catalysts

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Review

Biodiesel Production Using Solid Acid Catalysts Based on Metal Oxides

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Abstract: The development of solid acid catalysts, especially based on metal oxides and different magnetic nanoparticles, gained much awareness recently as a result of the development of different nano-based materials. Solid acid catalysts based on metal oxides are promising for the (trans)esterification reactions of different oils and waste materials for biodiesel production. This review gives a brief overview of recent developments in various solid acid catalysts based on different metal oxides, such as zirconia, zinc, titanium, iron, tungsten, and magnetic materials, where the catalysts are optimized for various reaction parameters, such as the amount of catalyst, molar ratio of oil to alcohol, reaction time, and temperature. Furthermore, yields and conversions for biodiesel production are compared. Such metal-oxide-based solid acid catalysts provide more sustainable, green, and easy-separation synthesis routes with high catalytic activity and reusability than traditionally used catalysts.

Keywords: biodiesel production; waste materials; free fatty acids; solid acid catalysts; mixed metal oxides; magnetic nanoparticles

1. Introduction

We are facing an energy crisis because of high energy demand from fossil fuels such as coal, petroleum, and natural gas, which compete with the feedstock requirements for different chemical industries. The demand for these non-renewable sources of energy is increasing rapidly. The rapid consumption of fossil and nuclear fuel reserves, greenhouse gas emissions (GHG), and associated climate change are stimulating the development of alternative and sustainable energy sources derived from renewable feedstocks [1]. Today, the predominant sources for of the global energy supply are coal, natural gas, and crude oil [2]. Attention is now shifting to the production of biomass-derived fuels, which are known as biofuels, for energy production. One such liquid biofuel is biodiesel. The advantages of biodiesel compared to conventional fossil diesels are its renewability, biodegradability, non-toxicity, and low exhaust emissions because of the absence of sulfur and aromatics in biodiesel [3].

Biodiesel is a real alternative to conventional fuels, due to its attractive properties such as reduced emissions, renewability, and sustainability. Additionally, biodiesel can be produced from naturally obtained renewable sources, such as plant oil, animal fat, and microorganisms, which makes it a promising fuel from a sustainability perspective [4]. Biodiesel is proven to be environmentally friendly, because of its reduced emissions during combustion and superior biodegradability when compared with fossil fuel. The cost of production of some of these fuels is still relatively high, however, despite the fact that they have lower environmental consequences than fossil fuels. The various production methodologies could be responsible for the high cost of these biofuels [5].

The need of energy security for economic development, as well as the demand for an alternative source of energy, promotes biodiesel production (mono-alkyl esters of long chain fatty acids) as a safe and novel technology [6]. It provides a sustainable, renewable, biodegradable, and non-toxic diesel fuel substitute that can be easily produced through base- or acid-catalyzed esterification and transesterification reactions [1]. Biodiesel is superior to diesel oil for health and the environment (it is low in sulfur, emits a low level of noxious particles like HC and CO, and is better in the CO_2 cycle in reducing global warming), as well as for engine performance (better lubrication, high cetane number, and more complete combustion) [7,8]. It has a high flash point, better viscosity, and similar caloric power to fossil fuels [9].

Biodiesel is usually produced by transesterification of vegetable oils or animal fats with chemical catalysts (Figure 1), especially in the presence of strong acidic or basic solutions, such as hydrochloric acid, sulfuric acid, sodium hydroxide, sodium methoxide, and potassium hydroxide. The catalyst is required to initiate the reaction and act as a solubilizer, which is needed because alcohol is sparingly soluble in the oil phase, and noncatalyzed reactions are extremely slow. The catalyst promotes an increase in alcohol solubility to allow the reaction to proceed at a reasonable rate [10]. Homogeneous alkali catalysts can convert triglycerides (TGs) to their corresponding fatty acid methyl esters (FAMEs) with high yield, less time, and low cost [11]. The properties of biodiesel fuel make it a promising substitute for diesel fuel; nevertheless, the production of biofuel is not economically feasible due to high raw material and production costs [12]. However, separating the catalyst from the product mixture for recycling is technically difficult. After the reaction, the catalyst should be neutralized or removed with a large amount of hot water, which will produce a large amount of industrial wastewater [13].

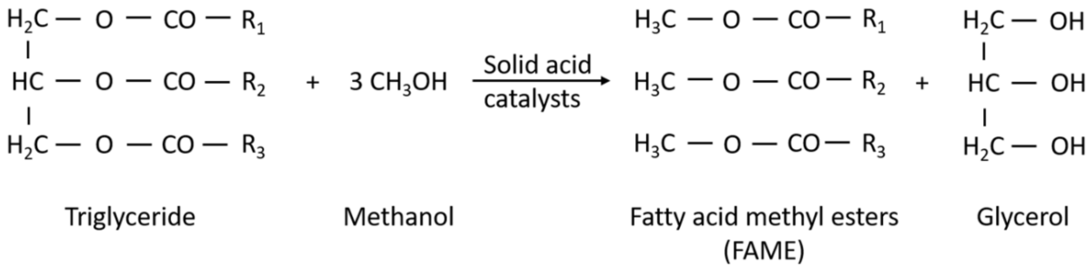

Figure 1. Solid acid-catalyzed transesterification reaction.

Two types of catalytic mechanisms, i.e., heterogeneous and homogeneous processes, can be used for biodiesel production. Heterogeneous catalysis can be identified as solid and enzymatic, where particularly lipases are used to improve reaction rates and yield [14]. In addition, solid heterogeneous catalysts can be classified as acids or bases [13]. Biodiesel production processes based on the use of acid catalysts are good alternatives to conventional processes because of their simplicity and the simultaneous promotion of esterification and transesterification reactions without soap formation. Thus, the acid catalysts can directly produce biodiesel from low-grade, highly acidic, and water-containing oils. Homogeneous acid catalysts, including strong Brønsted mineral acids (such as sulfuric acid or hydrofluoric acid) and *p*-toluenesulfonic acid, although effective, lead to serious contamination and corrosion problems that require the implementation of good separation and purification steps [15–17]. More recently, a "green" approach to biodiesel synthesis stimulated the application of sustainable solid acid catalysts as replacements for such liquid acid catalysts such that the use of harmful substances and the generation of toxic wastes are avoided; meanwhile, ease of catalyst separation after the reactions can be attained. Recent studies proved the technical feasibility and the environmental and economic benefits of biodiesel production via heterogeneous acid-catalyzed esterification and transesterification [18,19].

