. Sorbitan monopalmitate had a very poor conversion in the presence of all catalysts due to an ester bond between fatty acid and sugar molecules which hinders fatty acid from reacting. Nafion NR50 has shown great stability after five cycles of reactions without significant deactivation [94].

Table 1. Textural properties, acid site concentration and reactivity of acidic heterogeneous catalysts.

Catalyst	Surface Area ($m^2 \cdot g^{-1}$)	Acid Site Concentration ($\mu mol \cdot g^{-1}$)	Substrates with Higher Yields mol% of Methyl Palmitate Product [a]
Amberlyst 15	42	4700	1, 5, 3
Amberlyst 46	57	870	1, 5, 3
Smopex 101	0.15	4000	1, 5, 3
Nafion NR50	Very low	900	1, 5, 3, 2
Zeolite CBV8014	425	395	1, 3
Zeolite CBV600	660	712	1, 3, 5 (totally low)
Montmorillonite K-10	250	650	1

[a] Substrates: (1) palmitic acid; (2) glyceryl tripalmitate; (3) glyceryl dipalmitate; (4) sorbitan monopalmitate; (5) dipalmitoyl phosphocholine.

4.3. Biotransesterification Catalysts

Recently, the interest in enzymatic transesterification of lipids has increased due to medium reaction conditions and no soap or byproduct formations. Biotranesterification catalysts for algae conversion to biodiesel are classified as free, immobilized, cell-bound, and extracellular enzymes. However, the enzyme is the costly part of this new catalytic technology, and efforts were made on immobilization of enzyme to reduce the cost of the process and also improve the recyclability of catalyst [95–98]. Immobilization of lipase can be performed using several methods that covalent bonding is reported as one of the most common leading higher thermal stability and stronger enzyme interaction [99]. It was reported that free lipases could go through agglomeration in the aqueous reaction system, causes the weak access of the active catalyst phase to the substrate and decrease the efficiency of the biocatalyst. Preparation of cross-linked lipase-coated micro-crystals improved the pH, activity, and stability of lipase in the denaturing conditions [100–102]. Regarding appropriate biocatalyst for the transesterification process, very recent and interesting research demonstrated a modified super magnetic nano-biocatalyst which is particularly used for microalgal bio-oil (*Chlorella vulgaris*) conversion to biodiesel. The catalyst had a super magnetic core of Fe_3O_4 (MNP), functionalized by 3-amino propyl triethoxysilane (MNP-AP), and then with glutaraldehyde (MNP-AP-GA) and finally followed by an enzyme (*Rhizopus oryzae* lipase) immobilization of each step catalyst (ROL/MNP, ROL/MNP-AP, ROL/ MNP-AP-GA). It seems that presenting functional groups could have several advantages in the application of biocatalysts. For instance, in the case of grafting AP and GA to MNP surface, functional groups provided a wider space for enzyme connection and hence more active sites accessibility. In addition, providing dipolar interaction between enzyme and MNP because of amine groups in AP and also the covalent bond between aldehyde groups of GA and amine groups of ROL helped in preventing enzyme leaching and increasing biocatalyst stability for longer time reaction. The catalyst was stable through 5 cycles with 57.2% of biodiesel yield, which was comparable to the biocatalysts reported in the literature [103].

There are some other reports regarding biocatalysts in which the performance of a combination of free and immobilized lipase was investigated in the conversion of algal lipids to biodiesel. Chen et al. [104] used free lipase from Aspergillus niger (first step) and immobilized lipase from *Candida antarctica* (second step) as the biocatalysts for two steps transesterification and esterification of microalgal lipids considering that the second step was solvent-free and was carried out for FFAs esterification. They have demonstrated the optimization of reaction conditions such as methanol addition strategy, molecular sieve addition as a water-absorbent, molar ratio of methanol to lipid, lipase dosage, and temperature that were significant for increasing the activity of biocatalyst and biodiesel yield. The yield of biodiesel skyrocketed from 78% in first step to 97% in second step. Immobilization of lipase also helped enhance its stability, and hence it was stable over five cycles of reaction. A similar study was carried out by using both free and immobilized lipases from *Pseudomonas fluorescens* and *Candida* sp. and only with free lipase from wheat germ and porcine pancreas in the one-step transformation of *Scenedesmus obliquus* lipids. In optimum reaction conditions, immobilized lipase from *P. fluorescens* demonstrated the best activity with almost 90% biodiesel yield and best stability during four cycles batch reaction [105]. Bharathiraja et al. [106] compared the activity and stability of two different biocatalysts including "Intracellular Cal A and Cal B lipase producing recombinant *Pichia pastoris*" and "immobilized *Candida antarctica* lipase on calcium alginate" for biodiesel production from three marine macroalgae *Enteromorpha compressa*, *Gracilaria edulis*, and *Ulva lactuca*. The whole-cell catalyst was protected by a polar cell membrane which inhibits reactant to have free accessibility to the biocatalyst active sites and decrease biodiesel yield and hence increase catalyst stability, whereas immobilized lipase was denatured by ethanol without obstacle and showed higher activity. Thus, in optimum reaction conditions and in the case of all three macroalgae lipids transesterification, immobilized lipase has shown higher activity while whole cell biocatalyst has demonstrated higher stability. In addition, another research performed a comparison of free and immobilized whole-cell lipase (*Aspergillus* sp. and *Candida* sp.) for Scenedesmus obliquus lipids conversion to biodiesel. For immobilized whole-cell lipase, biomass particles were used as the support, and it has shown the highest biodiesel conversion. This catalyst was reusable for two cycles reaction. It seems that the long accessibility of immobilized lipase with methanol as reactant and hexane as solvent caused a change in lipase, and consequently, the whole-cell enzyme from biomass support particles was leaked [107].

