

Review

Current State and Perspectives on Transesterification of Triglycerides for Biodiesel Production

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Abstract: Triglycerides are the main constituents of lipids, which are the fatty acids of glycerol. Natural organic triglycerides (viz. virgin vegetable oils, recycled cooking oils, and animal fats) are the main sources for biodiesel production. Biodiesel (mono alkyl esters) is the most attractive alternative fuel to diesel, with numerous environmental advantages over petroleum-based fuel. The most practicable method for converting triglycerides to biodiesel with viscosities comparable to diesel fuel is transesterification. Previous research has proven that biodiesel–diesel blends can operate the compression ignition engine without the need for significant modifications. However, the commercialization of biodiesel is still limited due to the high cost of production. In this sense, the transesterification route is a crucial factor in determining the total cost of biodiesel production. Homogenous base-catalyzed transesterification, industrially, is the conventional method to produce biodiesel. However, this method suffers from limitations both environmentally and economically. Although there are review articles on transesterification, most of them focus on a specific type of transesterification process and hence do not provide a comprehensive picture. This paper reviews the latest progress in research on all facets of transesterification technology from reports published by highly-rated scientific journals in the last two decades. The review focuses on the suggested modifications to the conventional method and the most promising innovative technologies. The potentiality of each technology to produce biodiesel from low-quality feedstock is also discussed.

Keywords: triglycerides; biodiesel; esterification; transesterification; biodiesel feedstock

1. Introduction

The conversion of renewable energy sources to alternative fuels has been at the forefront of sustainable energy research due to the increased environmental awareness and worries from the expected depletion of fossil fuel resources [1–3]. Biodiesel is among the most promising alternative fuels produced from virgin and waste cooking vegetable oils or animal fats [4,5]. Due to its renewability, biodegradability, low emission profile, non-toxicity, and high flash point, biodiesel has a number of advantages over petroleum-based diesel [6–10]. In addition, biodiesel increases the operational lifetime of the compression

engine and reduces the consumption of the engine spare parts due to the high lubricity of biodiesel [11,12]. Therefore, biodiesel is an alternative fuel with the high potentiality to compete with petroleum fuel from environmental and economic points of view [7,13–15]. Using vegetable oil as a fuel dates back to the 1900s when Adolf Diesel used peanut oil as fuel in a diesel engine [16,17]. The main problem regarding vegetable oil as fuel is its greater viscosity besides its low volatility and bad cold flow properties, which affect the proper operation of the diesel engine [18,19]. The properties of vegetable oils can be improved in different ways, such as pyrolysis, dilution with liquid hydrocarbon (blending), micro emulsification, and transesterification process [20–23]. Transesterification is the most practicable process, among these four ways, for reducing the viscosities of vegetable oils and producing alkyl esters with characteristics comparable to diesel. This is the reason why transesterified vegetable oils are popularized as “biodiesel” [24,25]. Table 1 shows the difference in viscosity between oils and transesterified oils compared to diesel.

Table 1. The effect of transesterification on vegetable oils viscosities [26,27].

Fuel Type	Viscosity (mm ² /s) at 311 K	
	Raw Oil	Transesterified Oil
Sunflower oil	34.4	3.2
Cottonseed oil	33.0	3.1
Rapeseed oil	37.3	3.3
Karanja oil	38.7	4.5
Manilkara zapota oil	33.8	4.7
Diesel fuel no. 2		2.7

The transesterification reaction modifies one ester to another by changing its alkoxy part [28–30]. This is similar to hydrolysis; however, alcohol is used in this process instead of water and is thus known as alcoholysis [31]. Biodiesel is produced through transesterification by the reaction of lipids with alcohol. The major components of lipids (oil/fats) are triglycerides. Triglycerides are esters of three fatty acids and one glycerol. Thus, the alcoholysis of lipids produces monoalkyl esters, commonly named biodiesel, and glycerol as a by-product. The overall process of transesterification is a sequence of three consecutive and reversible reactions in which di and monoglycerides are formed as intermediates. The stoichiometric reaction requires one mol of triglyceride and three moles of alcohol. However, to maximize the yield of the alkyl ester, alcohol should be used in an excess amount. However, an excessive amount of alcohol makes the separation of the yields difficult. Therefore, the alcohol/oil molar ratio, besides the type of catalyst, temperature, and purity of the reactant, are the factors that affect the process of transesterification [32]. The purity of the reactants, mainly water content and free fatty acids, is the crucial factor that determines the convenient route of transesterification [33,34].

Commonly, the transesterification of lipids is applied by using a short-chain alcohol (C1 to C4). However, methanol is the most common alcohol because it is cheaper, and it is easier to recover unreacted methanol. On the other hand, ethyl esters are more renewable because ethanol is produced from agricultural resources [35]. In addition, ethyl esters were proved to have lower emissions of green gases and more biodegradability in the aquatic environment [36,37]. However, there are practical difficulties associated with the production of ethyl esters, as it suffers due to the fast saponification and solubility of ethyl esters in glycerol, which increases at a high oil/ethanol molar ratio [38].

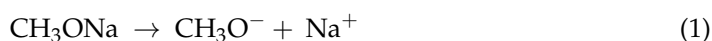
The cost of biodiesel production is high because more than 75% of its total cost is related to conventional raw materials, such as edible oils and animal fat [39]. On the other hand, using edible vegetable oils for biodiesel production leads to a food crisis [16]. A practical, sustainable transesterification route should produce biodiesel from low-cost feedstocks such as non-edible oils, waste cooking oils, or animal fats, increasing the cost-effectiveness of biodiesel production. Generally, the transesterification process is classified into catalytic and non-catalytic methods. Catalytic methods are categorized into

homogenous and heterogeneous processes [40]. The transesterification reaction's route determines the biodiesel industry's feasibility, considering economic and environmental constraints. Therefore, this paper aimed to review the progress in research, based on a bench scale, concerning the latest technologies of transesterification. The modifications to the conventional homogenous methods and the most promising innovative catalytic or non-catalytic technologies were critically reviewed.

2. Homogeneous Catalysis

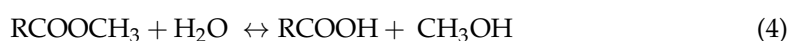
2.1. Homogenous Base-Catalyzed Transesterification

Basic metal alkoxide, hydroxide, and sodium and potassium carbonates are utilized in the homogeneous base-catalyzed transesterification process [26,41–43]. With virgin vegetable oil, base catalysts typically show high performance with oils containing more free fatty acids than the critical amount to produce soap that inhibits glycerol production and restrains the division of fatty acids to biodiesel and glycerin [44–46]. From an economic point of view, hydroxides are cheap and easy to handle during storage [16]. For continuous biodiesel production, methoxides in methanol are recommended [47]. In both cases, the active species is the methoxide ions resulting from the dissociation of the methoxide salt (Equation (1)) or when methanol reacts with the hydroxide alkaline metal (Equation (2)). The methoxide ions are strong nucleophiles and attack the carbonyl moiety in glyceride molecules to produce alkyl ester [48].



The comparison of different fundamental catalysts (sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide) was carried out for methanolysis of sunflower oil by Vicente et al. [49]. The results showed that the biodiesel purity was found to be 100 wt% for all catalysts. However, 100 wt% of biodiesel yields were only obtained with the methoxide catalysts. Singh et al. [50] studied the production of biodiesel from canola oil using different homogenous alkaline catalysts and revealed that potassium-based catalysts give a better yield than sodium-based catalysts, and methoxide catalysts give higher yields than corresponding hydroxide catalysts as follows: $\text{KOCH}_3 > \text{NaOCH}_3 > \text{KOH} > \text{NaOH}$. Biodiesel purities (i.e., methyl ester concentration in the biodiesel) reported for NaOH, KOH, NaOCH₃, and KOCH₃ were 99.70 ± 0.04 (%), 99.76 ± 0.05 (%), 99.73 ± 0.03 (%), and 99.52 ± 0.1 (%), respectively. Biodiesel yield (i.e., the relative amount of the methyl ester to the oil) reported for NaOH, KOH, NaOCH₃, and KOCH₃ were 86.71 ± 0.28 (%), 91.67 ± 0.27 (%), 99.33 ± 0.36 (%), and 98.46 ± 0.16 (%), respectively.

Industrial processes favor base catalysts for biodiesel production because they are less corrosive and produce biodiesel with high purity and yields in a short time compared to acid catalysts [51,52]. However, homogenous base catalysts are not tolerant to the free fatty acids (FFAs) in the feedstock with high concentrations. Feedstock has to comply with strict specifications. In particular, the total (FFAs) content must not exceed 0.5 wt% of oil. Otherwise, the catalyst is consumed due to the formation of soaps, as indicated in (Equation (3)). The base method is not suitable for feedstocks with high FFAs content, such as some non-edible vegetable oils, waste cooking vegetable oils, or animal fats. Further, alcohol and the catalyst must be essentially anhydrous because the water in the feedstocks promotes hydrolysis of alkyl esters to FFAs (Equation (4)) and, consequently, soap formation. Soap formation makes the separation of glycerol from alkyl ester complex [53]. From an environmental point of view, homogenous catalysis by alkali-hydroxides produces a large amount of wastewater discharged from the process to wash the dissolved catalyst off the produced biodiesel [54,55].



The fast saponification accompanying the production of ethyl esters by alkali base catalysts could be avoided by developing a process consisting of two reactions steps with glycerin separation and the addition of ethanol/alkali in each of them. A 99% conversion of sunflower oil to fatty acid ethyl ester by Mendow et al. [38] was achieved with low total consumption of ethanol during the whole process. The optimal reaction temperature was 55 °C at an ethanol/oil total molar ratio of 4.25:1. Sodium methoxide catalyst total concentration was 1.06 g catalyst/100 g oil; 50% of the catalyst was added in each reaction step. This two-stage alkali-catalyzed transesterification deserves to be industrially considered since biodiesel with required standard total glycerin content and low consumption of alcohol and catalyst, besides a higher biodiesel yield compared to one-stage transesterification, could be achieved.

2.2. Homogenous Acid-Catalyzed Transesterification

This method of production is the second conventional route to produce biodiesel. Sulfuric acid and sulphonic acids are most commonly used [56–58]. This type of catalyst gives very high yields in alkyl esters. However, it is industrially ignored, despite the advantage of its insensitivity to the presence of FFAs in the feedstock, because of its low reaction rate and requiring large quantities of alcohol [59,60]. The reaction kinetics of acid-catalyzed transesterification of waste frying oil was investigated by Zheng et al. [61]. They proved that the fatty acid methyl ester yield depended significantly on the temperature and the molar ratios between oil, methanol, and the acid catalyst. The transesterification reaction was a pseudo-first-order reaction because the maximum yield ($99 \pm 1\%$) was obtained using extensive methanol excess.

The effect of the methanol:oil molar ratios on the acid-catalyzed transesterification of soybean oil was studied by Fredman et al. [62] by using (1 wt%) concentrated sulfuric acid based on the oil weight at a temperature near the boiling point of methanol. They had conducted preliminary experiments with 6:1 and 20:1 molar ratios at 3 and 18 h, respectively. The conversion to esters was not satisfactory. However, a molar ratio of 30:1 resulted in a higher conversion to methyl ester after 69 h. The effect of the temperature on the methylation of crude palm oil was investigated by Crabbe et al. [63] at 75, 80, and 95 °C using 5% sulfuric acid and a 40:1 molar ratio methanol to the oil over 24 h. Biodiesel yield (99.7 wt%) was obtained at 95 °C after 9 h, while a similar yield was obtained at 80 °C after 24 h. Methylation at 75 °C was slow and incomplete, even after 24 h. Considering temperature, acid-catalyzed transesterification is energy-intensive.

Acids can catalyze both esterification and transesterification reactions by protonation of the fatty acids and triglycerides [59]. Hence, because acids can simultaneously catalyze both esterification and transesterification reactions, the acid-catalyzed method is suitable for producing biodiesel from low-cost feedstock with high FFAs content. From this point, acid-catalyzed production of biodiesel can compete economically with the base-catalyzed process [53]. According to a techno-economical assessment [64,65], an acid-catalyzed process using waste cooking oil was proved feasible with less complexity in equipment and more economical than the alkali-catalyzed process using waste cooking oil. This is because the alkali-catalyzed process requires an additional pretreatment unit for the FFAs removal.

