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Heterogeneous Solid Acid Catalysts for Sustainable Biodiesel Production from Wastewater-Derived Sludge: A Systematic and Critical Review

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Review

Heterogeneous Solid Acid Catalysts for Sustainable Biodiesel Production from Wastewater-Derived Sludge: A Systematic and Critical Review

Mohsen Ansari [1,2,3], Hamzeh Ali Jamali [1,2], Reza Ghanbari [1,2], Mohammad Hassan Ehrampoush [3], Parvin Zamani [3] and Behnam Hatami [3,*]

[1] Department of Environmental Health Engineering, School of Health, Qazvin University of Medical Sciences, Qazvin, Iran; mohsen.ansari90@yahoo.com

[2] Social Determinants of Health Research Center, Research Institute for Prevention of Non-Communicable Diseases, Qazvin University of Medical Sciences, Qazvin, Iran.

[3] Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran;

* Correspondence: bhatami88@yahoo.com; Tel.: (+98 (35) 3149 2299)

Abstract: This comprehensive review has systematically examined the use of heterogeneous solid acid catalysts in the production of biodiesel from wastewater-derived sludge by using the PRISMA methodology. The manuscript highlighted the composition and characteristics of wastewater-derived sludge, presenting both the opportunities and challenges associated with its use as a feedstock for biodiesel production. Various types of catalysts were dis-cussed, with a detailed exploration of heterogeneous solid acid catalysts, including zeolites, hetero-polyacid (HPA), mixed metal oxides, and sulphonic acid group catalysts. The advantages and limitations of these catalysts were critically analyzed, providing a balanced view of their potential in industrial applications. The application section delved into the catalytic transesterification reaction, mechanisms of biodiesel production, and the effects of catalyst loading on yield. Performance metrics such as catalytic activity, stability, recyclability, cost-effectiveness, and environ-mental impact were thoroughly evaluated, offering a clear understanding of the efficacy of these catalysts. Synthesis and characterization techniques were also reviewed, shedding light on the latest preparation methods and characterization techniques. Recent advances in catalyst development were presented, showcasing the innovative strides made in enhancing catalyst performance. The environmental and economic implications of using solid acid catalysts for bio-diesel production were assessed, emphasizing the importance of sustainability and economic viability.

Keywords: wastewater; sludge; heterogeneous catalysts; biodiesel production

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1. Introduction

Municipal wastewater-derived sludge (MWS), also known as sewage sludge, is a byproduct of the treatment of wastewater in municipal wastewater treatment plants. It consists of the solid material that settles out during the treatment process, as well as any other solids that are removed from the wastewater [1]. This sludge can contain a variety of organic and inorganic materials, including pathogens, heavy metals, persistent organic pollutants and organic trace pollutants [2].

MWS can be treated and used in various ways, such as being applied to agricultural land as a fertilizer by using a dewatered anaerobic sludge [3], soil conditioner by conditioning and dewatering [4], bubbling fluidized bed incineration process [5], bioenergy (biogas or syngas) production [6] or disposed of in landfills [7]. However, it is important to properly manage and treat MWS to minimize its environmental and health impacts.

The management of MWS is critically important for public health according to the United Nations' sustainable development goals (SDGs) [8], the sustainability and circular economy concepts [1], and energy usage, especially in the European sustainability plan [9]. Improper MWS management also causes the greenhouse gaseous (GHG) emissions [10], posing ecological risk [11] and

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contributing to climate change through technologies used for sludge treatment [12]. However, MWS has energy potential through chemical reactions to convert the biomass into renewable biofuels such as biogas and biodiesel [13].

Biofuels are a broad category of renewable fuels derived from biological materials, such as plant biomass, algae, and animal fats, and MWS [14]. Biodiesel is a specific type of biofuel produced from vegetable oils, animal fats, and MWS through a chemical process called transesterification [15].

The biodiesel produced from MWS can then be used as a renewable and sustainable fuel source for vehicles, machinery, and heating applications. This process helps to reduce the environmental impact of wastewater treatment and provides an alternative use for a waste product [16]. While the direct conversion of MWS into biodiesel is not straightforward, the indirect connections and potential synergies between the two processes offer opportunities for sustainable resource utilization and energy production [17]. These connections can contribute to the development of integrated, environmentally friendly approaches to waste management and renewable fuel production.