It was displayed that algal lipid purity and polarity are important features in biodiesel conversion and the reaction rate. In particular, this effect was investigated by a group of researchers using *Rhizopus oryzae* lipase as the biocatalyst for the conversion of *Nannochloropsis gaditana* lipids to biodiesel. The algal lipids were extracted by two approaches. In the first approach, the lipids were extracted by using a mixture of ethanol–hexane and then were purified by crystallization in acetone, while in the second approach, the extraction was performed using only hexane solvent. When crystallization in acetone was used for lipids purification after extraction, polar lipids (phospholipids and waxes) were precipitated while neutral saponifiable lipids stayed solubilized in acetone with more purity. A hexane extraction system has also shown a very good result of purified lipids. Hence, the reaction velocity, lipid conversion, and final biodiesel purification were raised for lipids with less polarity in the presence of *Rhizopus oryzae* lipase as biocatalyst. Moreover, when *Rhizopus oryzae* lipase was immobilized in biomass support particles and was used for polar lipids contained feedstock, less conversion to biodiesel and also less stability were achieved compared to non-immobilized whole-cell catalyst. It seems that polar lipids deactivated the immobilized *Rhizopus oryzae* lipase faster. In addition, the stability (three cycles) and activity of non-immobilized whole-cell catalyst were increased while hexane-extracted neutral saponifiable lipids were used as the reactant than ethanol-hexane extracted ones due to the presence of less polar lipids [108].

Kyung et al. [109] improved the activity of Novozyme 435 (immobilized type of lipase) biocatalyst in transesterification of extracted triglycerides from *Chlorella* sp. KR-1 due to using dimethyl carbonate (DMC) as the reaction medium and acyl acceptor. It seems that DMC can act as the extraction solvent during transesterification reaction. Carbon dioxide can also be produced through DMC reaction with triglyceride, which improves the reaction equilibrium shift toward product formation and increases biodiesel yield. In addition, the immobilized biocatalyst has shown very high stability after 10 cycles of batch reactions.

4.4. Advantages and Disadvantages of Algae Transesterification Methods

Up to now, two general methods have been mentioned for algae transesterification to biodiesel. The first method is a two-step process (conventional process) in which the lipid in the algal biomass structure can be extracted and then converted to biodiesel through catalytic transesterification. The second method is in situ (single step or direct) conversion of algal biomass to biodiesel in the presence of an acid catalyst. Every mentioned method has some pros and cons in the aspect of cost, time, biodiesel yield, and selectivity [110–112].

In the conventional process, different extraction and solid-liquid separation techniques were used to recover the oil from algal biomass. Biomass drying, the disruption of the cell wall, and solvent extraction are the common steps of algal oil recovery. Wet algae drying or dewatering before extraction of lipid is significant because the presence of water in the algal biomass can limit the mass transfer between lipids of the cells and reduce the extraction efficiency. Several techniques have been used for dewatering of algae, such as sun drying, centrifuges, spiral-plate, pressure, vacuum and membrane filtration, spray drying, heated-drum drying, and freeze-drying. Centrifuges, spiral-plate, spray drying, heated-drum drying, and freeze-drying are high-cost technologies even though they lead to high lipid extraction efficiency. On the other hand, pressure, vacuum and membrane filtration, and sun-drying are low-cost, but more time and wide drying surface area are needed for the sun-drying process [113–115]. In addition, for the disruption of the cell wall and solvent extraction, microwave and ultrasonic methods are more efficient in commercial-scale biodiesel plants compared to the traditional and chemical methods [116–118]. One of the disadvantages of the chemical method is the type of extraction solvents that are toxic organic solvents such as chloroform, hexane, and methanol in most cases and are not environmentally acceptable. In addition, using harsh extraction conditions such as high temperature and long time for some solvents is another disadvantage of the chemical method [119].

In the second step of the conventional process, the catalytic transesterification of extracted algal lipids to biodiesel is performed. All three introduced catalytic systems in this study have their own advantages and disadvantages for algae transesterification to biodiesel contribution to sustainable development, as are mentioned below:

1. Homogeneous transesterification catalysts:
    - Advantages: Since the homogeneous catalysts lead to the feasible mass transfer between lipids and catalysts, mild reaction conditions, including low temperature, low pressure, and short reaction time, are suitable for the transesterification process. This advantage is crucial in the economic aspect. In addition, the high reactivity of homogeneous catalyst, with the production of desirable yield and selectivity of biodiesel, is another prominent characteristic of this catalytic system [120].
    - Disadvantages: One of the most important disadvantages of homogeneous catalysts is saponification, especially for basic systems. The difficulty of catalyst separation from the reaction mixture, its recovery and reusability, and also product purification are the challenges of this catalytic system. Moreover, acidic homogeneous catalysts are corrosive for the reaction system [121].
2. Heterogeneous transesterification catalysts:
    - Advantages: Easy catalyst separation from reaction products, reusability of the catalyst, and lower waste generation are the prominent advantages of heterogeneous catalytic systems. In addition, there are some solid catalysts that can handle both transesterifications of lipids and esterification of FFAs in the algal feedstock to biodiesels and increase the efficiency of the process.
    - Disadvantages: Weak, porous structure of heterogeneous catalyst causes the mass transfer limitation between algal lipids and catalyst active sites. Therefore, harsher reaction conditions are needed, which reduce the overall catalytic efficiency and increase the cost of the process [122].
3. Biotransesterification catalysts:
    - Advantages: enzymatic catalysts are highly efficient systems with the production of pure product, without side reaction and soap formation. In addition, this catalytic system needs less energy compared to other catalytic systems due to its high activity and recyclability properties.

- Disadvantages: enzymatic catalysts are very expensive for being used at an industrial scale [123].

The second process meaning the in-situ algal transesterification is a combination of algal lipids extraction and their transesterification to biodiesel in the presence of acid catalyst and methanol or in supercritical conditions. Since in a single step, shorter time, lower solvent, and reagents are needed, the process is simplified and cheaper compared to the two-step process. On the other hand, due to the presence of both lipid and fatty acid in the reaction mixture, the final oil extraction is more difficult and hazardous and is required more energy [124].