2.3. Acid-Base Catalyzed Two-Step Process

This process is suitable for the production of biodiesel from feedstocks with high (FFAs). The first step is acid-catalyzed pretreatment to esterify FFAs to reduce their content to less than 1 wt%. The second step is transesterifying the triglycerides with an alkaline catalyst to complete the reaction [66–69]. Charoenchaitrakool and Thienmethangkoon [70] applied the two-step catalyzed pretreatment process to convert waste frying vegetable oil to biodiesel. The methyl ester content in the product was $90.56 \pm 28\%$. The optimum conditions in the first step to reducing the FFAs to less than 0.5 wt% were 6.1:1 methanol/oil

ratio, 0.68 wt% of H₂SO₄, at 51 °C and 60 min of reaction time. The second step consumed 1 wt% KOH with a methanol/oil ratio 9.1:1 at 55 °C and 60 min.

Ghadge and Raheman [71] reduced the FFAs content of mahua oil (*Madhuca indica*) from 19% to less than 1% through a two-step pretreatment process prior to alkaline catalyzed transesterification. They proved that FFAs content is influenced by both quantities of methanol and reaction time. It was apparent that a high amount of methanol was consumed during the two steps of pretreatment. To make this process feasible in a commercial application, part of methanol should be recovered from the water mix that is separated from the top after each step.

A novel homogenous catalysis route is present to produce biodiesel from feedstock with high FFAs in one step by using acidic ionic liquids (ILs) [72,73]. Although ionic liquids are costlier than regular catalysts, such as NaOH, KOH, and H₂SO₄, they offer advantages of reusability and biodegradability. Metal chlorides (MCl_n) were found to significantly increase the catalytic activity of acidic ILs to catalyze the esterification and transesterification reactions simultaneously. A maximum biodiesel yield of 99.7% was achieved from un-pretreated *Jatropha* with high FFAs (13.8 mgKOH/g) by adding a mixture of FeCl₃ and 1-butyl-3 methyl imidazolium-tosylate ([BMIm] [CH₃SO₃]); a Brønsted acidic ILs. However, from an economic point of view, ILs with metal chlorides need advancement in the techniques to compete for the conventional solvents and catalysts in the large-scale production of biodiesel [74]. Choline hydroxide (ChOH) was employed as a green ionic liquid catalyst by Phromphithak et al. [75] to produce biodiesel from palm oil. A maximum biodiesel yield of 89.72% methyl ester content was obtained at 1:13.24 oil to methanol molar ratio, a flow rate of 20 mL/min, microwave power of 800 W, and catalyst loading of 6% (*w/w*).

2.4. Transesterification Double Step Process (TDSP)

This method is found to be very effective in the separation of the biodiesel/glycerin phase. The first step is basic catalyzed transesterification, followed by the addition of an acidic catalyst. The addition of the acid in the second step breaks the soaps and catalyzes the reaction simultaneously. The overall process is swift and yields high purity due to the high conversion degree [53,76,77]. Samios et al. [77] produced biodiesel with high quality and purity, as indicated by ¹H-NMR, from sunflower and linseed oils using the TDSP. The evaluation of the ¹H-NMR data suggested that the oil conversion degree to fatty acid methyl ester was higher than 97%. Hydroxyl vegetable oil, such as castor oil, has a high solubility in ethanol and glycerin. Therefore, the ethanolysis of such vegetable oils by the conventional basic catalyst is not feasible. MontesD'Oca et al. [76] demonstrated that using the TDSP was necessary to improve the separation of glycerin and fatty acid ethyl ester produced from the transesterification of castor oil. They achieved high ethyl esters yields, glycerin with high purity (95.76%), and free and bound glycerol was less than the specified value. A modified TDSP was used to ethanololyse some vegetable oils and waste vegetable oils by Gazatto et al. [78]. The triglyceride conversion to biodiesel was higher than 97% for all oil used, and the yields were considerably high compared to single basic catalysis yields. TDSP is evaluated as a new method for biodiesel production with higher conversion than the basic one and sufficiently smaller operational time than acid catalysis. However, this method needs more investigations to be industrially competitive [77].

3. Heterogeneous Catalysis

The heterogeneous catalytic process seems to be an appropriate solution to overcome all problems associated with homogenous catalysts. The use of heterogeneous catalysts is currently preferred due to the main advantages of: (1) quickly separation and purification of final products, (2) it can be regenerated and recycled, and (3) it could be operated in continuous processes with no need for acid or water treatment in the separation step, so it is environmentally benign [79,80]. For all these advantages, heterogeneous catalysis has strongly drawn the attention of researchers. Heterogeneous catalysts can be solid base or solid acid [80]. The main mechanism of heterogeneous catalysis follows the principle

of homogeneous catalysis of either base or acid systems similarly [81]. In most cases, the solid catalyst is prepared by the impregnation of active compounds into the surface of porous material [82]. This method increases the catalytic activity and decreases the catalyst required during the transesterification process [83].

3.1. Heterogeneous Base-Catalyzed Process

Table 2 shows the conversion rate of some vegetable oils to biodiesel and optimized conditions using a solid base catalyst. Transesterification of soybean oil with a CaO/mesoporous silica catalyst was achieved by Samart et al. [83]. The optimized condition for the highest yield (95.2%), found to be 15 wt% of Ca loading on the mesoporous silica catalyst, was a 5% (*w/w*) catalyst to oil level, and reaction temperature of 60 °C for 8 h. Zeolites, such as MCM-41 and SBA-15, are considered promising support for various metals due to their catalytic surface properties and thermal stability. However, this support has a weak acidity due to the localized non-polar silanol groups on the pore walls. Liang et al. [84] impregnated Na precursor salts into SBA-15 and increased the surface acidity of the resultant catalyst (Na/SBA-15) by incorporating heteroatom Al. They used the modified catalyst (Na/Al SBA-15) to transesterify canola oil, 99% conversion to biodiesel was achieved at the optimum condition of 6:1 methanol to oil molar ratio, 65 °C temperature, and 6 h reaction time. The metal loading weight was 5%. Chen et al. [85] incorporated Zr atoms into the SBA-15 structure, facilitating the formation of Brønsted acid sites and decreasing the particle size of Na species. Catalysts with a higher Zr content enhanced the fatty acid methyl ester (FAME) yield as 99% were obtained at a 6:1 methanol/oil molar ratio, 12% catalyst content (wt% oil) with 15 wt% Na loaded into the support, reaction temperature of 70 °C, and a reaction time of 6 h.

Table 2. Solid basic catalysts for biodiesel production.

Catalyst	Catalyst to Oil %(<i>w/w</i>)	Feedstock	Conversion %	Reaction Parameters			Reference
				Methanol to Oil Molar Ratio	Reaction Time h	Temperature °C	
CaO/Mesoporous silica	5	Soybean oil	95.2	16:1	8	60	[83]
CaSn(OH) ₆	3	Oils with high free fatty acids	92–96	10:1	3–14	65	[86]
Na/Al-SBA-15	3	Canola oil	99	6:1	6	65	[84]
Na/Zr-SBA-15	NA	Canola oil	99	6:1	6	70	[85]
(BaAl ₂ O ₄)	12	Used cooking oil	93.28	21:1	2.5	65	[87]
(f-MgO)	NA	Canola oil	93.4	16:1	2.5	190	[88]

NA: not available.

Sandesh et al. [86] studied the transesterification of both edible and non-edible oils, such as sunflower, waste cooking oil, Jatropha, honge, and simarouba oils, using calcium hydroxy stannate (CaSn(OH)₆) as a strong heterogeneous solid base catalyst. Esterification of oils with an acid value greater than two was carried out first. The results showed that CaSn(OH)₆ showed varying performance for different studied oils with >90% biodiesel yield with 3 wt% catalysts. The oil to methanol ratio was 1:10, and the reaction temperature was kept at 65 °C. Yadav and Sharma [87] studied the transesterification of used vegetable oil using a heterogeneous base catalyst, barium aluminate (BaAl₂O₄), which was synthesized by the co-precipitation route. A 93.28% conversion of methyl ester was obtained at a methanol to oil molar ratio of 21:1, catalyst amount 4 wt%, reaction temperature of 65 ± 0.5 °C, for a 150 min reaction duration. Lee et al. [88] studied the canola oil biodiesel conversion using hierarchical flower-shaped hollow MgO (f-MgO) spheres as heterogeneous catalysts. Flower-like MgO nanostructures based on ultrathin petal-like nanosheets led to superior catalytic activity over commercial MgO. The experimental results for the

fatty acid methyl ester revealed that the maximum biodiesel conversion efficiency of f-MgO from canola oil is 93.4%.

3.2. Heterogeneous Acid-Catalyzed Process

Heterogeneous acid catalysts have a less corrosive and toxic effect and give rise to fewer environmental problems compared to homogeneous acid catalysts [52]. Single-process simultaneous esterification and transesterification of non-edible oils with high FFAs using solid acid catalysts have emerged as an alternative method to the more complex homogeneous two-step (acid-base) process [81]. Transesterification of refined and crude vegetable oils was carried out with a sulphonic acid-modified meso-structural catalyst. Regardless of the presence of free fatty acid, this catalyst showed high activity towards simultaneous esterification and transesterification reactions [89]. Malins et al. [90] compared the esterification reactions of rapeseed oil fatty acids (RFA) and RFA/rapeseed oil (RO) mixture (weight ratio 1/2) using 4-sulfophenyl activated carbon-based solid acid catalyst (ACPhSO₃H) and Amberlyst-15 (an industrial-grade solid acid catalyst). Esterification was carried out under the molar ratio of RFA to methanol (1/20), reaction time (0–7 h) at 65 °C. ACPhSO₃H catalyzed the conversion of RFA to RME using pure RFA, and the RFA/RO mixture was ~95% and ~92% after 7 h of reaction, respectively. For pure RFA using Amberlyst-15, the final conversion was similar, with a higher initial conversion of ~6–9% in the first ~4 h. However, for RFA/RO mixture, a conversion of ~96% was obtained in the presence of Amberlyst-15, which was 4.5% higher than that obtained with ACPhSO₃H as the catalyst. They attributed the higher conversion of Amberlyst-15 to the higher PhSO₃H density in comparison with ACPhSO₃H. Bhatia et al. [91] studied the transesterification of waste canola oil-based cooking oil using heterogeneous acidic biochar catalyst prepared by pyrolysis of waste cork (*Quercus suber*). The maximum fatty acids methyl esters (FAMES) conversion of 98% was obtained for the catalyst (pyrolyzed cork at 600 °C) with alcohol:oil (25:1), catalyst loading (1.5% w/v), and a temperature of 65 °C. Table 3 presents some novel heterogeneous solid acid catalysts for the production of biodiesel from the low-quality feedstock.

Lately, the single-step solid acid process has mainly been ignored mainly because of its relatively slower reaction rate [64,92]. Wang et al. [93] have developed a two-step catalyzed process (solid acid/alkaline base) to produce biodiesel from waste cooking oil. This process was presented as an industrial technique that is more feasible compared to the traditional homogeneous acid-catalyzed process. The first step was the esterification of the FFAs with ferric sulfate. The second step was transesterification of the oil with potassium hydroxide. This new two-step catalyzed process has the advantages of no wastewater, reusable catalyst, and low cost of reaction tank. They reported that with a 20:1 molar ratio of H₂SO₄ and 10 h reaction time, the biodiesel yield was 90 wt%, whereas, for Fe₂O₃/KOH, 97.22 wt% biodiesel yield was obtained with 10:1 molar ratio of catalyst and 4 h reaction time. Zhang et al. [94] have proven that biodiesel can be produced successfully from *Zanthoxylum bungeanum* seed oil with high FFAs through ferric sulfate-catalyzed esterification followed by transesterification using CaO as the alkaline catalyst. The acid value of the oil was reduced to less than 2 mg KOH/g from 41.02 mg KOH/g by the esterification process under the conditions of methanol-to-FFA molar ratio 40.91:1, ferric sulfate 9.75 wt% (of FFA), reaction temperature 95 °C, and reaction time 2 h. Transesterification of esterified oil was later carried out using CaO as a catalyst at optimized conditions with a methanol-to-oil molar ratio 11.69:1, catalyst amount 2.52 wt%, and reaction time 2.45 h, which resulted in a conversion to biodiesel above 96%.