There are several methods for producing biodiesel from MWS, each with its own advantages and challenges. Transesterification, as the most common method, involves reacting the sludge with an alcohol, such as methanol or ethanol, and a catalyst to convert the triglycerides in the sludge into biodiesel and glycerol [18]. Pyrolysis is a thermal decomposition process that can be used to convert sludge into bio-oil, which can then be further processed into biodiesel. This method involves heating the sludge in the absence of oxygen to break down the organic matter into liquid bio-oil, gases, and char [19]. As another method, supercritical transesterification involves using supercritical fluids, such as supercritical methanol or ethanol, to convert the sludge into biodiesel [20]. Supercritical transesterification can offer higher reaction rates and yields compared to conventional transesterification processes [21]. Hydrothermal liquefaction involves converting the sludge into biocrude oil through high temperature and pressure in the presence of water. The biocrude oil can then be upgraded into biodiesel [22]. Finally, microbial lipid extraction is known as using microorganisms to convert the organic matter in sludge into lipids, which can then be processed into biodiesel through transesterification [23]. Each of these methods has its own set of advantages and challenges, including varying energy requirements, yields, and byproduct generation. The choice of biodiesel production method from MWS will depend on factors such as the composition of the sludge, available resources, and desired end products [24].

Researchers are actively investigating catalytic processes as possible substitutes for conventional chemical methods in the sustainable production of biodiesel. These processes are appealing because they offer a unique set of characteristics, such as catalytic activity, affordability, ample supply, and environmentally friendly and efficient manufacturing methods [25]. Although, Guo et al. have reported that biodiesel from transesterification with heterogeneous catalysts shows potential as a petroleum diesel supplement. And they have reviewed various solid-acid catalysts for biodiesel production from any sources [26]. However, the lack of a comprehensive and systematic review of the current literature on sewage sludge hinders the identification of the most effective catalysts and optimal conditions for biodiesel production from MSW. This systematic review aims to address this gap by synthesizing and critically evaluating the existing research to provide valuable insights for future research and industrial applications.

The systematic review will focus on identifying the various types of heterogeneous solid acid catalysts used in biodiesel production from MWS, as well as the specific reaction conditions and performance metrics associated with each catalyst. Additionally, it will assess the environmental and economic implications of using these catalysts in biodiesel production, with a particular emphasis on sustainability and waste management. By consolidating and analyzing the available evidence, this review aims to provide a comprehensive understanding of the current state of research in this field and to identify potential areas for further investigation and improvement.

2. Review Methodology

In this study the Preferred Reporting Items for Systematic reviews and Meta-Analyses (PRISMA) method [27] was used to identifying eligible empirical studies from Scopus and Google scholar

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databases without time limit. Figure S1. Shows the PRISMA chart of study. The eligibility criteria aim to define studies that specifically focus on using heterogeneous solid acid catalysts for converting wastewater sludge to biodiesel, in order to comprehensively evaluate their efficacy for this application. The criteria also exclude inadequate or irrelevant types of studies that do not meet the systematic review objectives.

2.1. Inclusion Criteria

• Types of studies: Experimental studies, modeling studies, life cycle analyses that examine the production of biodiesel from MWS using heterogeneous solid acid catalysts.

• Types of biodiesel feedstock: Studies using primary, secondary, or digested MWS as feedstock. Studies using synthetic wastewater sludge mixtures are also eligible.

• Types of catalytic intervention: Use of heterogeneous solid acid catalysts, such as sulfated metal oxides, zeolites, heteropolyacids, and acid-modified silica, for the transesterification reaction to produce biodiesel from MWS.

• Types of outcome measures: Quantitative outcome measures like biodiesel yield, conversion rate, ester content, fuel properties, catalyst reusability and stability.