In view of these factors, the objective of this review is to highlight the latest synthesis protocols for the production of biodiesel from different types of materials using solid acid catalysts based on metal oxides. Synthesis protocols using different metal oxides from zirconia, zinc, iron, and titanium are presented. In addition, another highlight of this review is focused on using magnetic catalysts, which ease the separation process of the catalyst from the reaction media.

2. Technologies for Biodiesel Production

Using various methods, such as the non-catalytic supercritical method [20,21], the biox process [22], microwave heating [23], membrane technology [24], reactive distillation [25], and ultrasonication [26], the transesterification process for biodiesel production can also be performed.

The advantage of the supercritical method is that no catalyst is needed; however, on the other hand, there exists some disadvantages in the catalytic routes, such as the requirement to treat free fatty acids (FFAs) and triglycerides (TGs) in different reaction stages, inactivation of catalyst, occurrence of the repressive effects of water molecules in the mixture, low purity of glycerol, wastewater creation, and the catalyst separation from the mixture of product [27].

The advantage of this process is the high yield of FAMEs and low production of byproducts [28]. However, it is an energy-intensive and economically unfeasible process because it requires high operating temperatures (553–673 K) and pressures (10–30 MPa), as well as a high methanol-to-TG molar ratio, up to 42:1 [29]. Furthermore, this process has serious drawbacks, such as the corrosion of equipment and the difficult recovery of the catalyst [30]. In addition, the separation and purification of biodiesel is also a big problem.

In the biox process, a co-solvent tetrahydrofuran (THF) is used to accelerate the reaction by solubilizing methanol. Methanol (337.7 K) and THF (339 K) have similar boiling points, resulting in the removal of excess solvents in one step after the completion of the reactions [22]. Using this process, a conversion of oil feedstock with a high amount of FFA (to 10%) in biodiesel is possible in a two-step, single phase, continuous process at atmospheric pressures and a near-ambient operating temperature of 303.15 K [31]. The result is a fast reaction, on the order of 5–10 min, without catalyst residues in either the ester or the glycerol phase [32]. However, an economic barrier arises because of the similar boiling points of methanol and THF, resulting in the difficult separation of the products [33]. Furthermore, it is necessary to remove the co-solvent from glycerol and biodiesel due to its dangerous and toxic nature.

In the microwave method, energy consumption is 23 times lower in comparison to the standard transesterification method [34]. The microwave energy is transferred directly to the reactant and, therefore, no preheating is required. Moreover, the heat transfer system in the microwave process is more effective as in the conventional method, where the heat is transferred to the reaction through thermal heat reflux. Microwave transfers energy through electromagnetic waves, which results in acceleration of the transesterification process [35]. However, due to the low penetration depth of microwave radiation into materials, the ability to scale up on industrial levels is reduced [36].

Membrane technology connects, in a single step, the process of reaction and separation, thus leading to a reduction in separation costs and recycling requirements. There are two basic principles of operation in biodiesel production via membrane technology: separation based on oil droplet size [37] or use of a catalytic membrane [38]. Membranes are generally preferred in the refining processes for the following reasons: low energy consumption, safety, simple operation, elimination of wastewater treatment, easy change of scale, higher mechanical, thermal, and chemical stability, and resistance to corrosion [39]. Nonetheless, membrane technology certainly requires further purification since the FAME-rich phase still contains methanol, glycerol, and water [35,40].

In order to simplify the process operation, a single-unit combination of reaction and distillation in the reactive distillation process was invented [41]. Reactive distillation does not require additional quantities of alcohol, because the continuous removal of byproduct (water) can lower alcohol usage by 66%. The advantage of the process of distillation is that it is carried out at atmospheric pressure [42]. In the process of reactive distillation, fewer connections between instruments and equipment are required. Nevertheless, the requirement for a reboiler and condenser tremendously increases initial investment and operating costs [43,44].

The preferred operation process of ultrasonic homogenization between different phases in the alcoholysis process involves the enhancement of mixing and better heat and mass transfer [45]. In general, ultrasonic homogenization can reduce energy consumption and operating costs, while it has lower requirements regarding the molar ratio between alcohol and oil, a lower catalyst amount, and a shorter reaction time, while there is also no need for external heating requirement. Consequently, phase separation between biodiesel and glycerol is simpler with a shorter phase separation time. Due to superior properties in the transesterification reactions, ultrasonic homogenization offers the great possibility to be scaled up from laboratory to industrial scale [46,47].

Remarkably, many industrial processes shifted toward using solid acid catalysts [48]. The key benefit of solid acid catalysts is that no polluting byproducts are formed and the catalysts do not have to be removed, since they do not mix with the biodiesel product [49]. Byproducts formed in secondary reactions are likely to render the process uneconomical.

Figure 2 shows a schematic diagram of the processes involved in biodiesel production. Oil and methanol at a given ratio are combined, and the solid acid catalyst is added to the reactor. Then, the mixture is agitated for a specified time at a specific temperature. A stirrer is placed in the middle of the oil phase and set at a particular mixing speed in order to keep the interface between the two phases undisturbed. Excess methanol is removed by vaporization and recycled in the process with fresh methanol. When the reaction reaches equilibrium, the mixture is transferred to a funnel to separate the glycerol phase and the crude biodiesel phase [50].

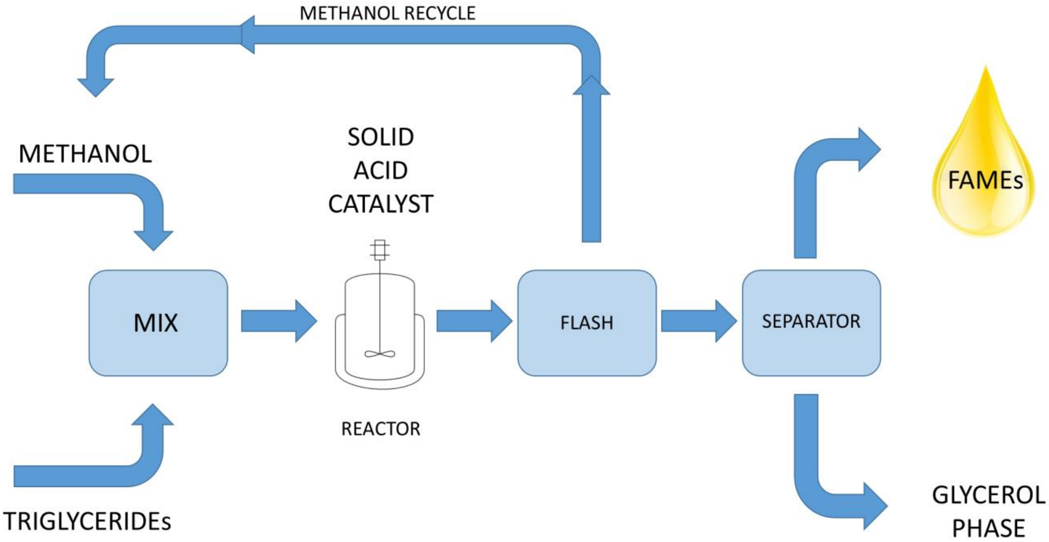

Figure 2. Simplified scheme of biodiesel production process.