Recently, new types of solid catalysts that have both acidic and basic sites on their surface have been investigated intensively. This type of catalyst, called acid-base bifunctional catalysts, can utilize the low feedstock with high FFAs for biodiesel production due to their efficient catalytic activity to esterify FFAs and transesterification of the triglycerides in the oil, simultaneously in one step. Moreover, these catalysts are insensitive to water present in the feedstock or produced during the reaction of esterification [95]. A novel and robust

calcium-boron solid bifunctional catalyst was prepared by sol-gel methods and calcined at 700 °C. The developed catalyst showed a smooth rod-like structure, proper surface area, identical pore size, and concentrated acid-base sites. A 4 wt% of this catalyst at 105 °C and 20:1 methanol to oil molar ratio successfully converted *Jatropha* oil with high FFAs (9.2 mg KOH/g) to biodiesel with a yield of 96% after only 2 h of reaction time. Ca-B exhibited high stability and reusability up to five cycles [96]. A bifunctional solid acid-base catalyst composed of CaO and La₂O₃, prepared by co-precipitation methods, was used to produce biodiesel from *Jatropha* oil with high FFAs. A high biodiesel yield (98.76%) was achieved under transesterification conditions of 160 °C, 3 h, 25 methanol/oil molar ratio, and 3 wt% catalyst. A Ca-La catalyst was used without much deterioration for four consecutive cycles [97]. Graphene Oxide-Alumina composite has been synthesized by a self-limiting hydrogel procedure and used for simultaneous esterification of FFAs and triglycerides in sunflower oil. The developed bifunctional catalysts exhibited superior acidic-basic properties. The composite with 5 wt% GO loading gave, after 10 h, oil conversion of 85.2% by using only 1.0 wt% catalyst to oil at 60 °C and 30:1 methanol to oil molar ratio, in a traditional batch reactor. Moreover, the same composite (GO (5 wt%)-alumina) gave higher oil conversion (97%) to methyl esters in an autoclave reactor at 120 °C. In addition, the same catalyst exhibited tolerance to water content up to 3 wt% and reusability six times [98].

Table 3. Some novel heterogeneous solid acid catalysts for the production of biodiesel from the low-quality feedstocks.

Catalyst	Feedstock	Acid Value (mgKOH/g)		Reaction Time	Biodiesel Yield wt%	Reference
		Initial Value	Final Value			
Fe ₂ O ₃ /KOH	Waste cooking oil	75.92	-	-	97.22	[93]
Fe ₂ O ₃ /CaO	<i>Zanthoxylum bungeanum</i>	41.02	2	4.45	96	[94]
Ca-B	<i>Jatropha</i> oil	9.2	0.5	2	96	[96]
Ca-La	<i>Jatropha</i> oil	16.03–22.85	0.5	3	98.76	[97]
Graphene Oxide—(5 wt%) Alumina	Waste sunflower oil	NA	NA	10	97	[98]
Fly ash (CaO/SO ₃)	Waste frying oil	6.35	NA	9	81.96	[99]

Fly ash that had a high content of CaO (47 wt%) and SO₃ (27 wt%) was used to produce biodiesel from waste frying oil in one step. A high yield of biodiesel (81.96%) was obtained after a 9 h reaction time by using 5 wt% fly ash and a 6:1 molar ratio methanol to oil at 45 °C reaction temperature. SO₃H group catalyzes the esterification of the FFAs, and CaO catalyzes the transesterification of the triglycerides in the raw material, and the two processes occur simultaneously [99].

3.2.1. The Role of Co-Solvent in Heterogeneous Catalyst

One of the significant problems associated with heterogeneous catalysis is the slow reaction rate due to forming a three-phase system, which inhibits the reaction [100]. Using a certain amount of a co-solvent, such as tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and n-hexane, is found to be a practical solution to increase the miscibility of oil and methanol and accordingly accelerate the reaction rate [101,102]. Using n-hexane as a co-solvent in the transesterification of soybean oil by Na/NaOH/ γ -Al₂O₃ base heterogeneous catalyst was adopted with a 5:1 oil n-hexane molar ratio [103]. Lam and Lee [104] demonstrated that biodiesel could be an effective co-solvent to accelerate the transesterification reaction catalyzed by a solid acid catalyst (SO₄²⁻/SnO₂–SiO₂). Fatty acid methyl ester yield was 30% higher than without using a co-solvent in short reaction times. Biodiesel, according to this study, is considered to be a better co-solvent than THF or n-hexane because it is not required to be separated from the product mixture. Gargari

and Sadrameli [105] studied the continuous transesterification of linseed oil in a packed bed reactor using CaO as a heterogeneous catalyst and diethyl ether (DEE) as a co-solvent. DEE plays a crucial role in the high yield of FAMEs as a continuous method is restricted by the absence of an appropriate agitator to disperse the oil and methanol during the reaction. Under optimal conditions of a molar ratio of DEE to methanol of 1.19:1, a molar ratio of methanol to oil of 9.48:1, and a flow rate of 1.37 mL/min, a FAMEs yield of 98.08% was achieved compared to 75.83% in the absence of DEE. Hájek et al. [106] studied the use of methanol together with butanol in the transesterification of rapeseed oil under heterogeneous catalysis. Mg-Fe mixed oxide with a molar ratio Mg/Fe of 3:1 was used as a heterogeneous catalyst. Transesterification was carried out at a constant 24:1 molar ratio of total alcohols to oil with various molar ratios between methanol and butanol, 1 wt% of catalyst to input rapeseed oil and 120 °C reaction temperature. The content of esters in the ester phase reached 97.5 wt% after 4 h. They showed that the addition of butanol caused a higher yield than for methanol or butanol only.

3.2.2. Nano-Heterogeneous Catalysis

Nanotechnology enables scientists to manipulate and produce new materials with specific physicochemical characteristics [107–109]. Hence, a new promising method to overcome the challenge of mass transfer depends on nanotechnology. The tremendous surface area on nanomaterials increases the reaction area and the active center extraordinarily and leads to catalytic reactions, a highly efficient and time-saving process. KF/CaO nano-catalyst (particle size 30–100 nm and average pore size 97 nm) was prepared by the impregnation method and used to convert Chinese tallow oil to biodiesel, a 96.8% yield was obtained at the optimized condition molar ratio 12:1 of alcohol to oil, the catalyst was 4% *w/w* of the oil, the reaction temperature was 65 °C, and reaction time was 2.5 h. The high catalytic ability was attributed to the formation of the new crystal KCaF_3 , as indicated by X-ray diffractometer (XRD) analysis. The active anion CH_3O^- is more easily released in the reaction media by KCaF_3 than CaO is due to the stronger Lewis F^- and stronger Lewis Ca^{2+} . These two species work simultaneously to deprotonate CH_3OH and attract the released CH_3O^- . In addition, the resultant crystal phase renders the KF/CaO nano-catalyst more stable than the CaO catalyst, considering the leaching effect and reusability. The biodiesel yield was over 91% even after 16 cycles. Moreover, the solid base nano-catalyst KF/CaO showed good anti-acid ability and more acidic tolerance than Ca/Mg catalysts [110]. In an attempt to increase the basicity and the catalytic activity of CaO, Degirmenbasi et al. [111] impregnated nanoparticles of CaO on K_2CO_3 at 773 K calcination temperature. A 3 wt% to canola oil of the resultant catalyst (K_2CO_3 (7%)/nano CaO) efficiently enhanced the transesterification of the triglycerides in canola oil, and the biodiesel yield reached $97.67\% \pm 1.7$ in 8 h of reaction time in a liquid batch reactor, at 338 K and a 9:1 methanol to oil molar ratio. The yield of methyl ester was only $60.33\% \pm 2.9$ for pure CaO. The basic degree of the functionalized Nano CaO catalyst did not decrease significantly and maintained its catalytic activity for five consecutive cycles.

Calcium aluminate nano-catalyst was prepared by using the novel method of microwave combustion. Impregnation of 23 wt% KOH to CaO- Al_2O_3 tremendously increased the catalytic activity of this catalyst towards the transesterification of canola oil. A high yield of biodiesel (96.7%) was obtained at the optimal condition of 65 °C, 3.5 wt% catalyst, 12:1 molar ratio of methanol-to-oil, and 4 h reaction time. KOH/calcium aluminate nano-catalyst was efficient for catalyzing the transesterification reaction at least three times.

Nano-magnetic catalysts have high catalytic activity and have the advantages of easy separation and recovery [112]. CaO was encapsulated on a magnetic core of $\gamma\text{Fe}_2\text{O}_3$ based on the sol-gel method using KNO_3 . The obtained magnetic catalyst $\text{CaO}@ \gamma\text{Fe}_2\text{O}_3$ performed high catalytic activity in the transesterification of soybean oil and produced 98.8% biodiesel yield at optimal parameters of catalyst dosage 2.0 wt%, the ratio of methanol and soybean oil 15:1, reaction temperature 70 °C, and reaction time 3 h. Moreover, magnetic catalyst $\text{CaO}@ \gamma\text{Fe}_2\text{O}_3$ showed high resistance to FFAs compared to pure CaO and high

reusability (4 times) [113]. A nano-magnetic solid base catalyst KF/CaO-Fe₃O₄ was synthesized by a facile impregnation method and used in the transesterification of Chinese tallow oil with over 95% biodiesel yield. Due to the magnetic separation, the catalyst recovery was more than 90%, and the catalyst was able to be reused up to 14 times without much deterioration in its activity [114]. Table 4 summarizes some novel nano-heterogeneous-based catalysts for biodiesel production.

Table 4. Some novel nano-heterogeneous-based catalysts for biodiesel production.

Catalyst	Method of Preparation	FeedStock (oil)	Reaction Parameters				Conversion or Yield wt%	Reusability	Ref.
			Catalyst Loading wt%	Methanol to Oil Molar Ratio	Temperature °C	Time h			
KF/CaO	Impregnation	tallow seed oil	4	12:1	65	2.5	96.8	16	[110]
(K ₂ CO ₃ (7%)/nano CaO	Impregnation	canola oil	3	9:1	115	8	97.67% ± 1.7	5	[111]
KOH (23 wt%)/Calcium aluminate nano-catalyst	Microwave combustion/impregnation	96.7%	3.5	12:1	65	4	96.7%	3	[112]
CaO@γ-Fe ₂ O ₃	CaO@γ-Fe ₂ O ₃ /encapsulation	Soybean oil	2	15:1	70	3	98.8	4	[113]
KF/CaO-Fe ₃ O ₄	facile impregnation	Stillingia oil	4	12:1	65	3	95	14	[114]
Fe ₃ O ₄ @SiO ₂ -SO ₃ H	Step-wise co-precipitation	Crude Jatropha oil	8	9:1	80	3.5	98	10	[115]
IL-Fe ₃ O ₄ @SiO ₂	Solvothermal method/Stöber method	Oleic acid	10.8	6:1	110	4	92.9	8	[116]
Polymeric acidic ILs/Fe ₃ O ₄ @SiO ₂	Solgel/acile chemical co-precipitation	Soybean with high FFAs	8	30:1	130	8	94.2	5	[117]

The catalytic activity and reusability of the solid acid catalyst can be increased substantially by loading it onto a magnetized support. Silica was coated on a magnetite Fe₃O₄ nanoparticle and functionalized by sulfonic acid using the step-wise co-precipitation method. The obtained Fe₃O₄@SiO₂-SO₃H nanoparticle catalyst was used for simultaneous esterification of free FFAs and transesterification of triglycerides in crude Jatropha oil that has a high initial acid value (AV) of 13.2 mg KOH g⁻¹. The catalyst showed 98 ± 1% conversion using the optimized reaction conditions of methanol:oil molar ratio of 9:1, 8 wt% catalyst loading, 80 °C, and 3.5 h. Magnetization of the catalyst facilitated the recovery and the reusability of the catalyst up to 10 cycles [115].

Ionic liquid (IL), which is emerging as a green catalyst for biodiesel production, can be significantly enhanced by loading it on magnetic nanoparticles [72]. A nano-magnetic particle Fe₃O₄ was prepared and coated by silica by Wu et al. [116]. The developed product, Fe₃O₄@SiO₂, was further functionalized using the dual Brønsted acidic ionic liquid [SO₃H-(CH₂)₃-HIM][HSO₄]. 3-chloropropyltrimethoxysilane was used as a linker. The performance of IL-Fe₃O₄@SiO₂ in the ethanolysis of oleic acid was investigated. High conversion (92.9%) of oleic acid to biodiesel was reached under suitable reaction conditions reaction time (4 h), reaction temperature (110 °C), catalyst dosage (10.8 wt%), and the molar ratio of ethanol to oleic acid (6:1). The catalyst was easily recovered and reused several times and retained its activity for eight cycles [116]. In a recent study, Xie et al. [117] developed a novel catalyst by functionalizing Fe₃O₄@SiO₂ magnetic nanoparticle using Polymeric IL to impart the composite support strong-acidic surface. They used, for this purpose, 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate as a monomer and 1,4-butanediyl-3,3'-bis-1-vinylimidazolium hydrogen sulfate as a cross-linker agent. They studied the efficiency of this solid acidic catalyst for simultaneous esterification and transesterification reactions of low-quality feedstock. This study proved that the combination of polymeric ILs and a magnetic porous support is very effective for utilization of low feedstock with

high free fatty acid for biodiesel production in one step as the developed polymeric acidic ILs/ $\text{Fe}_3\text{O}_4@\text{SiO}_2$ showed high tolerance to both FFAs and water. A 94.2% conversion of simulated low-quality soybean was achieved at optimized conditions (methanol/oil molar ratio, 30:1; reaction time, 8 h; reaction temperature, 130 °C; catalyst dosage, 8 wt%). Moreover, the solid catalyst was simply reused five times without much loss of its catalytic activity.