2.1. Exclusion Criteria

• Review papers, policy briefs, editorials, and other non-research articles

• Studies focused exclusively on catalyst development without application for biodiesel production

• Studies using only virgin vegetable oils, animal fats, palm or microalgae feedstock

• Studies using homogeneous acid or base catalysts

• Studies reporting insufficient data on quantitative outcome measures

• Duplicate studies or sub-studies of already included research

• Non-English studies

3. Overview of Biodiesel Production from Wastewater-Derived Sludge

3.1. Composition and Characteristics of Wastewater-Derived Sludge

MWS typically is characterized by its high moisture content, low organic matter content, and potential for odor generation [28]. The physical and chemical properties of MWS play a significant role in determining its suitability for various treatment and disposal options [29]. Sludge may also contain a significant amount of organic matter, such as proteins, carbohydrates, and lipids, which can contribute to its nutrient content. Antibiotic resistance genes and human bacterial pathogens [30] present in MWS pose a potential risk to human health and the environment. The microbial communities are influenced by treatment and nutrient load [31]. Heavy metals, such as lead, mercury, and cadmium, can also be the greatest barrier for the application of MWS to land [32] and posing a risk of contamination if released into the environment. Overall, the composition and characteristics of wastewater-derived sludge must be carefully considered when determining the most appropriate treatment and disposal methods to minimize potential risks and environmental impacts [17]. Wastewater treatment plants (WWTPs) produces primary and secondary sludges by utilizing wastewater treatment processes. Primary sludge is typically composed of organic matter, while secondary sludge contains a higher concentration of microorganisms. Both types of sludge also contain nutrients such as nitrogen and phosphorus, making them suitable for biodiesel production. Primary sludge also consist of floating oils and solids, differs from secondary sludge, which is primarily composed of microbial cells and suspended solids produced during aerobic biological treatment [33]. The lipid fraction of the mentioned sludges (fat, oil, and grease), with complex organic materials, can be converted into biodiesel. The characteristics of sludge-derived lipids are variable and highly dependent on the treatment technology used in the WWTP.

3.2. Opportunities and Challenges

Biodiesel production from wastewater-derived sludge can be considered as a solution for both waste management and renewable energy production. However, there are several challenges that need to be addressed in order to fully capitalize on this opportunity. One major challenge is the variability in sludge composition, which can affect the quality and yield of biodiesel produced. Additionally, identifying the optimal methods for collecting various fractions of waste sludge and processing them to achieve maximum lipid extraction poses a major challenge [34]. The presence of contaminants in the sludge, such as heavy metals and pathogens, can pose environmental and health risks if not properly managed [35]. Furthermore, the production process must be economically viable, which is a challenge given the current cost of lipid extraction techniques [36]. Intensive research and understanding of lipid accessibility mechanisms and mass transfer approaches are considered as challenges for the commercial-scale extraction of lipids from cell biomass. Despite these challenges, developing cost-effective and environmentally friendly extraction techniques will be key in scaling up lipid extraction processes for various applications in industries [37]. Additionally, continuous research and innovation in lipid extraction technology will drive advancements in the field and contribute to the sustainable production of lipids from diverse sources [38]. Collaboration between researchers, industry partners, and policymakers is essential to drive innovation and overcome technical barriers. Additionally, implementing strict quality control measures and monitoring protocols can help ensure the safety and sustainability of biodiesel production from wastewater-derived sludge [39]. Figure 1 shows opportunities and challenges of biodiesel production from wastewater-derived sludge.

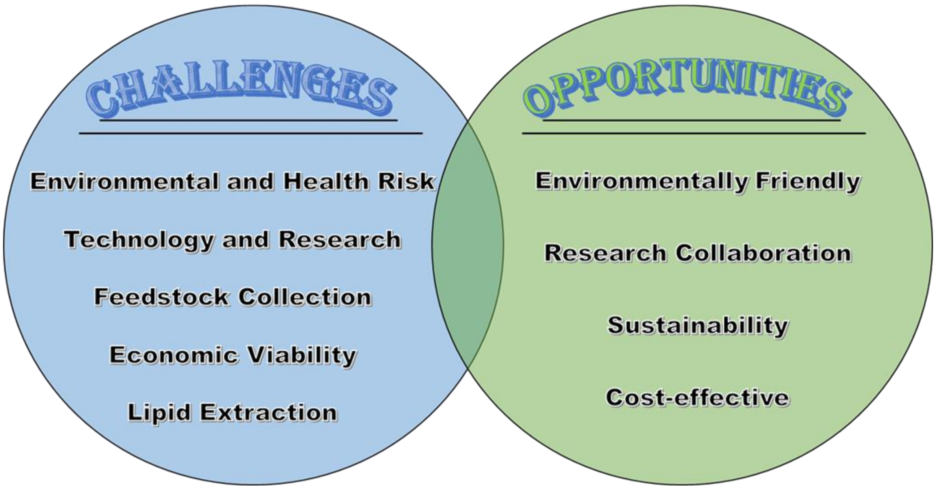

Figure 1. Opportunities and challenges of biodiesel production MWS.