The main byproduct of biodiesel production is glycerol, which is of interest to research scientists and companies, as it can be transformed into a series of useful chemicals and fuels through a range of chemical transformations. The rapid growth of the biodiesel industry (the global biodiesel market is expected to reach United States dollars (USD) $54.8 billion by 2025) generated a surplus of crude glycerol in the market. It was reported in various studies that 10%–20% of the total volume of biodiesel produced is composed of glycerol; for every 100 kg of biodiesel produced, 10 kg of glycerol is generated [51]. Glycerol is, thus, a cheap and abundant renewable feedstock, not only because of the huge amount produced, but also due to its low quality, since it is mixed with other products such as methanol, water, and salts [52]. On the other hand, it is a natural, sweet-tasting thick colorless liquid considered a base product, which has diverse applications in various industries such as pharmaceuticals, personal care, and food and beverages, as well as in the production of tobacco, alkyd resins, and polyether polyols; on the other hand, compounds of glycerol are used to preserve lotions, inks, fruits, and lubricants. The personal care and pharmaceutical industries account for more than one-third of the global glycerol market [11].

3. Mixed Metal Oxides in Biodiesel Production

The production of biodiesel rapidly increased in recent years as a result of the benefits associated with its ability to minimize environmental pollution. Heterogeneous catalysts are used in the production of biodiesel for easier recovery and to minimize demand for aqueous treatment. Transesterification of fatty acids into biodiesel using transition metal oxides gives higher conversion rates into their corresponding methyl esters in a short time, compared to other methods. In spite of the activity aspects of single metal oxides, such catalysts in biodiesel production are effective and offer a route to gain higher catalytic performance, because of the enhancement of surface properties. Supporting metal oxides on high-surface-area materials is a preferred method for increasing their stability as catalysts and reducing the costs of preparing the catalysts [53].

Among all different areas of heterogeneous catalysis, metal oxide-based catalysts are the most important catalysts, since a large number of catalytic processes are enabled by mesoporous or porous metal oxides. The importance of metal-oxide-based catalysts lies in their effective catalysis of different reactions, such as acid-base catalysis, oxidation reactions, photocatalysis, or biomass conversion, among others. Another benefit of metal-oxide-based catalysts is in many potential applications, such as in fuel cells or sensors [54]. Some metal oxides provide higher catalytic activities because of their large number of active acidic sites, thereby increasing the surface area for catalysis. Those properties increase reaction yield and reduce reaction times [55]. Enhanced activity, as well as product selectivity of a solid acid catalyst, can be achieved by manipulating its properties, such as turnover frequency (TOF), surface area, concentration and strength of catalytic sites, and Brønsted/Lewis acidity and porosity. Catalysts with multivalent metal cations can show Brønsted or Lewis acidity, which depends largely on the electronegativity of exchangeable cations. Therefore, the stronger catalyst acidity is because of its higher density of electronegative cations [56]. The efficiency of a catalyst is expressed by the TOF, which is a chemical reaction rate. Upon increasing the concentration of areal acid sites, TOF also increases; thus, higher TOF values mean shorter distances among the catalyst's acid sites. This means that the acidic strength of a solid acid catalyst determines the transfer of protons [57,58].

The necessary catalytic sites for methanolysis during the transesterification processes are provided by Brønsted and Lewis acid sites. Breaking of the O–H bond in the transesterification process results in the formation of hydrogen cations and methoxides, which accelerate the reaction between triglyceride molecules and methoxide anions to form FAME [59]. Most of these oxides are of transition metal group origin, such as zinc oxides, zirconium oxides, iron oxides, tungsten oxides, tin oxides, and titanium oxides, which are of interest to industries and research groups. Among these solid acid catalysts, sulfonated zirconia, tungstened zirconia, and CaO zirconia are promising for transesterifying TGs to fatty acid alkyl esters [60]. Iron oxide as a catalyst support can also be further developed by incorporating different catalytically active metals, as shown in Figure 3.

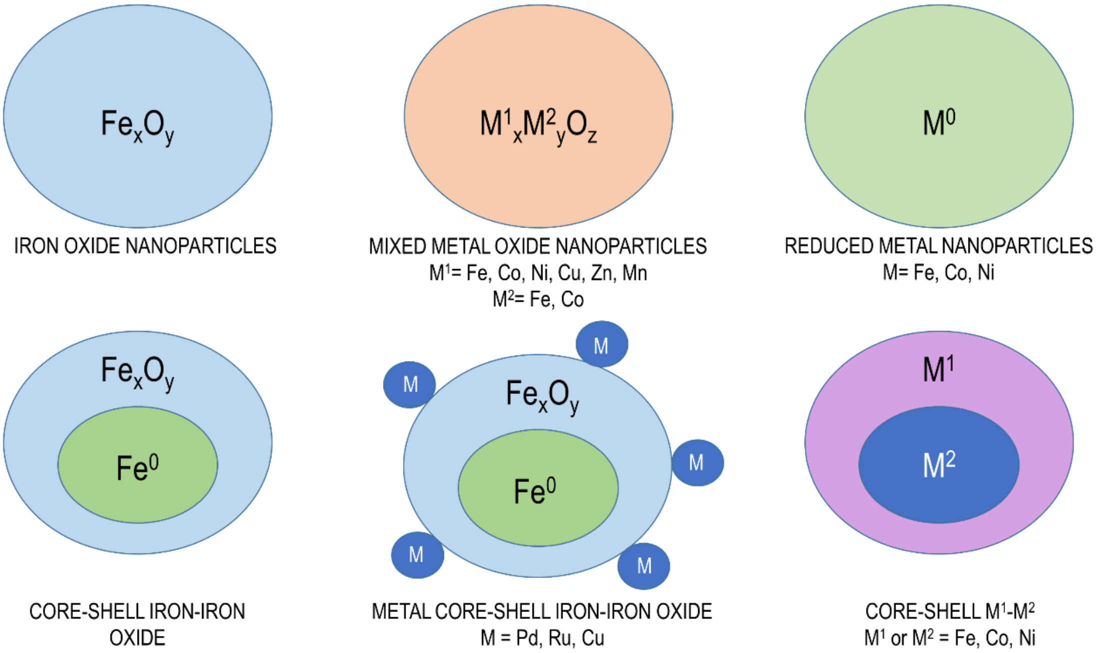

Figure 3. Types of catalysts based on magnetic nanoparticles.