3.3. Natural/Waste Based Heterogeneous Catalysis

Although various heterogeneous catalysts have been reported in the literature for biodiesel production, most of them are expensive or complicated to prepare. Thus, their industrial application is limited. Waste from industrial operations and the environment can help create a low-cost solid base catalyst that can encourage a sustainable and environmentally friendly approach to biodiesel synthesis [118,119]. In this field, many researchers are trying to develop low-cost and more natural heterogeneous catalysts. The utilization of industrial wastes for catalyst synthesis is considered adequate disposal and simultaneously reduces the costs of catalyst production [120]. Waste material with a wide source, low price, favorable biodegradability, and is environmentally friendly is suitable for preparing the catalyst [121].

3.3.1. Solid Basic Catalysis

Many researchers have proved industrial waste shells to be a cheap natural source of CaO for application as a solid base catalyst with high effective cost instead of high-cost analytical reagent-grade chemicals [122]. Table 5 shows the optimized condition for biodiesel production by solid-base catalysts derived from industrial waste shells. The derived catalysts were prepared by calcination at temperatures in the range of 700 to 1000 °C for a period range from 2 to 4 h. A combination of fly ash and the waste eggshell is considered as a novel route to produce low-cost supported-base catalysts with superior catalytic activity and reusability [122]. Waste shells with a low content of CaO activity could be increased by loading them on an active base. The KI impregnated shrimp shell-derived catalyst [121] was prepared by a novel tri-step synthetic strategy first, carbonization at 450 °C, loading KI of 25 wt%, and activation at 250 °C. The resultant active sites on the surface of the derived catalyst came from incompletely carbonized shrimp shells with KI during the activation process.

Table 5. Biodiesel production by solid base catalysts derived from industrial wastes.

Feedstock	Derived Catalyst	Active Phase	Loading Catalyst wt% of Oil	Methanol to Oil Molar Ratio	Temperature °C	Reaction Time h	Biodiesel Yield wt%	Catalyst Reusability	Ref.
Soybean oil	Clined waste eggshell	CaO	3	9:1	65	3	95	17	[123]
Soybean oil	Calcined waste Rohu fish (Labeo rohita)	β -tri-calcium phosphate	1.01	6.27:1	70	5	97.73	6	[124]
Rapeseed oil	KI impregnated shrimp shell	$\text{Ca}_3(\text{PO}_4)_2$,KI	2.5	9:1	65	3	89.1	3	[121]
Soybean oil	Fly ash supported CaO (waste eggshell-derived)	CaO	1.0	6.9:1	70	5	96.97	18	[122]
Palm oil	Calcined waste animal bones	hydroxyapatite	20	18:1	65	4	96.78	5	[125]
Soybean	Calcined waste mussel shell	CaO	5	12:1	70	1.5	>90	7	[126]
Waste frying soybean oil	Calcined snail shell	CaO	3.0–3.5	8.45:1	60	7	87.28	-	[127]

Table 5. Cont.

Feedstock	Derived Catalyst	Active Phase	Loading Catalyst wt% of Oil	Methanol to Oil Molar Ratio	Temperature °C	Reaction Time h	Biodiesel Yield wt%	Catalyst Reusability	Ref.
Palm oil	Calcined waste capiz (<i>Amusium cristatum</i>) shell	CaO	3	8:1	60	6	93	3	[128]
Soybean oil	Waste scale	CaO–MgO–Fe ₂ O ₃ –Al ₂ O ₃ –SiO ₂	1	12:1	70	5	93	-	[129]
Waste cooking oil	Waste chicken eggshells	Eggshell–CaO _{C-H-D} (calcination-hydration-dehydration) Eggshell–CaDG (calcium diglyceroxide)	1.5–3	10:1–12:1	60–65	50–90 min	93.10–96.07	-	[130]
Soybean oil	Calcined oyster shell	CaO	25	6:1	60	5	73.8	-	[131]
Jatropha oil	<i>Musa paradisiaca</i> trunk	Carbonates and oxides of alkali and alkaline earth metals	5	9:1	65	9 min	97.65	3	[132]
Leather tanning waste	Crab shell	CaO	3.87	12:1 (ethanol:oil)	60	3.58	98.7	4	[133]

3.3.2. Solid Acidic Catalysis

Inorganic-oxide acids catalysts, such as zeolite, Niobic acid, silica-supported zirconium sulfate, along with acidic acid exchange resins, such as Amberlyst-15 and Nafion-NR50, suffer from some common problems: low acid site concentration, micro-porosity and hydrophilic character of catalysts surface sites, leaching, and high cost. These problems can be avoided by sulfonating incompletely carbonized natural organic materials, such as sugar, starch, cellulose, and biomass wastes. Incomplete carbonization converts these materials to irregular aromatic carbon structures with large pores that trap the acidic groups (–SO₃H) by sulfonation. The resultant solid acid catalyst is highly stable due to the electron drawing effect caused by the aromatic groups. In addition, this derived catalyst is tolerant to the presence of water in the feeds stock due to its hydrophobic characteristics [123–125]. Thus, this method is considered to be a novel method to prepare high-performance carbon-based solid acid catalysts cheaply from naturally occurring molecules. Many researchers proved that carbon-based solid acid catalysts derived from industrial waste biomass are economical, eco-friendly, and promising sustainable catalysts to produce biodiesel from low-cost feeds stock with high FFAs or water. Deeba et al. [134] studied the transesterification of non-edible waste cooking oil using yeast residue-based solid acid (YSA) catalyst. YSA was produced from waste yeast residue via sulfonation. They showed that at 4 wt% catalyst concentration and 10:1 methanol to oil molar ratio, the fatty acid methyl ester (FAME) yield of waste cooking oil was 96.2 wt% at 60 °C and 94.8 wt% for yeast oil at 70 °C. Bagasse (waste biomass from a sugar refinery) was found by Lou et al. [127] to be a novel carbon-based solid acid catalyst. The optimized catalyst was produced under optimum carbonization at 648 K for 0.5 h and sulfonation at 423 K. The produced catalyst efficiently converted waste cooking oil with 38.6 wt% FFAs into biodiesel and afforded a high yield of about 93.8% within 12 h. The derived catalyst could be reusable for at least eight cycles without much deterioration in its catalytic activity. Glycerol, a by-product from biodiesel refineries, was used by Song et al. [135] to prepare carbon-based solid catalysts through in situ partial carbonization and sulfonation at 180 °C for 0.5 h. The derived catalyst showed high catalytic activity and recycling performance in the esterification of oleic acid and transesterification of triolein compared to commonly used Amberlyst-15. Therefore, according to this study, it is suggested that carbon-based solid acid catalyst is a sustainable route for the utilization of glycerol and the production of biodiesel. Shu et al. [124] had prepared a carbon-based solid acid catalyst by sulfonation of incompletely carbonized vegetable oil asphalt (a solid residue from biodiesel refinery)

and used it to catalyze the transesterification of cotton seed oil. Depending on the TGA analysis, the catalyst showed high thermal stability at 270 °C. Therefore, it was possible to obtain high biodiesel yield from the cotton seed oil (89.93%) at a shorter reaction time (3 h) and low methanol to oil mass ratio (18:1) when the reaction was processed at 260 °C. Such results, practically, could not be achieved with conventional homogenous sulfuric acid. Pau et al. [126] had successfully prepared carbon-based solid acid from kraft lignin (waste biomass from paper mills) via chemical activation by phosphoric acid, pyrolysis, and sulfuric acid. The resultant novel catalyst was used for biodiesel production from non-pretreated *Jatropha* oil with a high acid value (12.7 mg KOH/g) in a single-step process, 96.3% biodiesel yield was obtained. The catalyst could be used three times with little deactivation under optimized conditions.

Farabi et al. [136] presented a novel approach to cut down the cost of biodiesel production based on utilizing biomass wastes for both catalyst synthesis and biodiesel production. They used a palm kernel shell to prepare a carbon-based catalyst. The active sites of SO₃H were trapped on the surface of the carbonaceous catalyst by using chlorosulfonic acid (ClSO₃H) at 70 °C for 4. The produced sulfonated palm kernel shell catalyst (PKS-SO₃H) exhibited high catalytic activity to convert palm fatty acid distillate (a by-product in palm oil refining) to biodiesel. High biodiesel yield (95%) and FFAs conversion (97%) were achieved under optimized parameters, catalyst loading of 4 wt%, methanol-to-palm fatty acid distillate molar ratio of 15:1, reaction temperature of 65 °C, and the reaction time was 1 h. The prepared catalyst maintained its catalytic activity for up to four consecutive cycles. To facilitate the separation of PKS (PKS-SO₃H) catalyst from the reaction media, Quah et al. [137] used a magnetized form of PKS-SO₃H by sulfonating a composite of biochar derived from PKS and ferrite Fe₃O₄. The maximum biodiesel yield of 90.2% was obtained under these optimized temperature values at 65.07 °C, 102 min, 3.66 wt% of the catalyst loading, and the methanol/oil ratio of 13:1. The catalyst performance was acceptable during the first four cycles. The authors proposed coating the catalyst with an extra layer to reduce the leaching of Fe. Table 6 summarizes the studies on carbon-based solid acid catalysts for biodiesel production.

Table 6. Carbon-based solid acid catalysts for biodiesel production.

Carbonaceous Substrate	Feedstock	Reaction Parameter				Biodiesel Yield wt%	Reusability	Ref.
		Catalyst Loading wt%	Methanol to Oil Molar Ratio	Temperature °C	Time h			
Yeast residue	Waste cooking oil	4	10:1	60	8	96.2	4	[134]
Bagasse	Waste cooking oil 38.6 wt% FFAs	4	-	-	12	93.8	8	[127]
Glycerol	Oleic acid/triolein	10	60:1	80	10	99	5	[135]
Asphalt	cotton seed oil	0.2	18:1	260	3	89.93	3	[124]
Kraft lignin	<i>Jatropha</i> oil	5	12:1	80	5	96.3	3	[126]
Palm kernel shell	palm fatty acid distillate	4	15:1	65	1	95	4	[136]
Magnetized sulfonated Palm kernel shell	Waste cooking oil	3.66	13:1	65	1.42	90.2	4	[137]

4. Enzymatic Catalysis

The chemical catalysis process for producing biodiesel consumes energy and creates undesirable by-products, such as soaps and polymeric pigments, which impede product separation from glycerol and di- and monoacylglycerols, which can be eliminated using enzymatic catalysis [138]. Biodiesel production by enzymatic catalysis has emerged as the most promising new technology [139–141]. This is evidenced by the intensive publications on enzymatic transesterification of lipids (oils/fats) in the last two decades [142–146]. Lipases, which are glycerol ester hydrolases (EC 3.1. 1. 3.) [131], catalyze the hydrolysis of different esters. However, their synthetic activity is enhanced in low water mediums by catalyzing the reversible esterification and transesterification reactions. Microorganisms

present as a versatile source of lipases in nature [147]. Lipases can simultaneously catalyze the esterification and transesterification of FFAs and triglycerides present in the low-quality feedstock with no or less downstream operation, fewer processes, lower alcohol to oil ratio, easy separation of products with high purity at mild reaction conditions (low temperature and pressure). Hence, besides low energy consumption, enzymatic catalysis has numerous advantages over conventional chemical catalysis [148–151]. Moreover, the formation of undesired products is eliminated due to lipase's high specificity and selectivity towards the ester bond. The additional advantages of lipases are owed to their high thermo-stability at a wide range of pHs, easy handling, and the possibility of reusing and operating them on a continuous bed reactor when they are immobilized on suitable solid support [152,153]. The efficiency of lipase as a biocatalyst can be improved by protein engineering [154]. From an environmental point of view, lipases are considered to have major importance in natural ecosystems since they are involved in carbon storage in soil or litter. Therefore, enzymatic transesterification offers an environmentally more attractive option to conventional processes [149,155].