5. Conclusions

After considering the superiority of renewable energy resources over fossil resources, there are numerous advantages to making algal oils a suitable substitute for edible oils for biodiesel production. Algal biomass cultivation is feasible in wide kinds of environments with fewer limitations, even in salty water, without confronting hunger threats and competition with the human food industry. Furthermore, CO_2 consumption through the algal photosynthesis process and their fast growth would certainly prove them as sustainable and environmentally friendly feedstocks. Among others, biodiesel from transesterification of biomass is biodegradable, non-toxic, with slight CO_2 emission and low sulfur and aromatic contents, which could be a direct source of energy in petroleum-diesel engines with reasonable performance. In spite of the undeniable advantages of biodiesel from algae, several R&D works and attempts are necessary to overcome the challenges of algal biodiesel production systems. Some obstacles could be the lack of background knowledge on identifying potential industrial shifts. Therefore, composing biology, chemistry and engineering would be fundamental. The application of catalysts in the transesterification process has attracted industrial attention. Although acid and base homogeneous catalysts are cheaper with higher catalytic activity especially base catalyst, the challenge of corrosion and harsh reaction condition for acid catalysts, negative sensitivity to water and soap formation for base catalysts, and non-recyclability for both groups of homogeneous catalysts motivated researchers and industries in developing heterogeneous catalysts for the process. Solid base catalysts are recyclable and noncorrosive, but they are expensive and need severe reaction conditions, and also, they are not able to convert FFAs in algal lipids to biodiesel. Instead, acid solid catalysts are able to manage both transesterification and esterification reactions, while the issues of bulky lipids diffusion in their low porosity structure and their high cost should be taken into account. In addition, enzymes as the most recent transesterification catalysts are expensive, but they are highly recyclable with no soap formation. Hence, every group of catalysts has its own pros and cons for use at industrial scales, in which some criteria for selecting efficient catalysts must be considered. The catalysts should be (1) economically acceptable, (2) commercially available, (3) suitable for both transesterification of triglycerides and esterification of FFAs, (4) appropriate in having pore size and structure needed for bulky molecules penetration, (5) active at mild reaction condition, (6) stable in water without leaching active phase, (7) with an optimal hydrophobic/hydrophilic balance, (8) suitable for industrial-scale, and (9) reusability.