The overall process routes for sludge conversion into biodiesel involve several key steps (Figure 2), including the pre-treatment of raw sludge, lipid extraction from dried sludge, and chemical reactions for producing biodiesel [40]. Since free fatty acids (FFAs) and triglycerides (TGs) are the main lipid components extracted from wastewater, two reactions of esterification and/or transesterification are used to convert these components into biodiesel (Figure 3). In these reactions, stoichiometrically each mole of lipid is converted into three moles of fatty acid methyl ester (biodiesel) [41]. These chemical reactions require a technically suitable catalyst to expedite the reaction rate through lowering the activation energy and finally enhance the efficiency of biodiesel yield [42]. Considering the essential role of the catalyst in the biodiesel synthesis pathway, this issue is a major challenge for producing biodiesel on a commercial scale [43].

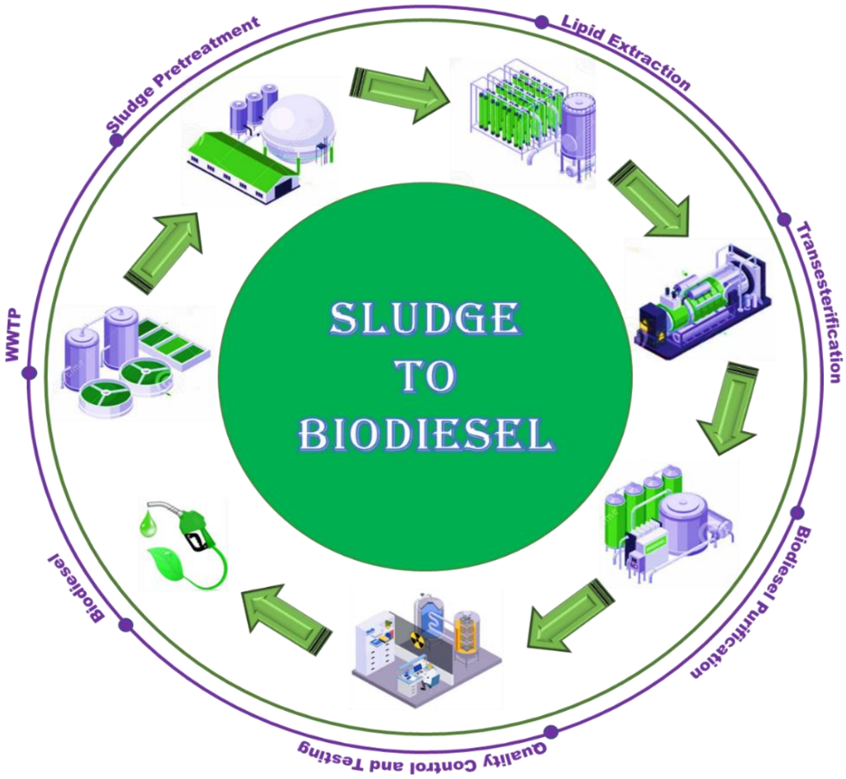

Figure 2. Diagram of process routes for sludge converting into biodiesel.