Although enzymatic catalysis seems to be an excellent alternative to conventional homogeneous-alkali catalysis, it is not industrially implemented. Only a small pilot plant of 20,000 tons/year is being tested in China [149]. The high cost of an enzyme, due to the complicated purification, recovery, and immobilization steps required, is the main barrier to its industrial application. In addition, the low rate of reaction, due to the deactivation of lipase, caused by the short-chain alcohol (co-substrate) and glycerol (by-product), these systems, economically, are not attractive for industrial-scale production of biodiesel [156,157].

In the enzymatic catalyzed-transesterification presence of FFAs and water in the feedstock effect the conversion of triglycerides to biodiesel products positively. Water assists in maintaining enzyme activity. While FFAs reduce the inhibition of lipase [158,159]. However, the excess of water resulting from the esterification reaction would reduce the biodiesel yield due to the hydrolysis reaction. Therefore, the effect of water should be maintained experimentally to aid biodiesel production at a large scale [160,161]. Moreover, the lipase activity is inhibited by the presence of phospholipids in the feedstock. Hence, the type of impurities of the feedstock is of great importance in lipase-catalyzed-transesterification [162].

4.1. Screening of Lipases

Lipases are classified into two broad categories: extracellular lipases and intercellular lipases. Extracellular lipases are extracted from the live-producing microorganism broth and then purified. The major microorganism producers for extracellular lipases are *Mucor miehei*, *Rhizopus oryzae*, *Candida antarctica*, and *Pseudomonas cepacia*. Intercellular lipase remains either inside the cell or in the cell-producing wall. In both cases, extracellular lipases and intercellular lipases are immobilized because pure lipase has shallow catalytic activity. However, free lipases are used to investigate their sensitivity towards the alcoholysis reaction [138]. Soumanou and Bornscheuer [163], in their study on the effects of different variables on the enzymatic alcoholysis reaction of sunflower oil, had screened six different crude microbial lipases (Table 7). They used triolein for methanolysis in n-hexane as an organic solvent. From the initial rate of alcoholysis reaction, only three enzymes showed considerable catalytic activity. *P. fluorescens* lipase was chosen for further investigation depending on the highest conversion after 24 h.

Table 7. Screening commercial crude lipases for alcoholysis of pure triolein with methanol in n-hexane (3:1 triolein to methanol ratio in 2 mL n-hexane, 10% lipase (*w/w* triolein), and 40 °C).

Lipase	Commercial Code	Initial Rate (μmol/mg/min)	Conversion (%)	
			5 h	24 h
<i>A. niger</i>	A 6	0	<0.01	<0.1
<i>C. rugosa</i>	AY 30	0	<0.4	<1.1
<i>P. cepacia</i>	PS	0.4	4.5	23.2
<i>P. fluorescens</i>	AK	1.3	17.0	48.0
<i>P. camembertii</i>	G 50	0.2	0.3	4.9
<i>R. oryzae</i>	F-AP 15	0	0.2	0.8

4.2. Treatments of Lipase Deactivation

The effect of methanol on lipase activity was investigated thoroughly by Shimada et al. [164]. They found that, by using immobilized *C. antarctica*, methanolysis of vegetable oil decreased significantly with the addition of methanol > 1/2 molar equivalent of methanol for the stoichiometric amount. To overcome the poisonous effect of methanol, they tried adding methanol step-wise in three successive additions of 1/3 molar equivalents of methanol. They achieved 98.4% oil conversion to its corresponding methyl esters after a total reaction time of 48 h. The catalyst was able to be reused with ester conversion of more than 95%, even after 50 cycles (100 days). Thus, step-wise addition of methanol could reduce the cost, especially if it is employed in a continuous fixed bed reactor. Chen and Wu [165] studied the deactivation of the enzyme by linear and branched alcohols. They used immobilized *C. antarctica* for the transesterification of soybean oil. They revealed that the enzyme was inhibited by linear alcohols more than the branched alcohols, which were more soluble in the triglyceride. Moreover, the degree of deactivation was inversely proportional to the length of the carbon chain of the linear alcohol. It was concluded that the deactivation of the enzyme was caused by the immiscibility of the short alcohol (methanol or ethanol) in the triglycerides, besides the adsorption of the alcohol droplet on the immobilized enzyme. Isopropanol, soybean oil, 2-propanol, and tert-butanol were used for washing the deactivated enzyme. The completely deactivated immobilized *C. antractia* had restored 56% and 75% of its original activity when washed with 2- butanol and tert-butanol, respectively. Meanwhile, immersion pretreatment by these alcohols could increase the activity of the enzyme tenfold compared to an un-pretreated enzyme. Such alcohols have the ability to dissolve the adsorbed methanol droplets around the enzyme. Therefore, Chen and Wu proposed the regeneration of lipase by washing it with C3 or C4 alcohol. This method was considered to be more practical compared to the step-wise addition of methanol, which needs high precision to maintain methanol at a low concentration, also the low rate of the reaction. Lu et al. [166] found a dissimilar result when *Candida* sp99-125 immobilized on a textile membrane was treated by short-chain alcohol from n-propyl alcohol to isobutyl alcohol. It seems that the pretreatment method depends on the origins of the lipase and the type of its immobilizing material.

The liberated glycerol, in a free solvent medium, inhibits the biocatalyst by blocking its entry pores [167]. The inhibitory effect of glycerol is significant, particularly in continuous operation [168,169]. In a systemic study, Xu et al. [170] investigated glycerol's inhibitory mechanism in ethanolysis of rapeseed oil. They concluded that the type of immobilizing support is the factor that influences the adsorption of the glycerol on the surface of the enzyme carrier. Supports for lipase immobilizing should not adsorb glycerol. They proved that supports, such as silica and polystyrene, which have a great affinity to glycerol, are not appropriate for immobilizing lipase. While supports with no affinity to adsorb glycerol, such as polymethyl methacrylate or polypropylene, are more convenient. Silica gel was found, among other solid materials, to be the most effective adsorbent to remove glycerol from the reaction media. Over 90% biodiesel yield was achieved in transesterification

reaction catalyzed by immobilized *Mucor Meiheini* in the presence of 1.25 silica weight equivalents to glycerol produced, regardless of the type of the oil or alcohol [171]. Adsorptive purification in a continuous process using ion exchange resin was satisfactory to maintain the content glycerol at a low concentration for more than 140-bed volumes and repeated after regeneration of the resin by using methanol [168].

Lately, there has been a trend to carry out enzymatic alcoholysis of triglycerides in an organic solvent. The reaction medium (oil, methanol, and glycerol) is partially soluble in hydrophilic solvents (e.g., acetone, acetonitrile) or in hydrophobic solvents (hexane, isooctane, and heptane). However, tert-butanol, a moderately hydrophilic solvent, can dissolve oil, methanol, and glycerol. Therefore, tert-butanol was considered a novel organic solvent to simultaneously eliminate the inhibitory effect of glycerol and methanol. In addition, lipases do not act on tertiary alcohol [172,173]. Among different organic solvents (hydrophilic, hydrophobic), tert-butanol was found to be the most suitable solvent in the methanolysis of cooking-waste palm oil. An 88% FAME yield was achieved under optimal conditions (methanol/oil molar ratio 4:1, 4% Novozyme 435 based on oil weight, 40 °C reaction temperature, 200 rpm, and 12 h reaction time) [172]. Li et al. [174] reported that a combined mixture of Lipozyme TL IM and Novozyme 435 maintained its catalytic activity, even after 200 cycles, in the methanolysis of rapeseed oil in the presence of tert-butanol as a reaction medium. A 95% biodiesel yield was achieved under the optimum conditions (tert-butanol/oil volume ratio 1:1, methanol/oil molar ratio 4:1, 3% Lipozyme TL IM, 1% Novozyme 435 based on the oil weight, 35 °C reaction temperature, 130 rpm, and 12 h reaction time).

However, flammable and volatile organic solvents diminish the green characteristics of bio-catalysis. ILs are emerging as a novel replacement for volatile organic solvents. ILs are organic salts remaining as a liquid at an ambient temperature. They are green solvents due to their undetectable vapor pressure. Their use can enhance the activity, selectivity, and stability of the enzyme. Moreover, it is possible to recycle both the biocatalyst and IL [163,175–177]. Many works demonstrate that ILs are superior solvents for lipase transesterification of triglycerides [178–180]. The high cost of ILs is the main barrier to their use in biodiesel production commercially [175]. Exploring friendly, inexpensive solvents for lipase-catalyzed biodiesel production is in progress. Solvent systems, such as a combination of supercritical fluids and ILs [181,182], choline-based eutectic solvents [183,184], and diether glycol (Glymes) [175], are being tried.

The negative effect of both methanol and glycerol could be avoided in free solvent systems by developing alternative acyl acceptors. In this field, methyl acetate presents as a novel acyl acceptor in lipase-catalyzed biodiesel production. Du et al. [185] investigated transesterification of soybean oil in the presence of Novozyme 435 by using different acyl acceptors. Repeatedly significant (100 cycles) lipase was found with methyl acetate. High biodiesel yields, 92%, could be obtained, from refined oil, under optimum conditions (methyl acetate/oil molar ratio 12:1, 30% Novozyme 435 based on oil weight, 40 °C, 150 rpm, and 14 h). The high enzyme consumption was attributed to the low reaction rate of methyl acetate. However, the high reusability of the lipase could minimize the impact of this negative effect. In addition, the dilution effect caused by the high methyl acetate/oil molar ratio could reduce the inhibitory effect of lipids, as indicated by an equal biodiesel yield produced from crude and refined soybean oils. Moreover, the production cost could be reduced by using acetyl acyl glycerol, a by-product, which has a higher value than glycerol. Ognjanovic et al. [186] demonstrated that methyl acetate is a promising acyl acceptor to improve the stability of the immobilized lipase on an industrial production scale. Eight consecutive, 8–10 h uses, with residual activity $93.6 \pm 3.75\%$ was achieved in a packed reactor [186].

Talukder et al. [187] tried to minimize the methanol deactivation of lipase by developing a two-step process, free of glycerol, to convert crude palm oil (CPO) to biodiesel. In the first step, CPO was hydrolyzed entirely to fatty acids by *Candida rugosa* under optimal conditions (buffer to CPO 1:1 (v/v), buffer pH 7.0, lipase 0.1 wt% to CPO, isooctane to

CPO 1:1 (*v/v*), temperature 30 °C, reaction time 4 h, and shaking speed 250 rpm). The second step was the esterification of the resultant fatty acids catalyzed by Novozyme 435 lipase in an excess amount of methanol. The high biodiesel yield of 98% was obtained when the reactions conditions were maintained at methanol/fatty acids molar ratio 1.2:1, 0.04 g Novozyme 435, temperature 40 °C, reaction time 2 h, and shaking speed 250 rpm. *C. rugosa* and Novozyme 435 lipases showed considerable repeated usage, 10 and 50 cycles, respectively. The significance of the developed two-step process is its ability to produce biodiesel from low feedstock with high FFAs or water, compared to single-step Novozyme 435 catalyzed methanolysis in *t*-butanol or step-wise addition of methanol in free solvent systems. Meng et al. [188] aimed to make the enzymatic two-step production of biodiesel more cost-effective and independent from petroleum sources. They used a comparatively cheap kind of lipase (*Yarrowia lipolytica*) and ethanol as the substrate to convert soybean oil to biodiesel. The hydrolysis of the acid oil was firstly carried out by the *Yarrowia lipolytica* crude broth lipase. In the second step, the fatty acids are esterified by ethanol in the presence of the immobilized *Yarrowia lipolytica* on fabric membrane. The degree of esterification was maintained over 82% with 25 reuses, each with a 3 h reaction time.

4.3. Immobilization of Lipases

The cost of the lipase enzyme is the main obstacle for the commercial production of biodiesel by enzymatic alcoholysis of triglycerides. The cost-effectiveness of immobilized lipases depends on support materials and immobilization methods. Support materials should be low cost and provide an adequate large surface and the least diffusion limitation in the transport of substance and product for the enzymatic reaction [189]. There are several methods for lipase immobilization, including physical adsorption onto a macro porous support [189–192], covalent bonding to a solid support [189,193–195], physical entrapment with a polymer matrix support [196–199], encapsulation [200,201], and cross-linking [160,202–204].