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References

1. Tang, X. Depletion of fossil fuels and anthropogenic climate change—A review. *Energy Policy* **2013**, *52*, 797–809. [CrossRef]
2. Le Page, M. Our advanced civilisation is built on easily exploited coal, oil and gas, World without fossil fuels. *New Sci.* **2014**, *224*, 34–39. [CrossRef]
3. Kumar, M.; Enamala, S.; Chavali, M.; Donepudi, J. Production of biofuels from microalgae—A review on cultivation, harvesting, lipid extraction, and numerous applications of microalgae. *Renew. Sustain. Energy Rev.* **2018**, *94*, 49–68. [CrossRef]
4. Fallot, A.; Girard, P.; De Coopération, C.; Agronomique, R.; Cirad, D.; Dameron, V.; Griffon, M. The assessment of biofuel potentials on global and regional scales in the tropical world. *Energy Sustain. Dev.* **2006**, *10*, 80–91. [CrossRef]
5. Fischer, G.; Prieler, S.; Van Velthuizen, H.; Berndes, G.; Londo, M.; De Wit, M. Biofuel production potentials in Europe : Sustainable use of cultivated land and pastures, Part II : Land use scenarios. *Biomass Bioenergy* **2010**, *34*, 173–187. [CrossRef]
6. Schut, M.; Slingerland, M.; Locke, A. Biofuel developments in Mozambique. Update and analysis of policy, potential and reality. *Energy Policy* **2010**, *38*, 5151–5165. [CrossRef]
7. Signoretto, M.; Taghavi, S.; Ghedini, E.; Menegazzo, F. Catalytic Production of Levulinic Acid (LA) from Actual Biomass. *Molecules* **2019**, *24*, 2760. [CrossRef] [PubMed]
8. Scott, S.A.; Davey, M.P.; Dennis, J.S.; Horst, I.; Howe, C.J.; Lea-smith, D.J.; Smith, A.G. Biodiesel from algae: Challenges and prospects. *Curr. Opin. Biotechnol.* **2010**, *21*, 277–286. [CrossRef] [PubMed]
9. Vassilev, S.V.; Vassileva, C.G. Composition, properties and challenges of algae biomass for biofuel application: An overview. *Fuel* **2016**, *181*, 1–33. [CrossRef]
10. Benedetti, M.; Vecchi, V.; Barera, S.; Dall'Osto, L. Biomass from microalgae: The potential of domestication towards sustainable biofactories. *Microb. Cell Fact.* **2018**, *17*, 1–18. [CrossRef]
11. Laurens, L.M. State of Technology Review—Algae Bioenergy. IEA Bioenergy Task 39. 2017. Available online: https://www.ieabioenergy.com/wp-content/uploads/2016/01/Laurens-Algae-Bioenergy-Report-IEA-webinar-170124-final-rev1.pdf (accessed on 10 September 2021).
12. Khan, M.I.; Shin, J.H.; Kim, J.D. The promising future of microalgae: Current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products. *Microb. Cell Fact.* **2018**, *17*, 1–21. [CrossRef] [PubMed]
13. Zhou, W.; Wang, J.; Chen, P.; Ji, C.; Kang, Q.; Lu, B.; Li, K.; Liu, J.; Ruan, R. Bio-mitigation of carbon dioxide using microalgal systems: Advances and perspectives. *Renew. Sustain. Energy Rev.* **2017**, *76*, 1163–1175. [CrossRef]
14. Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* **2007**, *25*, 294–306. [CrossRef] [PubMed]
15. McGinn, P.J.; Dickinson, K.E.; Bhatti, S.; Frigon, J.C.; Guiot, S.R.; O'Leary, S.J.B. Integration of microalgae cultivation with industrial waste remediation for biofuel and bioenergy production: Opportunities and limitations. *Photosynth. Res.* **2011**, *109*, 231–247. [CrossRef] [PubMed]
16. Sayre, R. Microalgae: The potential for carbon capture. *Bioscience* **2010**, *60*, 722–727. [CrossRef]
17. Ghasemi, Y.; Amini, S.R.; Naseri, A.T.; Najafabady, N.M.; Mobasher, M.A.; Dabbagh, F. Microalgae Biofuel Potentials (Review)^1. *Russ. Prikl. Biokhimiya i Mikrobiol.* **2012**, *48*, 150–168. [CrossRef]
18. Kojima, E.; Zhang, K.A.I. Growth and Hydrocarbon Production of Microalga Botryococcus braunii in Bubble Column Photobioreactors. *J. Biosci. Bioeng.* **1999**, *87*, 811–815. [CrossRef]
19. Demirbas, A. Combustion efficiency impacts of biofuels. *Energy Sources Part A Recover. Util. Environ. Eff.* **2009**, *31*, 602–609. [CrossRef]
20. Moroney, J.V.; Ynalvez, R.A. Algal Photosynthesis. *Encycl. Life Sci.* **2018**. [CrossRef]
21. Caliceti, M.; Argese, E.; Sfriso, A.; Pavoni, B. Heavy metal contamination in the seaweeds of the Venice lagoon. *Chemosphere* **2002**, *47*, 443–454. [CrossRef]
22. Obidike, L.I.; Yoro, K.O. Effect of zeolitic nano-catalyst on biodiesel yield and biochar formation during the pyrolysis of tallow. *Biofuels* **2021**. [CrossRef]
23. Taghavi, S.; Norouzi, O.; Tavasoli, A.; Di, F.; Signoretto, M.; Menegazzo, F.; Di, A. ScienceDirect Catalytic conversion of Venice lagoon brown marine algae for producing hydrogen-rich gas and valuable biochemical using algal biochar and Ni/SBA-15 catalyst. *Int. J. Hydrogen Energy* **2018**, *43*, 19918–19929. [CrossRef]
24. Demirbas, A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers. Manag.* **2000**, *41*, 633–646. [CrossRef]
25. Ohlrogge, J.B.; Jaworski, J.G. Regulation of fatty acid synthesis. *Annu. Rev. Plant Biol.* **1997**, *48*, 109–136. [CrossRef]
26. Lu, X.; Vora, H.; Khosla, C. Overproduction of free fatty acids in E. coli: Implications for biodiesel production. *Metab. Eng.* **2008**, *10*, 333–339. [CrossRef]
27. Voelker, T.A.; Worrell, A.C.; Anderson, L.; Bleibaum, J.; Fan, C.; Hawkins, D.J.; Radke, S.E.; Davies, H.M.; Voelker, T.A.; Worrell, A.C.; et al. Fatty Acid Biosynthesis Redirected to Medium Chains in Transgenic Oilseed Plants. *Science* **2016**, *257*, 72–74. [CrossRef] [PubMed]
28. Voelker, T.A.; Davies, H.M. Alteration of the specificity and regulation of fatty acid synthesis of Escherichia coli by expression of a plant medium-chain acyl-acyl carrier protein thioesterase. *J. Bacteriol.* **1994**, *176*, 7320–7327. [CrossRef] [PubMed]
29. Du, Z.; Li, Y.; Wang, X.; Wan, Y.; Chen, Q.; Wang, C.; Lin, X.; Liu, Y.; Chen, P.; Ruan, R. Bioresource Technology Microwave-assisted pyrolysis of microalgae for biofuel production. *Bioresour. Technol.* **2011**, *102*, 4890–4896. [CrossRef] [PubMed]
30. Topare, N.S.; Raut, S.J.; Renge, V.C.; Khedkar, S.V.; Chavan, Y.P.; Bhagat, S.L. Extraction of oil from algae by solvent extraction and oil expeller method. *Int. J. Chem. Sci.* **2011**, *9*, 1746–1750.