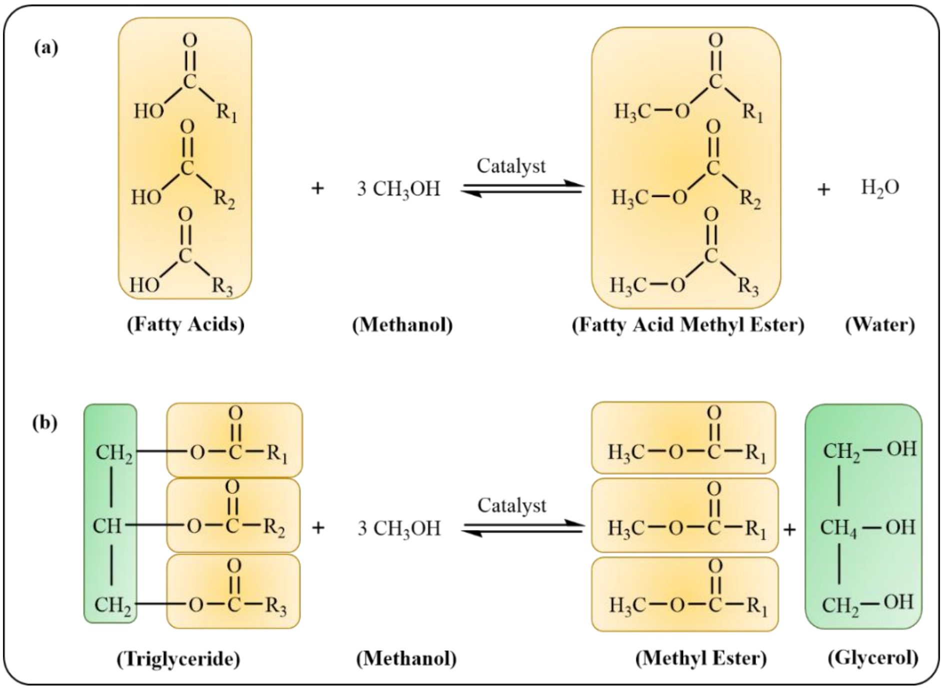

Figure 3. Chemical reactions for biodiesel production: (a) esterification of fatty acids (b) transesterification of triglycerides.

4. Types of Catalysts Used for Biodiesel Production

Various types of catalysts are generally classified as homogeneous (alkali or acid), heterogeneous (solid acid, solid alkali, and bifunctional), and biocatalysts that applied in the transesterification process (Figure 4) [44]. It is noteworthy that there is another reaction for the

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production of biodiesel in the absence of a catalyst, which is carried out under supercritical conditions [45].

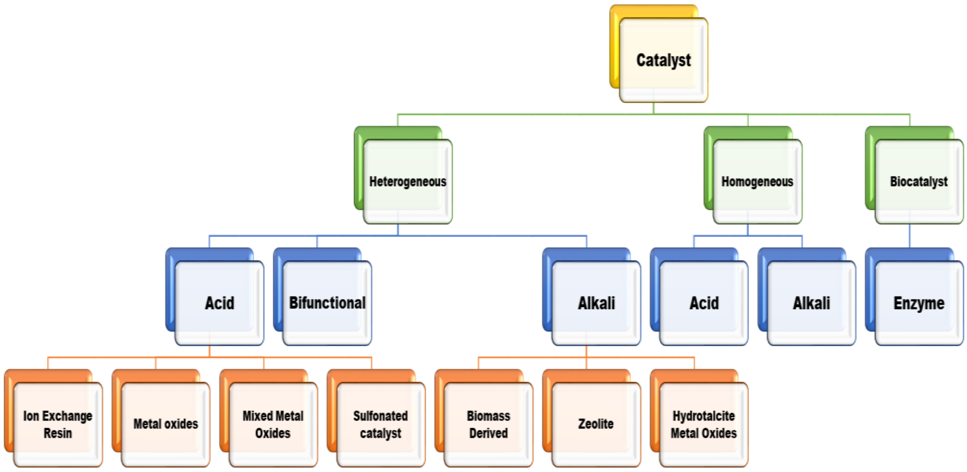

Figure 4. Classification of catalysts used for biodiesel synthesis.

Homogeneous alkali catalysts, which are usually found as soluble forms of compounds, play in the same liquid phase as the reaction mixture. The use of catalysts in the biodiesel industry is standardized because they are highly accessible, have a high reaction rate, and short reaction time [46]. The most frequently used reagents are strong alkalis, for example, NaOH and KOH which help to remove hydrogen (the proton) from alcohol molecules and activate triglyceride and form a biodiesel [47]. In Figure 5, a homogeneous alkaline catalyst that drives the transformation of lipid to its undergoing esterification is illustrated. Methanol is involved in the reaction of the catalyst which gives methoxide anion (CH_3O^-). Consequently, in the next step, the intermediates attack the carbonyl group of the triglyceride, which gives a tetrahedral intermediate. Accordingly, these are the final products of stepwise hydrolysis, which involves the formation of diglycerides, monoglycerides, and glycerol [17].