Lipase-catalyzed biodiesel production could be more cost-effective and environmentally friendly by using natural biopolymer as a matrix in the immobilization of lipase [200]. A novel method was developed by Shu et al. [205] to immobilize *Candida rugosa* lipase onto cotton cloth with the aid of polyethyleneimine and glutaraldehyde cross-linking processes. The enzymatic performance of the obtained immobilized lipase was examined in the ethanolysis of butyric acid. A conversion yield of 91.2% to ethyl butyrate was obtained at 25 °C. The immobilized lipase retained half of its initial activity after 12 repeated cycles, with a half-life of about 300 h. Microbial lipase from *Thermomyces launginosus* was immobilized on olive pomace, the industrial by-product of olive oil production, by Yücel [206]. The obtained immobilized lipase was influential in the production of biodiesel from olive oil by a three-step addition of methanol. A maximum biodiesel yield of 93% was achieved, under optimized conditions, at 25 °C in a 24 h reaction. The immobilized lipase retained its activity during ten repeated batch reactions. Plant fiber from *Cyperus papyrus* L. was used by Chauchinda et al. [207] to immobilize *Candida rugosa* for biodiesel synthesis from palm oil. Immobilization of the lipase by physical adsorption in heptanes gave satisfactory results in both transesterification and hydrolysis-esterification routes for methanolysis and ethanolysis of palm oil.

Compared to a free and immobilized enzyme, microbial whole-cells containing intracellular lipases immobilized onto biomass support particles (BSPs) are more effective in improving cost-efficiency. Immobilization can be achieved spontaneously during batch cultivation, and no purification of lipase is necessary [208]. A comparative study of immobilized-whole cell and commercial lipases was carried out by Tamalampui et al. [209] in the alcoholysis of *Jatropha* oil. They reported that *Rhizopus oryzae* immobilized onto BSPs made of reticulated polyurethane foams could catalyze the methanolysis of *Jatropha* oil more effectively than Novozyme 435. The maximum methyl ester content in the reaction mixture was 80 wt% and 76 wt% after 60 h and 90 h, respectively.

5. Transesterification by Ultrasonic and Microwave Irradiation

5.1. Ultrasonic Irradiation Assisted Catalysis

Molecules acquire unique physical and chemical properties when exposed to ultrasonic radiation. Ultrasonic cavitation has emerged as a new technique for mass transfer in chemical processes. The production of biodiesel by the ultrasonic irradiation method is found to have the advantages of reducing processing time, amount of catalyst and alcohol required, separation time, and reaction temperature [210–213]. Investigations on the effect of ultrasound radiation on the transesterification of triglycerides to develop sonochemical reactors for biodiesel production are in progress. Teixeira et al. [214] investigated both conventional mechanical stirring and ultrasonic irradiation of the alkali-catalyzed transesterification of beef tallow. Under similar reaction conditions, ultrasonic treatment (400 W and 20 kHz) could achieve similar FAME in a shorter reaction time (70 s) compared to 1 h in the conventional process. In the ethanolysis of coconut oil assisted by ultrasonication [215], 98.3 wt% FAEE yield was obtained under optimal reaction conditions (oil /ethanol molar ratio 1:6, 0.75 wt% KOH to oil, and a reaction time of 7 min), while 94 wt% FAME yield was achieved by conventional stirring at an oil/methanol molar ratio of 1:8, 1 wt% KOH to oil, 60 °C and a reaction time of 120 min). It is evident that ultrasonic irradiation could reduce, considerably, consumption of alcohol, amount of catalyst, and time. Hingue et al. [216] illustrated that transesterification of waste cooking oil in sonochemical reactors is a promising new route for biodiesel synthesis. Ultrasound power 200 W treatment for 40 min led to an 89.5% conversion to FAME at 1:6 oil/methanol molar ratio, 1 wt% KOH to oil, and a 45 °C reaction temperature. Compared to conventional stirring (54 blade turbine with diameter 1.5 cm operating at 1000 rpm), only 57% conversion was achieved under optimal conditions. Deng et al. [217] demonstrated that the two-step process, acid esterification and base-transesterification, coupled with ultrasonic irradiation, is an efficient route for biodiesel production with high yields and stability from crude oils with high FFA. A 96.4% biodiesel yield with only 0.32 mg KOH/mg acid value was achieved for *Jatropha curcas seed* oil with 10.45 mg KOH/mg, by the new two-step process, in an ultrasonic reactor at 210 W and 60 °C. The reaction time required for the ultrasonic-assisted two-step process was half of the time required for the conventional two-step process.

Ultrasonic radiation is effective in heterogeneous catalysis as well as in homogenous catalysis. Investigations on transesterification of *Jatropha curcas* oil by mesoporous solid base catalyst (Na/SiO₂) were carried out by Kumar et al. [215]. Maximum biodiesel yield, more than 98%, was obtained under optimal reaction conditions (1:9 oil to methanol molar ratio, catalyst percentage 3 wt% to oil, ultrasonic wave amplitude 50%, ultrasonic irradiation pulse 0.7 cycle each second, and processing time 15 min compared to 3–6 h in conventional methods). The solid catalyst could be reused successfully for three cycles after appropriate thermal treatment. These results indicate that ultrasonic treatment could increase the efficiency of the heterogeneous catalyst. Moreover, optimum conversion can be attained at a lower amount of the catalyst.

Ultrasound-assisted lipase-catalyzed transesterification of triglycerides has also emerged as one of the latest trends in the research efforts concerning the application of ultrasound irradiation for biodiesel production. Batistella et al. [218] studied the influence of ultrasound irradiation on lipase-catalyzed ethanolysis of soybean oil, without agitation, in the presence of hexane as a solvent. They were able to obtain high biodiesel yield (≈90 wt%) at reaction temperature 60 °C in a relatively short reaction time, 4 h, by using Lipozyme RM IM as a catalyst. The catalyst was reused successfully for two cycles without significant decay in its activity. The effect of ultrasound irradiation on lipase-catalyzed transesterification in the presence of different solvents and in the absence of solvent, as well as the behavior of the lipase in the ultrasound systems, are hot topics to be investigated by researchers.

5.2. Microwave Irradiation Assisted Catalysis

Microwave radiation can change the magnetic field of weak polar molecules, such as alcohols. As a result, the rotational movement of the molecules is accelerated, and heat is generated. In chemical reactions, microwave irradiation leads to more effective heat transfer than conventional heating in a much shorter reaction time. The major disadvantage or restriction of microwave heating is its shallow penetration depth. The microwave has a few millimeters of penetration depth, indicating a fast reduction in microwave intensity in a reaction setting. The non-thermal effect associated with microwave heating is also debatable. Another difficult issue is choosing suitable building materials because microwave susceptibility in some materials, sparks in metal, and high-temperature zones at welded or sharp edges may all be lethal.

Microwave irradiation is one of the most effective methods to obtain high biodiesel yields in a concise reaction time [219–221]. Azcan and Danisman [222] studied the alkali-catalyzed transesterification of cotton seed oil to compare microwave heating to conventional heating techniques. Three parametric conditions were varied (catalyst amount, temperature, and reaction time). The optimum reaction parameters were found to be 1.5% (*w/w*) catalyst to oil, 333 K temperature, and a seven-minute reaction time to obtain biodiesel with high yield and purity. Similar results were achieved by conventional heating but in a 30 min reaction time. Perin et al. [223] demonstrated that microwave heating effectively increases the rate of heat transfer in the reaction medium between alcohol and oil in the presence of a solid basic or acidic catalyst and in homogenous catalysis. They used acidic silica gel ($\text{SiO}_2/50\% \text{H}_2\text{SO}_4$) and basic alumina ($\text{Al}_2\text{O}_3/50\% \text{KOH}$) to transesterify castor oil in the presence of methanol or ethanol. The reaction conditions were adjusted to a 1:6 oil to alcohol molar ratio, 10 wt% catalysts to oil, and a 60 °C reaction temperature. Conventional heating resulted in high yields after 1 and 3 h for acidic and basic catalysis, respectively, while microwave heating afforded similar biodiesel yields after 30 and 5 min for acidic catalysis and basic catalysis.

Combining ultrasound mixing with microwave heating in transesterification of triglycerides increases the mass transfer and heat transfer in the reaction media simultaneously. Therefore, a discrete two-step process was proposed by Hiaso et al. [224] to attain high biodiesel yield and conversion from soybean oil in the presence of methanol and alkaline catalyst. The authors aimed to obtain the optimal ultrasonic mixing and closed microwave irradiation. In the first step, the reaction of reagents was assisted by ultrasound mixing. In the second step, the reaction of reagents was assisted by closed microwave irradiation. A high rate of conversion (97.7%) was achieved by 1 min ultrasound mixing followed by 2 min closed microwave irradiation at optimal conditions: methanol to oil molar ratio, 6:1; the amount of catalyst, 1.0 wt%; and reaction temperature of 333 K. It is worth mentioning that assisting the reaction in one step within a short time, by ultrasound mixing without microwave irradiation or by microwave irradiation without ultrasound mixing, led to very poor methyl ester conversion. A comparative study of the sequential effect of microwave and ultrasound compared to individual approaches of microwave and ultrasound was carried out by Gole and Gogate [225] to produce biodiesel from high acid value Nagchampa oil. By an individual approach of ultrasound, the initial acid value of the oil was reduced from 18.9 to 1.7 mg KOH/g of oil by the optimized condition: methanol to oil molar ratio 1:4, 3 wt% H_2SO_4 to oil, and 60 min reaction time.

In contrast, the individual microwave approach required a 1:3 methanol to oil molar ratio, 3 wt% H_2SO_4 to oil, and a 25 min reaction time to achieve the same result. However, the sequential approach of microwave followed by ultrasound, to reduce the acid value in the range, required a considerably smaller methanol to oil ratio, amount of catalyst, and reaction time (1:2 M, 2 wt%, and 15 min), respectively. For the transesterification reaction, ultrasound, microwave, and the sequential approach required (1:6, methanol to oil molar ratio, 1 wt% NaOH to oil, and a reaction time of 20 min at 50 °C reaction temperature), (1:6 methanol to oil molar ratio, 1 wt% NaOH to oil, 350 rpm, and 15 min), (1:4 methanol to oil molar ratio, 1 wt% NaOH to oil, and 6 min reaction time), respectively. The sequential

process should start with the microwave since the heat released by the microwave effect accelerates the ultrasonic mixing. In their study, Gole and Gogate [225] illustrated that a sequential combination of microwave and ultrasound is economically more feasible in producing biodiesel because it reduces the amount of the catalyst and the reaction time. Moreover, the requirement of less amount of methanol reduces the consumption of energy in methanol recovery.

6. Non-Catalytic Biodiesel Production

The transesterification reaction between supercritical alcohol and triglycerides occurs in the absence of any catalysts. Once the alcohol molecules reach the supercritical region, hydrogen bonding in the alcohol dramatically decreases, allowing alcohol molecules to behave similar to an acid catalyst [226–228]. At particularly high pressure and temperature, for instance, 240 °C and 78.60 bar, methanol behaves similarly to a supercritical fluid, and the nature is similar to a compressible fluid with an intermediate density between a liquid and a gaseous fluid that allows excellent mass transfer characteristics due to the low surface tension and viscosity. The increase in temperature decreases the ionic product of different polar solvents, such as alcohols, CO₂, and water, converting them into a non-polar solvent. Supercritical alcohol technology can eliminate the drawbacks of homogenous and heterogeneous conventional catalytic processes as it does not use any catalyst. At supercritical conditions, alcohol has unique properties, such as gas-like high kinetic energy and liquid-like high density. Furthermore, supercritical alcohol has a low dielectric constant compared to alcohol liquid. This results in a reduced negative effect of alcohol polarity when reacting with the non-polar triglycerides. The process forms an entirely miscible 1-phase system of triglycerides and alcohol, and full conversion to fatty acids alkyl ester is accomplished in a concise time without a catalyst. The process involves heating alcohol until its critical temperature and pressure are reached [229–232]. Table 8 illustrates the critical temperature and pressure of some alcohols and solvents.

Table 8. Critical properties of various alcohols and other solvents [233–236].

Alcohol/Solvent	Critical Temperature (°C)	Critical Pressure (MPa)
Methanol	239	8.09
Ethanol	243	6.38
1-propanol	264	5.06
1-butanol	287	4.9
1-octanol	385	2.86
Water	373.95	22.12
Methyl acetate	234	4.69
Dimethyl carbonate	283	4.63
Acetic acid	317	5.80

6.1. One-Step Catalyst-Free Supercritical Alcohol Transesterification

Saka and Kusdaina [237] studied the production of methyl esters from rapeseed oil using supercritical methanol instead of sodium hydroxide as a catalyst. The authors reported that methyl esters produced in supercritical methanol have similar fatty acid composition comparable to that of the conventional method. Moreover, they reported higher biodiesel yield for the supercritical method compared to biodiesel yield derived using an alkaline catalyst; this can be attributed to simultaneous transesterification and esterification of FFAs. As supercritical alcohol transesterification required a more straightforward purification process, the authors claimed the process to be more environmentally friendly. Alcohol to oil molar ratio, temperature, and alcohol type are the factors that affect this process. Saka and Kusdaina [238] carried out a detailed kinetic study in free catalyst transesterification of rapeseed oil using supercritical methanol. The authors varied the controlling factors, such as temperature and reaction time and methanol to oil molar ratio. The authors reported maximum biodiesel yield at 350 °C, 43 MPa, and 1:42 methanol to oil molar ratio. Warabi

et al. [239] reported that, by using supercritical conditions, short-alkyl chain alcohols could achieve 100% conversion of triglycerides to biodiesel. They also reported a higher FFAs esterification reaction rate compared to triglycerides transesterification rate.