31. Al hattab, M.; Ghaly, A. Microalgae Oil Extraction Pre-treatment Methods: Critical Review and Comparative Analysis Fundamentals of Renewable Energy and Applications. *J. Fundam. Renew. Energy Appl.* **2015**, *5*, 1000172. [CrossRef]
32. Brown, T.M.; Duan, P.; Savage, P.E. Hydrothermal Liquefaction and Gasification of *Nannochloropsis* sp. *Energy Fuel* **2010**, *24*, 3639–3646. [CrossRef]
33. Carrero, A.; Vicente, G.; Rodríguez, R.; Linares, M.; Peso, G.L. Hierarchical zeolites as catalysts for biodiesel production from Nannochloropsis microalga oil. *Catal. Today* **2011**, *167*, 148–153. [CrossRef]
34. Ranjan, A.; Patil, C.; Moholkar, V.S. Mechanistic Assessment of Microalgal Lipid Extraction. *Ind. Eng. Chem. Res.* **2010**, *49*, 2979–2985. [CrossRef]
35. Rawat, I.; Kumar, R.R.; Mutanda, T.; Bux, F. Biodiesel from microalgae : A critical evaluation from laboratory to large scale production. *Appl. Energy* **2013**, *103*, 444–467. [CrossRef]
36. Li, W.; Zheng, P.; Guo, J.; Ji, J.; Zhang, M.; Zhang, Z.; Zhan, E. Bioresource Technology Characteristics of self-alkalization in high-rate denitrifying automatic circulation (DAC) reactor fed with methanol and sodium acetate. *Bioresour. Technol.* **2014**, *154*, 44–50. [CrossRef]
37. Puri, M.; Sharma, D.; Barrow, C.J. Enzyme-assisted extraction of bioactives from plants. *Trends Biotechnol.* **2012**, *30*, 37–44. [CrossRef] [PubMed]
38. Chan, W.; Schenk, P.M. Minireview Progress on lipid extraction from wet algal biomass for biodiesel production. *Microb. Biotechnol.* **2016**, *9*, 718–726. [CrossRef]
39. Kumar, R.R.; Rao, P.H.; Arumugam, M. Lipid extraction methods from microalgae : A comprehensive review. *Front. Energy Res.* **2015**, *2*, 1–9. [CrossRef]
40. Liu, X.; He, H.; Wang, Y.; Zhu, S.; Piao, X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel* **2008**, *87*, 216–221. [CrossRef]
41. Liu, X.; He, H.; Wang, Y.; Zhu, S. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. *Catal. Commun.* **2007**, *8*, 1107–1111. [CrossRef]
42. Anbessie, T.; Mamo, T.T.; Mekonnen, Y.S. Optimized Biodiesel Production from Waste Cooking Oil (WCO) using Calcium Oxide (CaO) Nano-catalyst. *Sci. Rep.* **2019**, *9*, 1–8. [CrossRef]
43. Chouhan, A.P.S.; Sarma, A.K. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4378–4399. [CrossRef]
44. Ma, H.; Li, S.; Wang, B.; Wang, R.; Tian, S. Transesterification of Rapeseed Oil for Synthesizing Biodiesel by K/KOH/γ-Al_2O_3 as Heterogeneous Base Catalyst. *J. Oil Chem. Soc.* **2008**, *85*, 263–270. [CrossRef]
45. Kim, H.J.; Hilger, H.; Bae, S. $NiSO_4/SiO_2$ catalyst for biodiesel production from free fatty acids in brown grease. *J. Energy Eng.* **2013**, *139*, 35–40. [CrossRef]
46. Han, F.Y.; Komiyama, M.; Uemura, Y.; Rabat, N.E. One-path catalytic supercritical methanothermal production of fatty acid methyl ester fractions from wet microalgae Chlorella vulgaris. *Biomass Bioenergy* **2020**, *143*, 105834. [CrossRef]
47. Jafari, A.; Esmaeilzadeh, F.; Mowla, D.; Sadatshojaei, E.; Heidari, S.; Wood, D.A. New insights to direct conversion of wet microalgae impregnated with ethanol to biodiesel exploiting extraction with supercritical carbon dioxide. *Fuel* **2021**, *285*, 119199. [CrossRef]
48. Ramachandran, K.; Suganya, T.; Gandhi, N.N.; Renganathan, S. Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst : A review. *Renew. Sustain. Energy Rev.* **2013**, *22*, 410–418. [CrossRef]
49. Issariyakul, T.; Dalai, A.K. Comparative kinetics of transesterification for biodiesel production from palm oil and mustard oil. *Can. J. Chem. Eng.* **2012**, *90*, 342–350. [CrossRef]
50. Sivaramakrishnan, R.; Incharoensakdi, A. Production of methyl ester from two microalgae by two-step transesterification and direct transesterification. *Environ. Sci. Pollut. Res.* **2017**, *24*, 4950–4963. [CrossRef] [PubMed]
51. Venkatesan, H.; Godwin, J.J.; Sivamani, S. Data in Brief Data set for extraction and transesteri fi cation of bio-oil from Stoechospermum marginatum, a brown marine algae. *Data Br.* **2017**, *14*, 623–628. [CrossRef]
52. Plata, V.; Kafarov, V.; Moreno, N. Optimization of Third Generation Biofuels Production: Biodiesel from Microalgae Oil by Homogeneous Transesterification. *Chem. Eng. Trans.* **2010**, *21*, 1201–1206. [CrossRef]
53. Narula, V.; Thakur, A.; Uniyal, A.; Kalra, S.; Jain, S. Process parameter optimization of low temperature transesteri fi cation of algae-Jatropha Curcas oil blend. *Energy* **2017**, *119*, 983–988. [CrossRef]
54. Dong, T.; Wang, J.; Miao, C.; Zheng, Y.; Chen, S. Biore source Tec hnology Two-step in situ biodiesel production from microalgae with high free fatty acid content. *Bioresour. Technol.* **2013**, *136*, 8–15. [CrossRef] [PubMed]
55. Kusdiana, D.; Saka, S. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresour. Technol.* **2004**, *91*, 289–295. [CrossRef]
56. Freedman, B.; Pryde, E.H.; Mounts, T.L.; Regional, N. Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils. *Jaocs* **1984**, *61*, 1638–1643. [CrossRef]
57. Ma, F.; Hanna, M.A. Biodiesel production: A review. *Bioresour. Technol.* **1999**, *70*, 1–15. [CrossRef]
58. Suganya, T.; Kasirajan, R.; Renganathan, S. Bioresource Technology Ultrasound-enhanced rapid in situ transesterification of marine macroalgae Enteromorpha compressa for biodiesel production. *Bioresour. Technol.* **2014**, *156*, 283–290. [CrossRef] [PubMed]