3.1. ZrO_2-Based Catalysts

Zirconia is a well-known and widely used catalyst in various industrial applications. It is thermally stable and has very strong acidic sites. Its large pores reduce diffusional limitations, since they can accommodate large molecules of fatty acids (FAs) [61,62]. Zirconia is also not prone to side reactions of etherification and dehydration [63]. Based on the treatment used during preparation, sulfonated zirconia can act as a superacid. High temperatures above 873.15 K destroy the crystal growth of zirconium oxide and transform the tetragonal phase to a monoclinic phase upon cooling at low temperatures as a result of volume increase.

Many applications use zirconium oxides, such as water-resistant zirconium sulfate tetrahydrate [$Zr(SO_4)2{\cdot}4H_2O$]/tubular carbon membranes (TCM), which are prepared using wet impregnation of TCM with different zirconium sulfate loadings. They are used as a heterogeneous solid acid catalyst for the esterification of acidified oil with methanol. Because of the high specific area of TCM, the catalytic activity of 11.4% zirconium sulfate/TCM can be improved by 1.8 times compared with bulk zirconium sulfate [64]. Solid acid is prepared by sulfonation of surface-modified α-zirconium phosphate (ZrP) single-layer nanosheets (SO_3H@ZrP), and the prepared solid acid was investigated for the esterification of oleic acid with methanol to produce biodiesel. Results showed that the SO_3H@ZrP solid acid catalyst has a superior catalytic efficiency for the esterification reaction, as well as excellent recyclability. The SO_3H@ZrP single-layer solid acid catalyst can be uniformly dispersed in the reaction medium, but it remains heterogeneous and, thus, can be easily separated via centrifugation and recycled. However, SO_3H@ZrP exhibits higher catalytic activity than commercial catalysts. This can be ascribed to the high density of the sulfonic acid groups on the surface of ZrP nanosheets and their high dispersion and, thus, high accessibility in the reaction system [65].

Another mesoporous sulfated Zr-KIT-6 (x) (x = Si/Zr) solid acid catalyst can be successfully synthesized via the hydrothermal method, where different weights of zirconium are loaded into a fixed gel in the acidic medium and then sulfated to obtain sulfated Zr-KIT-6 (x) catalysts. Experiments performed showed that sulfated Zr-KIT-6 (20) demonstrates the highest catalytic conversion for esterification of oleic acid (96%) and transesterification of jatropha oil (85%) in optimized reaction conditions of 393.15 K, 20:1 methanol-to-reactant molar ratio, 4 wt. % catalyst loading, and 6 h reaction time [66].

Enascuta et al. developed a new environmentally friendly heterogeneous superacid catalyst (SO_4^{2-}/SnO_2-ZrO_2), which was tested in the esterification reaction of FFAs with ethanol. The reaction was found to follow a Langmuir-Hinshelwood (L-H) dual-site mechanism, and demonstrated that both Brønsted and Lewis acid centers participate equally in the esterification reaction [67].

Shi et al. prepared sulfonated zirconia directly by impregnating ammonium persulfate on crystalline zirconia, which was followed by calcination temperatures of 573.15–773.15 K. Their catalyst exhibited high activity in the transesterification of soybean oil with methanol and achieved an 84.6% yield of biodiesel because of the preferable superacid sites on the surface of the catalyst [68]. Many researchers investigated different oils for biodiesel production, including sunflower oil, where sono-sulfated zirconia nanocatalyst was prepared via an ultrasound-assisted impregnation/hydrothermal hybrid method. The performance of sulfated zirconia nanocatalyst in biodiesel production from sunflower oil showed that ultrasound-assisted synthesized nanocatalysts gave higher conversion in comparison to non-sonicated catalysts. Biodiesel conversion in a catalyst with ultrasonic irradiation exceeded 96.9% under constant conditions at 333.15 K reaction temperature, with a methanol/oil molar ratio of 9:1 and 5% catalyst concentration. Biodiesel conversion of sonicated catalyst was well maintained to a high extent (71.4%) after five cycles, while biodiesel conversion of non-sonicated catalyst barely reached 43.5% [69].

Another study investigated bamboo leaf ash, which was utilized as ZrO_2 support for a heterogeneous catalyst application. The preparation of ZrO_2-supported bamboo leaf ash (ZrO_2/BLA) was conducted via the impregnation method with a metal content of 20 wt. %. The results showed that the physicochemical characteristics of ZrO_2/BLA facilitated catalytic activity in biodiesel conversion. The microwave-assisted method gave yields comparable to those obtained via the reflux method in less time. The optimized conditions of FAME production using the microwave-assisted reaction method were a 15:1 methanol-to-oil molar ratio, 30 min of reaction time, and 12 wt. % catalyst weight. The catalyst exhibited reusability properties, as indicated by its relatively similar yields, initial rates, and turnover frequencies observed when fresh and reused catalysts were used [70].

Another zirconium-based carbonaceous catalyst was synthesized, where a two-step method (metal ion chelation and sulfonation) was used at low temperature. The catalyst obtained 8.45 mmol/g acid content for esterification of oleic acid, at which it managed to obtain 99% biodiesel yield at 313.15–365.15 K. After three cycles, the biodiesel yield was still 82%, 93%, and 90%, respectively. Such a catalyst had a high activity, which was due to low activation energy, and it showed a potential application for a greener production of biodiesel [71].

Calcium-based catalysts derived from waste shells were synthesized via the wet impregnation method. Biodiesel via transesterification was synthesized to FAME, where methanol was used. Such a catalyst showed excellent catalytic performance, where biodiesel was yielded at 90.1% in three hours. Reusability after three times was investigated as well, where the catalyst yielded around 70% [72].

Another study produced biodiesel from waste *Phoenix dactylifera* L. kernel oil in the presence of synthesized efficient heterogeneous metallic oxide catalyst (Mn@MgO-ZrO_2). The performance of the synthesized metallic oxide catalyst was based on biodiesel yield and optimized. The optimum biodiesel yield was 96.4%, when the process temperature was 363.15 K and catalyst loading was 3 wt. %. Methanol-tooil ratio was 15:1 with a reaction duration of 4 h [73].