Madras et al. [240] investigated the biodiesel synthesis process under supercritical methanol and ethanol from refined sunflower oil. They observed a nearly complete conversion rate around 80–100% when the reaction occurred in the presence of supercritical ethanol and methanol, and they reported the transesterification at temperature 200–400 °C, pressure 20 MPa for a molar ratio of 40:1 alcohol to oil molar with a reaction time of 30 min. Moreover, they determined the reaction kinetics and reaction relevant activation energy from temperature relied on the rate coefficients. He et al. [241] examined the continuous biodiesel synthesizing process from soybean oil utilizing supercritical methanolysis by a tube reactor and reported catalyst-free optimum reaction achieved under a constant reaction temperature with an alcohol to oil molar ratio of 40:1, under 310 °C, and 35 MPa for 25 min residence time. Their maximum production yield is 77%, and they proposed a gradual heating method and obtained more than 96% methyl ester conversion.

Hawash et al. [242] reported biodiesel preparation from the transesterification of *Jatropha* oil, and they used a supercritical methanol catalyst-free process under various test conditions. They maintained a temperature from 512 to 613 K, pressure 5.7 to 8.6 MPa, and 10:43 molar ratio of alcohol to fuel. They reported biodiesel from *Jatropha* oil via supercritical methanol transesterification and reported a 100% yield in under 4 min at 320 and 8.4 MPa with a 43:1 molar ratio of methanol to oil. Demirbas et al. [243] examined that 250 and 41:1 molar ratios of methanol to hazelnut kernel oil are suitable to produce biodiesel with a yield of 95% in 5 min. The free catalyst method necessitates high energy consumption for reaching high reaction pressure-temperature conditions and recovering unreacted alcohol. Santana et al. [244] studied continuous biodiesel production using supercritical ethanol on an ion exchanging resin catalyst with an additional co-solvent carbon-di-oxide for pressure 15–25 MPa, 150 to 200 °C, and oil to ethanol molar ratio 1:20 to 1:45 by varying residence time. Micic et al. [245] studied continuous biodiesel production using supercritical ethanol on an ion exchanging resin catalyst with an additional co-solvent carbon-di-oxide for pressures 15–25 MPa, 150 to 200 °C, and oil to ethanol molar ratio 1:20 to 1:45 by varying residence time.

Water affects the formation of biodiesel in the catalyst-free supercritical methanol process positively. Vegetable oils that contain water, transesterification, hydrolysis of triglycerides, and methyl esterification of fatty acids proceed simultaneously during the treatment and result in high yields [246]. Thus, supercritical methanol transesterification technology is deemed economically more feasible due to higher biodiesel yield in a short reaction time with lower methanol consumption from low feedstock with high FFAs or water contents. Palm fatty acids distillate (PFAD), which is a by-product from palm oil refineries, consists of 93% FFAs and is esterified by Yujaroen et al. [234] in supercritical methanol conditions. A high biodiesel yield was obtained (95%) at 300 °C with 1:6 PFAD to methanol molar ratio and a 30 min reaction time. Compared to the transesterification of pure palm oil (PPO) in supercritical methanol, a relatively low biodiesel yield (80%) was reached at 300 °C with higher methanol requirements (1:45 PPO to methanol) and 50 min reaction time. Acid-catalyzed-esterification of the PFAD produced only 75% biodiesel yield in a 5 h reaction time. Wet algae biomass containing 90% water was converted to biodiesel at much milder reaction conditions, a wet algae to methanol (wt./vol) ratio of 1:9, with a reaction temperature and reaction time of 255 °C and 25 min, respectively [235]. Hegel et al. [247] used free-catalyst supercritical ethanol transesterification of the bio-oil to obtain biodiesel. The authors reported higher lipid extraction yields using ethanol with respect to n-hexane. The authors further reported that the transesterification of crude lipids extracted with ethanol as the solvent at 305 °C and 40 min produced up to 15.9 wt% of biodiesel with respect to dried biomass processed.

6.2. Acyl Acceptors as an Alternative to Alcohol

Saka and Isayama [248] developed a new method for the transesterification of triglycerides in order to avoid the formation of glycerol as a by-product in biodiesel production. In its supercritical condition, they used methyl acetate to convert triglycerides of rapeseed oil to biodiesel in one step without catalyst. The new by-product was triacetin, which is a valuable biodiesel additive. Triacetin has the ability to improve cloud points and oxidative stability of biodiesel. Patil et al. [249] studied the effect of lipid to methyl acetate molar ratio, reaction temperature, and reaction time on the FAME yield and algal biodiesel fuel yield. The authors concluded that this glycerin-free and non-catalytic transesterification process is more economical and environmentally friendly due to the simplification of the downstream separation and purification process. Tan et al. [250] studied FFAs and water's effect on the supercritical methyl acetate (SCMA) process. PO was treated with a predetermined amount of FFAs and water. Their results conclude that the SCMA process is insensitive to the presence of FFAs or water. FFAs react with methyl acetate to produce FAME and, a by-product, acetic acid, which catalyze the reaction and convert glycerol, as a result of the hydrolysis of the triglycerides to triacetin, simultaneously. Glycerol carbonate and citramalic acid were produced as two other valuable by-products of the non-catalytic one-step transesterification of rapeseed oil by supercritical dimethyl carbonate by Ilaham and Saka [251].

Li et al. [252] first studied ethanol and obtained it as an acyl acceptor during the deacidification of high-acid rice bran oil (RBO) esterification catalysis process through immobilized partial glycerides selective lipase SMG1-F278N from *Malassezia globosa*. The strong specificity of immobilized SMG1-F278N toward MAG and diacylglycerol (DAG) assures the intactness of triacylglycerol (TAG) while converting FAs to FA ethyl esters [252,253]. Sun et al. [254] studied phoenix tree seed oil (PTSO) as the novel feedstock to prepare fatty acid ethyl ester (FAEE), where ethanol as a fatty acyl acceptor and NaOH as a catalyst and the impact of transesterification conditions are observed in the order of NaOH concentration > substrate ratio > transesterification temperature. In Li et al. [255], methanol, ethanol, and glycerol were utilized as a novel acyl acceptor by deacidification of high-acid rice bran oil (RBO), and methanol showed a higher deacidification efficiency of RBO compared with glycerol and ethanol due to the distance of glycerol being more distant from catalytic serine (Ser-171) of SMG1-F278N, having a critical distance of approximately 4.6 Å. Methanol and ethanol potentially react with fatty acids, and a close distance was observed between them, and they approximately maintained a binding distance of 3.6 and 3.7 Å from the catalytic serine. As a final product, the acid value was 0.09 g KOH/g.

6.3. Production of Biodiesel by Supercritical Technology at Mild Conditions

Conventional free catalyst supercritical methanol treatment of triglycerides (lipids/oils) is economically not feasible, although they achieve high conversion to FAME, because of the harsh conditions, of high temperature and pressure required, besides the thermal degradation of FAME, especially those with a high unsaturation degree and isomerization of fatty acids to trans-type at high temperatures. Imahara et al. [256] investigated the effect of high temperature and pressure (270 °C/17 MPa to 380 °C/56 MPa) on the thermal stability of biodiesel derived from supercritical methanol conditions for various plant oils. Temperatures lower than 300 °C, preferably 270 °C, with a minimum pressure of 8.09 MPa, were proven to be appropriate to maintain the maximum yields and thermal stabilization of biodiesel. Therefore, researchers were motivated to develop new supercritical fluid technology to produce biodiesel at mild reaction conditions.

6.3.1. Supercritical Methanol and Co-Solvent

According to Yin et al. [257], the presence of propane in the reaction mixture, as a co-solvent, simultaneously reduces the temperature and pressure required for the methanolysis of vegetable oils in supercritical conditions. Propane is a good solvent for vegetable oils. Hence, a single-phase (methanol/oil) can be achieved at a lower temperature and methanol

to oil molar ratio. The reduction of methanol in the reaction mixture, consequently, reduces the pressure required for a supercritical state. Yin et al. [257], in their study of supercritical methanol reactions with soybean oil, obtained a 98% biodiesel yield at optimal conditions propane/methanol molar ratio 0.05, methanol/oil molar ratio 24, reaction temperature 280 °C, reaction pressure 12.8 MPa, and a 10 min reaction time. Furthermore, propane has the advantage of being reused after some pretreatments.

6.3.2. Subcritical Methanol and Co-Catalyst

Some heterogeneous catalysts are capable of transesterifying triglycerides at much milder reaction conditions at subcritical conditions of methanol. A maximum conversion of sunflower oil to biodiesel was achieved at (252 °C, 3% CaO to the oil weight, 41:1 methanol to oil molar ratio, and 6 min reaction time) [258]. Combining heterogeneous catalysts with subcritical methanol conditions gives more convenient temperature and pressure requirements compared to supercritical methanol-free catalysts. A minimal amount of tri-potassium phosphate in subcritical methanol exhibited high catalytic activity in the transesterification of soybean oil. A maximum biodiesel yield (95.6%) was obtained at optimal conditions (1% K₃PO₄ to oil weight, 220 °C, methanol/oil molar ratio 24:1 and 30 min reaction time. The catalyst retained 90% of its initial activity after two cycles [257]. This method was limited by the maximum presence of water and FFA 5% and 3%, respectively [257]. More satisfactory results were obtained when soybean oil was treated by subcritical methanol in the presence of a minimal amount of potassium hydroxide (KOH/oil = 0.1 wt%) as a catalyst, 98% biodiesel yield was obtained after 10 min at 160 °C and molar ratio (methanol/oil) 24:1 [259].

6.3.3. Two-Step Supercritical Methanol Transesterification

Kusdiana and Saka [260] have developed a new two-step process for the methanolysis of triglycerides. The first step involves the hydrolysis of triglycerides at a subcritical state of water. The second step is supercritical methanol treatment of fatty acids (FA) results from the hydrolysis, together with the FFAs, initially exist in the reaction mixture to achieve FAME conversion. The two-step process was applied to convert rapeseed oil to FAME in a considerably shorter reaction time and milder condition (270 °C/7–20 MPa) than direct supercritical methanol condition treatment. Furthermore, biodiesel produced by the two-step process has shallow glycerol content due to the continuous reaction removal of glycerol in the first step before the methyl esterification. Detailed kinetic study carried by Minami and Saka [261] revealed that the hydrolysis of triglycerides in a subcritical state of water is an autocatalytic reaction due to the considerable role of the resultant FAs. According to their proposed mechanism, the reaction propagates by the dissociation of the FAs to eliminate proton, which causes the protonation of the carbonyl oxygen of the triglycerides (TG), providing nucleophilic site to be attacked by the water. This theoretical approach coincides very well with experimental results since the FAs yield was observed to be low at the earlier stage of the reaction and increase gradually when the rate of FAs formation increase in the course of time. Ilham and Saka [262] investigated transesterification of *Jatropha curcas* oil in dimethyl carbonate supercritical condition, applying the two-step process. More than 97% biodiesel yield was achieved by subcritical water treatment (270 °C/27 MPa) for 25 min followed by subsequent supercritical dimethyl carbonate treatment (300 °C/9 MPa) for 15 min. There was no thermal decomposition of unsaturated fatty acid methyl ester derived from *Jatropha curcas*, observed.

A novel two-step process to convert triglycerides to biodiesel at mild reaction conditions without glycerol production was developed by Saka et al. [236]. It includes treatment of triglycerides with subcritical acetic acids followed by supercritical methanol treatment. Rapeseed oil was converted in the first step to FA and triacetin by subcritical acetic acid under optimal conditions (300 °C/20 MPa, 30 min reaction time, and 1:54 oil to acetic acid molar ratio equivalent to 1:3.2 volumetric ratio). After removal of triacetin from the reaction mixture, supercritical methanol treatment required 270 °C/17 MPa for 15 min at a

molar ratio of FAs to methanol 1:14 (1:1.6 volumetric ratio) the yield of FAME was 97 wt% and that for triacetin was 20 wt% totally being 117 wt% out of theoretical value 125 wt%.