59. Vieira, C.; Hachemi, I.; Pereira, S.; Mäki-arvela, P.; Aho, A.; Hemming, J.; Smeds, A.; Heinmaa, I.; Batista, F.; Cristina, D.; et al. A route to produce renewable diesel from algae: Synthesis and characterization of biodiesel via in situ transesterification of Chlorella alga and its catalytic deoxygenation to renewable diesel. *Fuel* **2015**, *155*, 144–154. [CrossRef]
60. Mathimani, T.; Uma, L.; Prabaharan, D. Homogeneous acid catalysed transesteri fi cation of marine microalga *Chlorella* sp. BDUG 91771 lipid—An efficient biodiesel yield and its characterization. *Renew. Energy* **2015**, *81*, 523–533. [CrossRef]
61. Chamola, R.; Khan, M.F.; Raj, A.; Verma, M.; Jain, S. Response surface methodology based optimization of in situ transesterification of dry algae with methanol, H_2SO_4 and NaOH. *Fuel* **2019**, *239*, 511–520. [CrossRef]
62. Ma, Y.; Liu, S.; Wang, Y.; Adhikari, S.; Dempster, T.A.; Wang, Y. Direct biodiesel production from wet microalgae assisted by radio frequency heating. *Fuel* **2019**, *256*, 115994. [CrossRef]
63. Wahidin, S.; Idris, A.; Yusof, N.M.; Kamis, N.H.H.; Shaleh, S.R.M. Optimization of the ionic liquid-microwave assisted one-step biodiesel production process from wet microalgal biomass. *Energy Convers. Manag.* **2018**, *171*, 1397–1404. [CrossRef]
64. Malekghasemi, S.; Kariminia, H.R.; Plechkova, N.K.; Ward, V.C.A. Direct transesterification of wet microalgae to biodiesel using phosphonium carboxylate ionic liquid catalysts. *Biomass Bioenergy* **2021**, *150*, 106126. [CrossRef]
65. Chen, L.; Liu, T.; Zhang, W.; Chen, X.; Wang, J. Bioresource Technology Biodiesel production from algae oil high in free fatty acids by two-step catalytic conversion. *Bioresour. Technol.* **2012**, *111*, 208–214. [CrossRef] [PubMed]
66. de Jesus, S.S.; Ferreira, G.F.; Moreira, L.S.; Filho, R.M. Biodiesel production from microalgae by direct transesterification using green solvents. *Renew. Energy* **2020**, *160*, 1283–1294. [CrossRef]
67. Schenk, P.M.; Thomas-hall, S.R. Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *Bioenergy Res.* **2008**, *1*, 20–43. [CrossRef]
68. Mcneff, C.V.; Mcneff, L.C.; Yan, B.; Nowlan, D.T.; Rasmussen, M.; Gyberg, A.E.; Krohn, B.J.; Fedie, R.L.; Hoye, T.R. Continuous catalytic system for biodiesel production. *Appl. Catal. A Gen. A* **2008**, *343*, 39–48. [CrossRef]
69. Krohn, B.J.; Mcneff, C.V.; Yan, B.; Nowlan, D. Bioresource Technology Production of algae-based biodiesel using the continuous catalytic Mcgyan Ò process. *Bioresour. Technol.* **2011**, *102*, 94–100. [CrossRef] [PubMed]
70. Umdu, E.S.; Tuncer, M.; Seker, E. Bioresource Technology Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts. *Bioresour. Technol.* **2009**, *100*, 2828–2831. [CrossRef] [PubMed]
71. Rahman, M.A. Valorization of harmful algae E. compressa for biodiesel production in presence of chicken waste derived catalyst. *Renew. Energy* **2018**, *129*, 132–140. [CrossRef]
72. Hwa, S.; Islam, A.; Taufiq-yap, Y.H. Chemical Engineering Research and Design Algae derived biodiesel using nanocatalytic transesterification process. *Chem. Eng. Res. Des.* **2016**, *111*, 362–370. [CrossRef]
73. Lotero, E.; Liu, Y.; Lopez, D.E.; Suwannakarn, K.; Bruce, D.A.; Goodwin, J.G. Synthesis of Biodiesel via Acid Catalysis. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353–5363. [CrossRef]
74. Environ, E.; Shimizu, K.; Satsuma, A. Environmental Science Toward a rational control of solid acid catalysis for green synthesis and biomass conversion. *Energy Environ. Sci.* **2011**, *4*, 3140–3153. [CrossRef]
75. Misono, M.; Ono, I.; Koyano, G.; Aoshima, A. Heteropolyacids. Versatile green catalysts usable in a variety of reaction media *. *Pure Appl. Chem.* **2000**, *72*, 1305–1311. [CrossRef]
76. Borges, M.E.; Díaz, L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2839–2849. [CrossRef]
77. Okuhara, T. Water-Tolerant Solid Acid Catalysts. *Chem. Rev.* **2002**, *102*, 3641–3666. [CrossRef] [PubMed]
78. Kiss, A.A.; Dimian, A.C.; Rothenberg, G. Solid Acid Catalysts for Biodiesel Production—Towards Sustainable Energy. *Adv. Synth. Catal.* **2006**, *384*, 75–81. [CrossRef]
79. Suppes, G.J.; Dasari, M.A.; Doskocil, E.J.; Mankidy, P.J.; Goff, M.J. Transesterification of soybean oil with zeolite and metal catalysts. *Appl. Chem. A Gen.* **2004**, *257*, 213–223. [CrossRef]
80. Macario, A.; Giordano, G.; Onida, B.; Cocina, D.; Tagarelli, A.; Maria, A. Applied Catalysis A: General Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid-base catalyst. *Appl. Chem. A Gen.* **2010**, *378*, 160–168. [CrossRef]
81. Melero, J.A.; Bautista, L.F.; Morales, G.; Iglesias, J.; Briones, D. Biodiesel Production with Heterogeneous Sulfonic Acid-Functionalized Mesostructured Catalysts. *Energy Fuel* **2009**, *23*, 539–547. [CrossRef]
82. Serrano, D.P.; Escola, M.; Rodrı, M.; Juan, R.; Uni, C. Hierarchical Zeolites with Enhanced Textural and Catalytic Properties Synthesized from Organofunctionalized Seeds. *Chem. Mater.* **2006**, *18*, 2462–2464. [CrossRef]
83. Macario, A.; Giordano, G. Catalytic Conversion of Renewable Sources for Biodiesel Production: A Comparison between Biocatalysts and Inorganic Catalysts. *Catal. Lett.* **2013**, *143*, 159–168. [CrossRef]
84. Qu, S.; Chen, C.; Guo, M.; Jiang, W.; Lu, J.; Yi, W.; Ding, J. Microwave-assisted in-situ transesterification of Spirulina platensis to biodiesel using PEG/MgO/ZSM-5 magnetic catalyst. *J. Clean. Prod.* **2021**, *311*, 127490. [CrossRef]
85. Bala, D.D.; Misra, M.; Chidambaram, D. Single step esterification of algae oil using mesoporous solid acid catalyst. *Fuel* **2014**, *117*, 1093–1095. [CrossRef]
86. Rana, A.; Alghazal, M.S.M.; Alsaeedi, M.M.; Bakdash, R.S.; Basheer, C.; Al-saadi, A.A. Preparation and Characterization of Biomass Carbon—Based Solid Acid Catalysts for the Esterification of Marine Algae for Biodiesel Production. *BioEnergy Res.* **2019**, *12*, 433–442. [CrossRef]