Another heterogeneous acid catalyst supported by zirconia tungstophosphoric heteropolyacid was obtained through the sol–gel method combined with a subsequent hydrothermal treatment under mild conditions. The zirconia support was generated by hydrolysis of an alkoxyde precursor in the presence of the heteropolyacid, which led to materials with homogeneously well-dispersed clusters, as well as to an increasing contribution of the tetragonal ZrO_2 crystalline phase. A sample with a 30% mass percentage of heteropolyacid was identified as the most efficient catalyst because it afforded conversions above 90% and showed lower loss of activity over successive reaction runs among the studied materials [74].

Another process for catalytic conversion in biodiesel production uses microalgae. Guldhe et al. used a heterogeneous acid catalyst, tungstated zirconia (WO_3/ZrO_2), which was evaluated for conversion of *Scenedesmus obliquus* lipids. The tungstated zirconia catalyst displayed maximum biodiesel conversion of 94.58% at 373.15 K, with 12:1 methanol-to-oil molar ratio and 15% of catalyst amount, which was based on oil weight after 3 h. Tungstated zirconia showed comparable biodiesel conversion to homogeneous catalysts, while, for the enzyme catalysts, the conversion was higher [75].

Kalavathy used *Ulva lactuca* marine microalgae for the production of biodiesel, where oil extracted from microalgae was transesterified into biodiesel using silica doped with zinc oxide as a novel heterogeneous nanocatalyst. The maximum biodiesel yield of 97.43% was achieved at the optimized calcination temperature (1073.15 K), with a catalyst concentration of 8%, along with 9:1 methanol-to-oil ratio, 328.15 K reaction temperature, and 50 min reaction time. The marine microalgae *Ulva lactuca* was found to be a potential source for biodiesel production [76].

3.2. ZnO-Based Catalysts

Using zinc in catalyst formation was the topic of many research papers. Sodium/ZnO-loaded SBA-15 was prepared using a one-pot method under atmospheric conditions without employing hydrothermal treatment and following the wet impregnation method. The catalyst was utilized for transesterification from virgin cotton seed oil, and the catalyst activity was dependent on its basic strength. Under optimal reaction conditions of catalyst amount (12 wt. %), methanol-to-oil molar ratio (24:1), and reaction temperature (338.15 K), the prepared catalyst yielded more than 98% FAME in 4 h of reaction. The catalyst was able to yield a conversion level as high as approximately 74% even in the fifth cycle after regeneration [77].

Baskar et al. developed manganese-doped zinc oxide, which was used as a heterogeneous catalyst for the production of biodiesel from Mahua oil. The 8% (*w*/*v*) catalyst concentration, 1%:7% (*v*/*v*) oil-to-methanol ratio, 50 min of reaction time, and 323.15 K reaction temperature were found to be the optimum process conditions for a maximum biodiesel yield of 97% [78]. The same research group also investigated heterogeneous Ni-doped ZnO nanocatalyst for biodiesel production from castor oil with high FFA. The optimum conditions for transesterification were an oil/methanol molar ratio of 1:8, catalyst loading of 11% (*w*/*w*), and reaction temperature of 328.15 K for 60 min of reaction time using the response surface method. The study also confirmed that the Ni-doped ZnO nanocatalyst can be reused efficiently for three cycles [79].

Another study was focused on the use of cobalt-doped zinc oxide nanocatalyst for the production of biodiesel from *Mesua ferrea* oil, which under optimal reaction conditions achieved maximum biodiesel conversion of 98.03% after 3 h at 333.15 K with 2.5 wt. % catalyst loading and 1:9 oil-to-methanol molar ratio [80].

Soltani et al. investigated the use of mesoporous $SO_3H\text{-}ZnAl_2O_4$ solid acid catalyst using a microwave irradiation heating system for one-step esterification of palm fatty acid distillate (PFAD). The investigated mesoporous $SO_3H\text{-}ZnAl_2O_4$ catalyst displayed unique properties and achieved the highest FAME yield of 94.59% at 20 min under optimum esterification conditions with a catalyst concentration of 1.5 wt. %, methanol-to-PFAD molar ratio of 9:1, reaction temperature of 333.15 K, and mixing intensity of 300 rpm using a microwave irradiation heating system [81].

A heterogeneous catalyst composed of Mn-ZnO capped with polyethylene glycol (PEG) was utilized for transesterification of oil extracted from *Nannochloropsis oculata* into biodiesel using methanol as an acyl acceptor. The process parameters for heterogeneous catalysis of *N. oculata* to biodiesel were optimized (oil/methanol molar ratio of 1:15, catalyst loading of 3.5% (*w*/*w*), reaction temperature 333.15 K for 4 h). The yield of biodiesel obtained from *N. oculata* species using the Mn–ZnO nanocomposite capped with PEG was 87.5%, and it could efficiently be reused for four cycles [82].

Another lithium/zinc-based catalyst from chicken bones (Li/Zn-Cb) was synthesized using the wet impregnation method using different metal ratios (Li:Zn = 1:2, 2:2, and 2:1). The synthesized Li/Zn-Cb catalyst displayed feasibility and activity for transesterification of waste canola oil (WCO), which was investigated under different operating conditions. The results showed that integrating the chicken bone powder with Li:Zn = 2:2 could enhance the FAME content significantly (by more than four-fold), resulting in a 98% yield (at 333.15 K reaction temperature with 3.5 h of reaction time, catalyst dosage of 4%, and 18:1 molar ratio of MeOH/WCO) [83].

Escorsim et al. developed zinc stearate as a catalyst for the production of non-ionic surfactants and FAs that can be converted to FAMEs (biodiesel) by esterification. Their experiments were performed in a continuous stirred tank reactor (CSTR), where the effect of temperature (413.15–463.15 K), palm-oil-to-water molar ratio (1:10–1:53), and catalyst amount (2–10 wt. %) were evaluated. High contents of FFAs (up to 60 wt. %) with 35 wt. % diacylglycerol and 20 wt. % monoacylglycerol were obtained. In addition, zinc stearate maintained its catalytic activity for palm oil hydrolysis and could be reused for five cycles [84].

3.3. TiO_2-Based Catalysts

Titanium-dioxide-based catalysts were also investigated [85]. Gardy et al. reported that a novel, efficient, and recyclable mesoporous $TiO_2/PrSO_3H$ solid acid nanocatalyst was synthesized by the post-synthetic grafting of propyl sulfonic acid groups onto a mixed phase of a TiO_2 support. The catalytic performance of $TiO_2/PrSO_3H$ on the production of FAME via simultaneous esterification and transesterification reactions from used cooking oil was studied. Here, 98.3% FAME was obtained after 9 h of reaction time with a 1:15 molar ratio of oil to methanol, 333.15 K reaction temperature, and 4.5 wt. % catalyst loading. The solid acid nanocatalyst was recycled four times without significant loss of catalytic efficiency [86].