7. In Situ Transesterification

Conventional biodiesel production involves, prior to esterification/transesterification, extraction and purification of oils from triglycerides-bearing materials. Refined feedstock constitutes 70% of the total cost of biodiesel because of the required multi-processing stages technologies. In situ transesterification is a route of biodiesel production, which was developed to cut down the cost of biodiesel production. In situ transesterification involves one step of direct extraction and transesterification, in which alcohol acts as solvent extraction and transesterification reagent. In situ transesterification, commonly termed reactive extraction has the advantages of reducing the processing time and the amount of solvent [263–265]. In addition, it is environmentally benign since hazardous air pollutants, such as hexane, can be avoided [266].

Production of biodiesel by direct alkali-catalyzed transesterification of soybeans was examined by Haas et al. [266]. With the aid of thin-layer chromatography, it was apparent that even the brief incubation (2.5 h) of soy flakes (5 g) in 15 mL of alkaline solution (0.33 N NaOH) and simple alcohol (methanol, ethanol, isopropanol) at 60 °C resulted in fatty acid alkyl ester, suggesting that this phenomenon is a general one. Quain et al. [267] investigated the in situ transesterification of cottonseed oil by sodium hydroxide. Their study revealed that extraction and conversion of cottonseed oil increased significantly by increasing the amount of the catalyst, methanol loading, reaction time, and decreasing the moisture content and the size of the seed particles. The effect of temperature on biodiesel yield was not significant. A total of 99% and 98% of cottonseed oil extraction and conversion, respectively, were achieved by the optimal condition: less than 2% moisture content in cottonseed flour, 0.3–0.335 mm particle solid size, 0.1 mole/L methanolic sodium hydroxide solution, 135:1 methanol/oil molar ratio, 40 °C reaction temperature, and a 3 h reaction time. The presence of petroleum ether as a co-solvent substantially increased the extraction and conversion of the oil, with the optimal volume ratio of 1:3 ether/methanol. Moreover, the cottonseed oil extraction and conversion remained constant by using a mixture of fresh methanol and recycled methanol with 0.2 ratios (of recycled methanol/total reaction methanol, v/v).

The acidic in situ transesterification process presents as a novel route for direct extraction, esterification, and transesterification of low feedstock with high FFA, instead of the conventional acid-base two-step process. Shuit et al. [268] investigated the feasibility of acidic in situ transesterification of *Jatropha curcas* L. seeds to biodiesel. Oil extraction efficiency (91.2%) and FAME yield (99.8%) was achieved by using seeds with a size less than 0.335 mm and n-hexane as the co-solvent with the following reaction conditions; reaction temperature 60 °C, reaction period of 24 h, methanol to seed ratio 7.5 mL/g, and 15 wt% of H₂SO₄. The in-situ transesterification process was used by Ehimen et al. [269] as a cost-reducing scheme for microalgae biodiesel production. They aimed to provide information on the optimal condition required for high biodiesel yield with the least material and energy requirements. The conversion process was monitored by the specific gravity of the biodiesel product, as the specific gravity decreased by increasing the concentration of a lighter FAME. The results revealed that the lowest FAME specific gravity was achieved with increasing methanol to oil molar ratios, temperature, and stirring the reaction vessel. Regarding the effect of moisture, it was found that the oil conversion to biodiesel was completely inhibited by water content beyond 115% (w/w).

Su et al. [270] examined the feasibility of biological in situ reactive extraction of oilseed with short-chain alkyl acetate for alkyl ester production. Firstly, they demonstrated that methyl acetate and ethyl acetate were capable of extracting oil from *Pistacia chinensis* Bunge seed and *Jatropha curcas* L, as well as n-hexane. Crude oil extracted by alkyl acetates had, remarkably, a lower phospholipids content compared to extract of hexane. Afterward, they compared the in situ transesterification versus conventional two-step

extraction/transesterification in the presence of Novozyme 435 in both cases. The yields of methyl esters and ethyl esters in reactive extraction were considerably higher than those obtained by methanolysis and ethanolysis of the hexane extracted oil. The losses in yields may be attributed to the multi-step operations in the conventional extraction and transesterification, or the possible inhibition of lipase by methanol or ethanol and phospholipids. Furthermore, the effects of solvent, seeds, and seed water content on in situ reactive extraction were investigated. Methyl/ethyl esters' yields decreased by incomplete oil extraction due to the too low ratio of solvent/seed or the excessive dilution caused by higher ratios. Regardless of the kind of seeds or alkyl acetates used, the optimum solvent/seed ratio for high yields was 7.5 mL/g at the fixed condition of 5 g oilseed, 50 °C, 30% (w/w) Novozyme 435 to theoretical oil content, 10 h, and 180 rpm.

The presence of water in the reaction medium enhances biological activity. However, the excess of water leads to hydrolytic reaction and, consequently, decreases the esters' yields. The highest ester yields were achieved at 4.26% and 4.62% water contents for *Pistacia chinensis* and *Jatropha curcas* L. seeds, respectively, regardless of the kind of alkyl acetate used, at the established solvent/seed ratio. Su et al. [271], in their further investigations on in situ reactive extraction of *Pistacia chinensis* and *Jatropha curcas* L. seeds, demonstrated that short-chain dialkyl carbonates act as not only an extraction solvent but also as a transesterification agent. The optimum solvent/seed ratio for the highest biodiesel yields was 10 mL/g, at fixed conditions: 5 g oilseed, 50 °C, 10% (w/w) Novozyme 435 to oil content, 10 h, and 180 rpm, regardless of the kinds of seeds and dialkyl carbonates used. Regarding the effect of water content at the optimized solvent/seed ratio, for *Pistacia chinensis* Bunge seed by using dimethyl carbonate, the highest methyl ester yields were attained at 3.14% water content. In comparison, the highest ethyl ester yields were attained at 2.34% by using diethyl carbonate. However, the highest ester yields were achieved at 3.02% of water content for *Jatropha curcas* L. seeds regardless of the kind of dialkyl carbonates used. At these optimized conditions, for both seeds, the yields of methyl esters and ethyl esters were almost constant after 24 h, with a rapid increase in the first 16 h.

A combination of supercritical methanol technology with reactive extraction was present as a novel method for producing biodiesel by Lim et al. [272]. They aimed to investigate the feasibility of non-catalytic reactive extraction of *Jatropha curcas* L. seeds in a high-pressure batch reactor in the presence of n-hexane as a co-solvent. The effects of temperature and the size of the solid particles of *Jatropha curcas* L. seeds on the FAME yields and the oil extraction efficiency were investigated extensively. The particle size of the seeds varied in the range of 0.5–2.0 mm, and the temperature varied in the range of 200–300 °C. Their study revealed that ≤ 1.0 mm particle solid size, the reaction temperature of 300 °C, and 240 MPa operational pressure are optimal conditions to achieve maximum extraction efficiency and FAME yield at 10 mL/g solvent to seed ratio, 2.5 mL/g co-solvent to seed ratio, and relatively short reaction time (45 to 80 min). The maximum FAME yield (103.5%) beyond the theoretical value (100%) was due to the excess oil being extracted based on n-hexane Soxhlet extraction of *Jatropha* oilseeds due to the significant effect of the co-solvent at the low temperature.

8. Perspectives and Challenges

Homogeneous acid/base catalysis is the most preferred method used to produce biodiesel as they are simple to use and require less time to achieve a complete reaction. In addition, metal ions in ILs are novel methods for the esterification and transesterification of low feedstock with high FFAs. Moreover, TDSF is a suitable route for the utilization of the renewable acyl acceptor, ethanol. Heterogeneous catalysis is the most promising alternative technology to homogeneous catalysis. Research is going on to minimize mass transfer problems by using co-solvents or developing superior nano-solid acidic or basic catalysts. Waste-based catalysts are a promising solution to cut down the high cost of analytical-grade chemical catalysts. The industrial waste shells are the sources for CaO as a base catalyst, whereas cellulosic waste biomass materials are carbon-based solid

acid catalysts. A bio-heterogeneous catalyst was proven to be efficient in converting the low-quality feedstock to biodiesel. Intensive research is being carried out to avoid lipase inhibition by methanol or glycerol. More research is required to reduce the cost of enzymes and immobilization methods besides the research into the types of the carriers. Further investigation into industrial enzymatic biodiesel production for ensuring viable future options is necessary.

The application of ultrasound irradiation and microwave radiation enhances mass and heat transfer and reduces the time required for the transesterification process compared to conventional stirring and heating systems. More in-depth studies should be performed dealing with the reaction pathway of triglycerides on solid acid catalysts. In addition, more parametric studies are also required for two-step heterogeneous ultrasound-assisted transesterification of non-edible feedstocks with different types of catalyst (enzymatic and nano-catalysts). The influence of different parameters, such as catalyst loading, reactor volume, reactor design, and flow rate, on the behavior of microbubbles in ultrasound synthesis at the pilot or industrial scale also has to be investigated further. The selection of appropriate materials of construction for the reaction vessel, microwave leakage and its harmful effect on the human body, and selection of an appropriate catalyst are some of the challenges in implementing microwave-assisted transesterification that needs addressing.

Supercritical alcohol transesterification represents a neat route for biodiesel production since there is no catalyst used. However, this method is energetically intensive, and it affects the thermal stability of the FAME due to the high temperature and pressure required. Co-solvent, co-catalyst, and subcritical water are being investigated for biodiesel production by supercritical technology at mild reaction conditions. Valuable by-products more than glycerol, such as triacetin, were produced by using supercritical methyl acetate and dimethyl carbonate. Developing an alternative acyl acceptor is a promising aspect of a solvent-free system. For solvent systems, the environmental, friendly, and inexpensive solvent should be sought.

In situ transesterification of the seed oil is expected to substantially reduce biodiesel production's cost since the extraction, degumming, and refining processes could be eliminated, and the methanol can be recycled. However, the solid particle size, the solvent/seed ratio, and water content in the raw materials should be maintained to achieve high biodiesel yields. Recent studies demonstrated that a combination of in situ transesterification and supercritical methanol in the presence of co-solvent produces biodiesel yields beyond the expected theoretical yields.

9. Conclusions

Fatty acid methyl ester (FAME), known as biodiesel, is a fuel generated from renewable sources used in traditional compression ignition engines. In response to the need to create sustainable energy supplies and combat climate change, the interest in and development of biofuels has increased dramatically in recent years. The commercial and environmental sustainability of the biodiesel industry is still under debate. There is rapid progress in research to make biodiesel production more cost-effective and environmentally benign. Special attention needs to be given to developing new routes of transesterification that render the utilization of low-quality feedstock feasible for biodiesel production, with fewer downstream processes.

There are many non-edible plant oils used for biodiesel synthesis through the transesterification of lipids. Stable catalysts in terms of catalytic life, recyclability, and reduced cost are essential since they directly influence the total cost of the process. The studies on heterogeneous catalysts primarily focused on evaluating the appropriate oil supply, methanol to oil molar proportion, and measuring the accessibility of catalysts owing to their less expensive and more environmentally beneficial properties since they may be recovered and reused. Solid acid catalysts may convert high free fatty acid (FFA) oils into biodiesel in one step despite their lower reaction rate and side reactions. Nano-heterogeneous catalysts have a large active surface area and excellent selectivity, which increase the reaction rate

and efficiency of nano-catalyzed transesterification. Given the benefits of homogeneous catalysts (high contact surface) and heterogeneous catalysts (easy selectivity), and if the preparation time is short and the cost is low, nano-catalysts may be the best option in synthesizing biodiesel through transesterification.

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Abbreviations

KOCH ₃	Potassium methanolate
OCH ₃	Methoxide
KOH	Potassium hydroxide
FFA	Free Fatty Acid
H ₂ SO ₄	Sulphuric Acid
BMIIm-CH ₃ SO ₃	1-butyl-3 methyl imidazolium- tosylate
TDSP	Transesterification Double Step Process
NMR	Nuclear Magnetic Resonance
MCM	Mobil Composition of Matter
SBA	Santa Barbara Amorphous
FAME	Fatty Acid Methyl Ester
RFA	Rapeseed oil fatty acids
RO	Rapeseed oil
ACPhSO ₃ H	4-sulfophenyl activated carbon-based solid acid catalyst
RME	Rapeseed methyl ester
GO	Graphene Oxide
SO ₃	Sulfur trioxide
THF	tetrahydrofuran
DMSO	dimethylsulfoxide
DEE	Diethyl ether
KF	Potassium Fluoride
XRD	X-ray diffractometer
CH ₃ OH	Methanol
O ₂	Oxygen
YSA	Yeast residue-based solid acid
TGA	Thermogravimetric analysis
CPO	Crude palm oil
BSP	Biomass Support Particles
FAEE	Fatty Acid Ethyl Ester

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