87. Gurusamy, S.; Kulanthaisamy, M.R.; Hari, D.G.; Veleeswaran, A.; Thulasinathan, B.; Muthuramalingam, J.B.; Balasubramani, R.; Chang, S.W.; Arasu, M.V.; Al-Dhabi, N.A.; et al. Environmental friendly synthesis of TiO_2-ZnO nanocomposite catalyst and silver nanomaterilas for the enhanced production of biodiesel from Ulva lactuca seaweed and potential antimicrobial properties against the microbial pathogens. *J. Photochem. Photobiol. B Biol.* **2019**, *193*, 118–130. [CrossRef]
88. Sala, J.G. *Ethyl Octyl Ether Synthesis from 1-Octanol and Ethanol or Diethyl Carbonate*; University of Baecelona: Barcelona, Spain, 2013.
89. Karinen, R. Etherification of some C_8-alkenes to fuel ethers. In *Industrial Chemistry Publication Series*; Helsinki University of Technology: Espoo, Finland, 2002.
90. Lopez, D.E.; Jr, J.G.G.; Bruce, D.A.; Lotero, E. Transesterification of triacetin with methanol on solid acid and base catalysts. *Appl. Catal. A Gen.* **2005**, *295*, 97–105. [CrossRef]
91. Ravenelle, R.M.; Schü, F.; Amico, A.D.; Danilina, N.; Van Bokhoven, J.A.; Lercher, J.A.; Jones, C.W.; Sievers, C. Stability of Zeolites in Hot Liquid Water. *J. Phys. Chem.* **2010**, *114*, 19582–19595. [CrossRef]
92. Laitinen, A.; Harlin, A. Production of p-Cymene from Crude Sulphate Turpentine with Commercial Zeolite Catalyst Using a Continuous Fixed Bed Reactor. *Org. Process. Res. Dev.* **2014**, *18*, 1468–1475. [CrossRef]
93. Cseri, T.; Bkassy, S.; Figueras, F.; De Menorval, L.; Dutartre, R. Characterization of clay-based K catalysts and their application in Friedel-Crafts alkylation of aromatics. *Appl. Catal. A Gen.* **1995**, *132*, 141–155. [CrossRef]
94. Asikainen, M.; Munter, T.; Linnekoski, J. Conversion of polar and non-polar algae oil lipids to fatty acid methyl esters with solid acid catalysts—A model compound study. *Bioresour. Technol.* **2015**, *191*, 300–305. [CrossRef]
95. Sánchez, D.A.; Tonetto, G.M.; Ferreira, M.L. Burkholderia cepacia lipase: A versatile catalyst in synthesis reactions. *Biotechnology* **2017**, *115*, 6–24. [CrossRef]
96. Nielsen, P.M.; Brask, J.; Fjerbaek, L. Review Article Enzymatic biodiesel production: Technical and economical considerations. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 692–700. [CrossRef]
97. Mukherjee, J.; Nath, M. Dual bioimprinting of Thermomyces lanuginosus lipase for synthesis of biodiesel. *Biotechnol. Rep.* **2016**, *10*, 38–43. [CrossRef] [PubMed]
98. Rodrigues, J.; Canet, A.; Rivera, I.; Osório, N.M.; Sandoval, G.; Valero, F.; Ferreira-dias, S. Bioresource Technology Biodiesel production from crude Jatropha oil catalyzed by non-commercial immobilized heterologous Rhizopus oryzae and Carica papaya lipases. *Bioresour. Technol.* **2020**, *213*, 88–95. [CrossRef]
99. Mohamad, N.R.; Haziqah, N.; Marzuki, C.; Buang, N.A.; Wahab, R.A. An overview of technologies for immobilization of enzymes and surface analysis techniques for immobilized enzymes. *Biotechnol. Biotechnol. Equip.* **2015**, *29*, 205–220. [CrossRef] [PubMed]
100. Kensingh, P.; Chulalaksananukul, W.; Charuchinda, S. Lipase immobilization on Scirpus grossus L.f. fiber support by glutaraldehyde-crosslinked technique for biodiesel synthesis. *J. Biotechnol.* **2010**, *150*, 163. [CrossRef]
101. Yan, J.; Yan, Y.; Liu, S.; Hu, J.; Wang, G. Preparation of cross-linked lipase-coated micro-crystals for biodiesel production from waste cooking oil. *Bioresour. Technol.* **2011**, *102*, 4755–4758. [CrossRef] [PubMed]
102. Kumari, V.; Shah, S.; Gupta, M.N. Preparation of biodiesel by lipase-catalyzed transesterification of high free fatty acid containing oil from Madhuca indica. *Energy Fuels* **2007**, *21*, 368–372. [CrossRef]
103. Nematian, T.; Salehi, Z.; Shakeri, A. Conversion of bio-oil extracted from Chlorella vulgaris micro algae to biodiesel via modified superparamagnetic nano-biocatalyst. *Renew. Energy* **2020**, *146*, 1796–1804. [CrossRef]
104. Chen, J.Z.; Wang, S.; Zhou, B.; Dai, L.; Liu, D.; Du, W. A robust process for lipase-mediated biodiesel production from microalgae lipid. *RSC Adv.* **2016**, *6*, 48515–48522. [CrossRef]
105. Guldhe, A.; Singh, B.; Rawat, I.; Permaul, K.; Bux, F. Biocatalytic conversion of lipids from microalgae Scenedesmus obliquus to biodiesel using Pseudomonas fluorescens lipase. *Fuel* **2015**, *147*, 117–124. [CrossRef]
106. Bharathiraja, B.; Kumar, R.R.; Praveenkumar, R.; Chakravarthy, M.; Yogendran, D.; Jayamuthunagai, J. Bioresource Technology Biodiesel production from different algal oil using immobilized pure lipase and tailor made r Pichia pastoris with Cal A and Cal B genes. *Bioresour. Technol.* **2016**, *213*, 69–78. [CrossRef] [PubMed]
107. Guldhe, A.; Singh, P.; Kumari, S.; Rawat, I.; Permaul, K.; Bux, F. Biodiesel synthesis from microalgae using immobilized Aspergillus niger whole cell lipase biocatalyst. *Renew. Energy* **2016**, *85*, 1002–1010. [CrossRef]
108. López, E.N.; Medina, A.R.; Antonio, P.; Moreno, G.; Cerdán, L.E.; Valverde, L.M.; Grima, E.M. Bioresource Technology Biodiesel production from Nannochloropsis gaditana lipids through transesterification catalyzed by Rhizopus oryzae lipase. *Bioresour. Technol.* **2016**, *203*, 236–244. [CrossRef] [PubMed]
109. Kyung, O.; Hyun, Y.; Na, J.; Oh, Y.; Yeol, E. Bioresource Technology Highly efficient extraction and lipase-catalyzed transesterification of triglycerides from *Chlorella* sp. KR-1 for production of biodiesel. *Bioresour. Technol.* **2013**, *147*, 240–245. [CrossRef]
110. Veillette, M.; Chamoumi, M.; Nikiema, J.; Faucheux, N.; Heitz, M. Production of Biodiesel from Microalgae. *Adv. Chem. Eng.* **2012**, *10*, 245–260. [CrossRef]
111. Prommuak, C.; Pavasant, P.; Quitain, A.T.; Goto, M.; Shotipruk, A. Microalgal lipid extraction and evaluation of single-step biodiesel production. *Eng. J.* **2012**, *16*, 157–166. [CrossRef]
112. Martinez-Guerra, E.; Gude, V.G.; Mondala, A.; Holmes, W.; Hernandez, R. Extractive-transesterification of algal lipids under microwave irradiation with hexane as solvent. *Bioresour. Technol.* **2014**, *156*, 240–247. [CrossRef]
113. Fasaei, F.; Bitter, J.H.; Slegers, P.M.; van Boxtel, A.J.B. Techno-economic evaluation of microalgae harvesting and dewatering systems. *Algal Res.* **2018**, *31*, 347–362. [CrossRef]