Titanium was also used in the preparation of a nanocatalyst consisting of TiO_2-Cu_2O nanoparticle composites. TiO_2 nanoparticles were prepared via an ultrasonic-assisted sol–gel method using titanium tetra-isopropoxide, and TiO_2-Cu_2O nanoparticle composites were later prepared via an electrochemical method. They were effectively used as a catalyst in the synthesis of thumba ethyl ester (biodiesel) via a transesterification reaction between thumba oil and ethanol. Prepared TiO_2-Cu_2O nanoparticles were useful for biodiesel production and yielded a 60% conversion rate of TGs from thumba oil [87].

Another environmentally friendly synthesis method of a TiO_2-ZnO heterogeneous catalytic system was described where *Ulva lactuca* seaweed was effectively utilized for biodiesel production. Optimized conditions for higher conversion to FAME (15.8 mL) included 4 wt. % catalyst for 4 h at 333.15 K. The total product yield was calculated as 82.8% of conversion to FAME [88].

A tungsten (W)-supported TiO_2/SiO_2 catalyst for triglyceride transesterification using a sol-gel method was also reported. Optimized reaction conditions of 5 wt. % catalyst, 30:1 methanol-to-oil molar ratio, and 338.15 K reaction temperature yielded more than 98% fatty acid ethyl ester (FAEE), which was obtained in 4 h [89].

Two new and efficient titanium-based sulfonated catalysts, designed as ZrO_2–TiO_2–SO_3H nanorods and ZrO_2-TiO_2@SO_4^{2-} nanorods, were prepared for biodiesel production via esterification of palmitic acid. The two catalysts had a high content of sulfate groups, which was demonstrated by the weight ratio of S/(Zr + Ti) and obvious peaks of Brønsted acid sites. As a result, ZrO_2-TiO_2-SO_3H and ZrO_2-TiO_2@SO_4^{2-} revealed strong catalytic activities in the esterification of palmitic acid. ZrO_2-TiO_2-SO_3H nanorods exhibited higher reusability, and the yield of biodiesel was more than 85% after five recycles [90].

A solid acid S-TiO_2/SBA-15 catalyst was synthesized using a direct wet impregnation process for biodiesel production from hydrolyzed waste cooking oil through esterification reaction. Biodiesel yielded at 95% and was obtained under optimum reaction conditions with 1% catalyst loading. The catalyst exhibited 90% efficiency for three recycles, without regeneration. A purification step is unnecessary for such a catalyst, which simplifies the process and leads to no generation of wastewater, which makes such a catalyst an environmentally friendly replacement of conventional catalysts [91].

Li_2TiO_3 was used for the transesterification of soybean oil into biodiesel and prepared through a solid-state reaction that involved mixing and grinding TiO_2 and Li_2CO_3, followed by calcination at

1073.15 K for 2 h. A biodiesel conversion rate of 98.5% was obtained under optimal reaction conditions of a methanol-oil molar ratio of 24:1, catalyst amount of 6 wt. %, and a reaction temperature of 338.15 K for 2 h [92].

Another lithium/titanium-based catalyst was investigated by Alsharifi et al., for transesterification using the wet impregnation method with lithium implanted on TiO_2. Such a catalyst yielded at 98% of transesterification, with 5 wt. % catalyst loading in optimum conditions, such as a reaction temperature of 328.15 K, a 24:1 methanol-to-oil ratio, and 3 h of reaction time [93].

3.4. MgO-Based Catalysts

Reports showed the investigation of nano-composite MgO, Al_2O_3-CaO, and TiO_2 for efficient conversion of novel non-edible seed oil of *Silybum eburneum* into liquid biodiesel. The highest conversion efficiency of 91% biodiesel yield was achieved using MgO catalyst followed by Al_2O_3-CaO and TiO_2 at 0.1% catalyst loading, with an optimal molar ratio of 1:3, temperature of 343.15 K, reaction time of 3 h, and stirring rate of 600 rpm using the reflux transesterification route [94].

3.5. Magnetic Catalysts

The magnetic properties of solid acid catalysts are excellent for separating the catalyst from the reaction medium. However, since the surface of magnetic oxide materials is unstable under acidic conditions and very sensitive (compared to titanium), the particles can easily be aggregated into large clusters. Such large clusters cause anisotropic dipolar interactions, which result in loss of their catalytic activity [95,96]. Magnetic particles are based on compounds with magnetic characteristics, such as those containing iron, cobalt, and nickel. Magnetic catalysts can easily be separated and recovered from reaction mixtures, compared to heterogeneous catalysts that use centrifugation and filtration as forms of separation. Therefore, the main advantage of magnetic catalysts is their simple and rapid recovery through magnetic separation (Figure 4). Another advantage is the property of high specific surface area, which increases catalytic activity via active sites [97]. For example, impregnation of iron particles not only provides magnetism to the catalyst, but also enhances the release of volatile substances, which increases the surface area and volume of the particles. Yet another advantage of magnetic catalysts is that there is almost no loss of catalytic activity after several cycles of reusability [2,98].

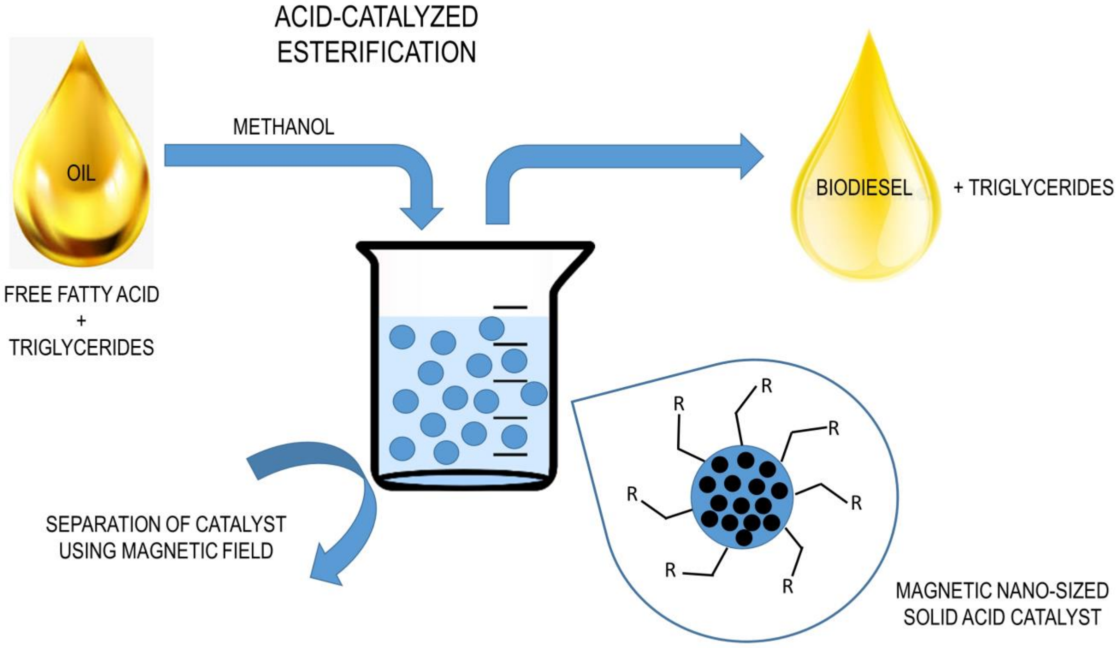

Figure 4. Scheme of magnetic solid acid-catalyzed esterification for biodiesel production.

Magnetic ZnO/$BiFeO_3$ was prepared using a co-precipitation method and later applied as a cheap magnetic nanocatalyst for biodiesel production from canola oil through a transesterification reaction. The optimum conditions for the process consisted of a molar ratio of methanol/canola oil of 15:1, a reaction temperature of 338.15 K, and a catalyst amount of 4 wt. %, in which the conversion of canola oil yielded 95.43%. The catalyst was recycled five times and FAME yield was maintained at more than 92.08% [99].

Another study reported on the use of nanoferrites $NiFe_2O_4$ and $Ni_{0.3}Zn_{0.7}Fe_2O_4$. Nickel–ferrite and mixed nickel-zinc ferrite were successfully synthesized via a combustion reaction using a conical reactor. The catalysts were used to convert soybean oil into biodiesel. A biodiesel yield of 94% was obtained with $Ni_{0.3}Zn_{0.7}Fe_2O_4$ and a yield of 49% was obtained with $NiFe_2O_4$ [100].

Another magnetic core-shell SO_4/Mg-Al-Fe_3O_4 catalyst was synthesized via stepwise co-precipitation, encapsulation, and surface functionalization. The catalyst was active for waste cooking oil transesterification and oleic acid esterification. Optimum conditions for the transesterification of waste cooking oil over the sulfated solid acid catalyst were 368.15 K, a methanol-oil molar ratio of 9:1, and 300 min duration of reaction. Under these conditions, 98.5% FAME yield was achieved. Esterification of oleic acid to methyl oleate resulted in 88% yield after 150 min under the same reaction conditions. The magnetic solid acid catalyst exhibited good thermal and chemical stability and enabled facile catalyst separation post-reaction and the production of high-quality biodiesel [101].

Gardy et al. also reported on the use of novel magnetic SO_4/Fe-Al-TiO_2 solid acid catalyst for biodiesel production via transesterification of waste cooking oil. The nanocomposite catalyst was prepared with TiO_2 nanoparticles with alumina as a buffer layer. The catalyst reportedly achieved 96% yield from waste cooking oil after 2.5 h of reaction at 363.15 K, using 3 wt. % magnetic catalyst, and a methanol-oil molar ratio of 10:1. The catalyst was also effective for feedstocks containing up to 20 wt. % FFA and was stable for over 10 recycles [48].

An investigation into the catalytic activities of magnetic solid acid catalyst via biodiesel synthesis from waste oils was reported by Li et al. The magnetic catalyst was synthesized via immobilization of an ionic liquid precursor obtained from (3-aminopropyl)trimethoxysilane onto a magnetic core. The solid acid exhibited a higher activity than traditional acid catalysts and ionic liquid precursors. The core-shell structure and magnetic attraction between the particles provided strong ionic interactions which resulted in high activity and stability. The main advantages of the magnetic catalyst were easily accessible acidic sites, simple magnetic separation, and high waste oil utilization [102].

Using cassava peel biochar, a magnetic sulfonated solid acid catalyst was synthesized by incorporating Fe_3O_4 nanoparticles, which were synthesized via the co-precipitation method and incorporated in the sulfonated biochar via ultrasonication, to obtain a magnetized sulfonated biochar catalyst. The acid sites on the shell structure are easily accessible to reactant sites as a result of Fe_3O_4 nanoparticles' excellent stability. Magnetic properties also improve the separation of catalyst after the transesterification process. Under optimal parametric conditions, biodiesel yield was 98.7% and the enhanced stability and activity of the magnetic catalyst were a result of strong ionic interactions between particles, high sulfonic acid group density, and higher accessibility of reactants toward acidic sites. The catalyst was recycled five times and obtained a yield of more than 75% [103].

Finally, Zhang et al. reported improved biodiesel production process efficiencies using a series of magnetically acidic poly(ionic liquid) catalysts with varying hydrophobicity and controllable acidity. The investigated catalyst exhibited 96.1% biodiesel yield for oleic acid esterification and 91.7% biodiesel yield in transesterification of crude *Euphorbia lathyris* L. oils. Moreover, the catalyst managed to sustain constant activity with biodiesel yield of 87.5% after five cycles in transesterification and was easily separated using a magnet [104].

4. Use of Solid Acid Catalysts in Recent Studies

Careful design of robust, efficient, and stable solid acid catalysts that can dramatically improve the efficiency of biodiesel production is still an important challenge. The ideal solid acid catalyst for esterification and transesterification reactions should have characteristics such as strong Brønsted and/or Lewis acid properties, unique porosity or textural properties, and a hydrophobic surface [1]. On the other hand, deactivation, poisoning, and leaching of acid sites in the reaction medium should be avoided. Considering these characteristics, the paragraphs below summarize recent advances in biodiesel production using novel solid acid catalysts.

Acid catalyst (tetraoxosulfate VI acid) was used instead of alkali catalyst (NaOH or KOH) to lower the activation energy for quick formation of esters and glycerin. The available literature is mainly focused on researching biodiesel production with the use of new solid acid catalysts, where a high percentage of conversion rate was reached [105].

Gaurav et al. developed a kinetic model to describe the esterification and transesterification reactions for biodiesel reactions from high FFA yellow grease feedstocks via simultaneous esterification and transesterification on a solid catalyst prepared by supporting a heteropolyacid (HSiW) on alumina (HSiW/Al_2O_3). The conversion of a model yellow grease to biodiesel was faster than pure canola oil at 423.15 K because of the faster esterification of FFA with solid acids [106].