114. Lee, Y.L.; Chuang, Y.C.; Su, H.M.; Wu, F.S. Freeze-dried microalgae of Nannochloropsis oculata improve soybean oil's oxidative stability. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 9675–9683. [CrossRef]
115. Chen, C.L.; Chang, J.S.; Lee, D.J. Dewatering and Drying Methods for Microalgae. *Dry. Technol.* **2015**, *33*, 443–454. [CrossRef]
116. Melgar, B.; Dias, M.I.; Barros, L.; Ferreira, I.C.F.R.; Rodriguez-Lopez, A.D.; Garcia-Castello, E.M. Ultrasound and microwave assisted extraction of Opuntia fruit peels biocompounds: Optimization and comparison using RSM-CCD. *Molecules* **2019**, *24*, 3618. [CrossRef] [PubMed]
117. Kapoore, R.V.; Butler, T.O.; Pandhal, J.; Vaidyanathan, S. Microwave-assisted extraction for microalgae: From biofuels to biorefinery. *Biology* **2018**, *7*, 18. [CrossRef]
118. Gim, G.H.; Kim, S.W. Optimization of Cell Disruption and Transesterification of Lipids from Botryococcus braunii LB572. *Biotechnol. Bioprocess Eng.* **2018**, *23*, 550–556. [CrossRef]
119. Miao, X.; Li, P.; Li, R.; Zhong, J. In situ biodiesel production from fast-growing and high oil content chlorella pyrenoidosa in rice straw hydrolysate. *J. Biomed. Biotechnol.* **2011**, *2011*, 141207. [CrossRef]
120. Polshettiwar, V.; Varma, R.S. Green chemistry by nano-catalysis. *Green Chem.* **2010**, *12*, 743–775. [CrossRef]
121. Jiang, C.; Jia, J.; Zhai, S. Mechanistic understanding of toxicity from nanocatalysts. *Int. J. Mol. Sci.* **2014**, *15*, 13967–13992. [CrossRef]
122. Mohammed, N.I.; Kabbashi, N.A.; Alade, A.O.; Sulaiman, S. Advancement in the Utilization of Biomass-Derived Heterogeneous Catalysts in Biodiesel Production. *Green Sustain. Chem.* **2018**, *8*, 74–91. [CrossRef]
123. Ranganathan, S.V.; Narasimhan, S.L.; Muthukumar, K. An overview of enzymatic production of biodiesel. *Bioresour. Technol.* **2008**, *99*, 3975–3981. [CrossRef]
124. Amin Umar, A. Feasibility Study of Algae Biodiesel Production in the Cambois Peninsular (UK). *Int. J. Energy Environ. Res.* **2014**, *2*, 21–54.