Wang et al. synthesized novel sulfonated magnetic solid acid catalysts (ZrFe-SA-SO_3H) with both Brønsted and Lewis sites to obtained high yields of biodiesel (92.7%–99.5%) for the first catalytic cycle at 363.15 K for 4 h [107].

Concurrently, Sandouqa et al. revealed that a lignin-based solid acid catalyst has high potential to esterify waste vegetable oil to about 92% conversion. Furthermore, it demonstrated about 57% conversion to fatty acid methyl esters (FAME) after sulfonation time of 1 h, catalyst loading of 10 wt. %, a methanol-to-WVO molar ratio of 35:1, a reaction temperature of 338.15 K, and reaction time of 6 h. Furthermore, the results showed that the lignin-based acid catalyst can be reused at least 10 times with high FFA conversion (> 75%) [108].

Ibrahim et al. used ZrO_2 loaded on different supports (Al_2O_3, Fe_2O_3, TiO_2, and SiO_2) in environmental applications such as the production of biodiesel, where the conversion rate reached 48.6% after a reaction time of 3 h and reaction temperature of 393.15 K [109].

In another recent study, Masteri-Farahani et al. prepared a graphene-based acid catalyst, GO–PrSO_3H, through a simple two-step process. Surface modification with (3-mercaptopropyl)trimethoxysilane followed by oxidation of sulfide groups led to the production of sulfonic acid sites on graphene oxide nanosheets. Biodiesel as a clean fuel was produced with acceptable yield over GO-PrSO_3H compared to a blank test using oleic acid and methanol as substrates [110].

Yang et al. indicated the possibility of biodiesel production at room temperature using a Na_2SO_3 catalyst with a biodiesel yield of more than 96% [111].

Additional studies not described in the text above are presented in Table 1, where examples of the use of solid acid catalysts in biodiesel production are compared.

Table 1. Examples of the latest use of solid acid catalysts in biodiesel production.

Oil Feedstock (Molar Ratio)	Catalyst	Operating Conditions	Conversion/Yield	References
Sewage sludge + methanol	$SO_4^{2-}/Al_2O_3-SnO_2$	403.15 K 4 h 8 wt. % catalyst	73.3% yield	[112]
Oleic acid + methanol (120:1)	Bismuth silicate (BS_{30})	353.15 K 2 h 0.3 g of catalyst	90% conversion	[113]
Palm fatty acid distillate (PFAD) + methanol (21:1)	BSY-SO_3H (brewer's spent yeast (BSY))	338.15 K 3 h 8 wt. % catalyst	87.8% conversion	[114]
Waste frying oil + methanol (12:1)	Al_2O_3-supported coconut chaff	338.15 K 2.5 h 1.5 wt. % catalyst	91.05% yield	[115]
Soybean oil + methanol (35:1)	Fe_3O_4/SiO_2	393.15 K 6 h 9 wt. % catalyst	93.3% conversion	[116]
Pongamia pinnata raw oil + methanol (12:1)	Fe_3O_4-loaded catalytic eggshell (CES-Fe_3O_4)	338.15 K 2 h 2 wt. % catalyst	98% yield	[117]
Palm oil + methanol (15:1)	4-Benzenediazonium sulfonate; SO and SO_3H sulfonic groups on carbon catalyst	473.15 K 7 h 20 wt. % catalyst	98.1% yield	[118]
Soybean oil + methanol (20:1)	Reduced graphene oxide	353.15 K 3 h 3 wt. % catalyst	99% yield	[119]
Castor oil + ethanol (12:1)	MgO-Urea-800	348.15 K 1 h 6 wt. % catalyst	96.5% yield	[120]
Waste frying oil + methanol (12:1)	Anthill-eggshell-Ni-Co (AENiCo)	343.15 K 2 h 3 wt. % catalyst	90.23% yield	[121]
Rubber seed oil + methanol (12:1)	Calcium oxide (CaO) derived from eggshells	N.D. 4 h 5 wt. % catalyst	97.84% conversion	[122]

N.D.—not determined.

Low-cost raw materials, such as waste cooking oils and non-edible oils, were identified as an attractive oil feedstock with the potential to reduce production costs and, therefore, improve the economic feasibility of biodiesel production. Generally, acid catalysts are insensitive to FFAs and water and, therefore, can catalyze the transesterification of TGs and esterification of FFAs into biodiesel more significantly. Furthermore, the acid-catalyzed process, in addition to being an efficient approach for biodiesel production, especially from low-cost oil feedstocks, can also address waste disposal issues [116].

5. Future Prospects

Solid acid catalysts are efficient in producing biodiesel from feedstocks with high FFA content. Nevertheless, the insufficiency of researched processes using different metal oxides, as well as magnetic nano-sized materials, is an indication that solid acid catalysis based on these materials may be more comprehensively and intensively explored. New research in this field will help to establish the potential of catalysts based on different metal oxides, as well as ensure the importance of biodiesel.

Despite all of the challenges the world was forced to witness regarding environmental damage and climate change, catalysis offers potential solutions for the problems inherent in most industrial processes (such as petrochemistry and bulk chemistry); these new catalytic solutions can help to secure an environmentally and climate-friendly industrial society. The use of solid acid catalysts based on metal oxides, especially based on magnetic nano-sized materials, will simplify the catalysis process, as well as ensure more sustainable implementation of different solid acid catalysts in biodiesel production. It will provide greener synthesis routes for biofuel production, which will have potential as simple and cost-effective routes with high catalytic activity and reusability.

6. Conclusions

The aim of recent studies was to bring down the cost of production, in which the reusability of catalyst plays a major role. These studies showed that a great deal of effort is directed toward reusing of the catalyst, where the yield of the biodiesel production is still high (more than 90%). Nevertheless, there are still some drawbacks that highlight the continuing need to design improved catalysts for esterification and transesterification of different feedstocks. It must be taken into account that the choice of feedstock for biodiesel production depends greatly on environmental conditions, agricultural practices, soil availability and characteristics, and geographical locations, which vary from country to country [123]. The feedstock used for biodiesel production is a critical parameter in estimating the total cost of biodiesel production and revenue [124]. These new methods for reducing biodiesel production costs offer improved production technologies for better yield, reduced capital costs, and reduced raw material costs, of which feedstock cost is the most dominant [125]. Therefore, many studies of various non-food feedstocks including waste cooking oil (WCO), microalgae, and non-edible seed oils such as *Jatropha*, *Pongamia*, neem, *Camelina*, soapberries, and animal fats, along with low-cost technologies, were performed in attempts to reduce the cost of biodiesel and to commercialize its products in both developing and developed countries [126,127].

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