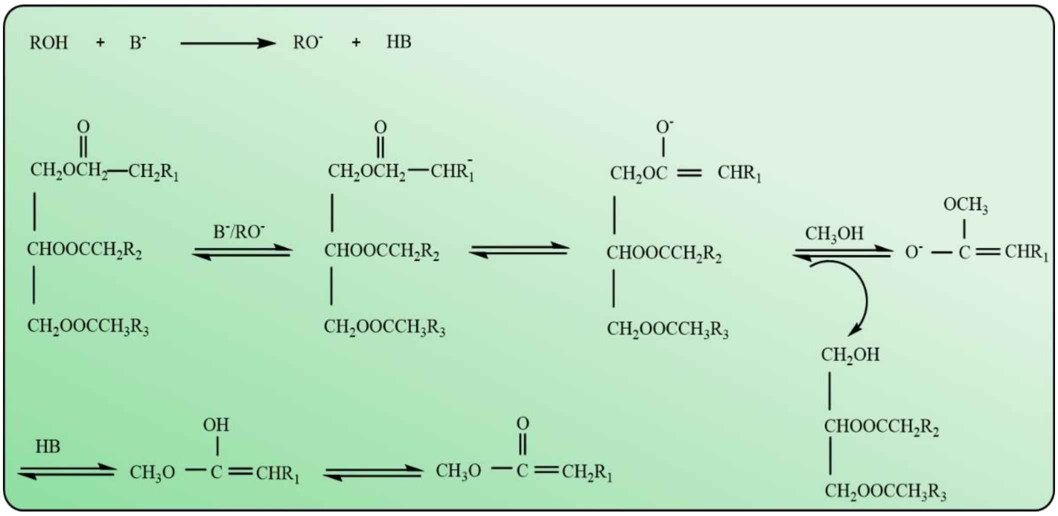

Figure 5. Mechanism of a homogeneous alkaline catalyst transesterification.

Nevertheless, one of the limitations of using alkaline catalysts in producing biodiesel from sewage sludge is the saponification of the reaction mixture [33]. Sewage sludge contains high FFAs (more than 1%), therefor, the reaction catalyzed by the alkali was hindered by the FFAs, resulting in the formation of soap rather than biodiesel (Figure 6). Increasing the viscosity of the products and the difficulty in separating them from the mixture are other consequences of using this type of catalyst [47].

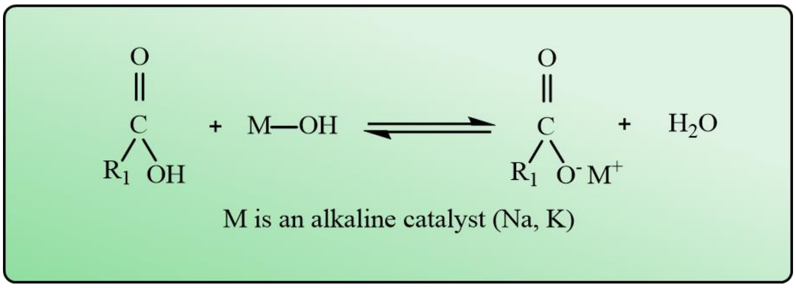

Figure 6. Soup formation during the esterification of sewage sludge in presence of a homogeneous alkaline catalyst.

Homogeneous acidic is another common catalyst used for producing biodiesel. The activity of this catalyst is significantly lower than alkali type, but nevertheless, they are not sensitive to the presence of FFAs in the feedstock [47]. Therefore, they seem to be a suitable option for transesterification of the sludge-derived lipid. Figure 7 illustrates the mechanisms of a homogeneous acidic catalyst during conversion of lipid into its corresponding esters. As shown in Figure 7a, to expedite esterification by an acidic homogeneous catalyst, first, during a bimolecular reaction, the protons of the catalyst are attached to FFAs, and by connecting alcohol molecules to this part, intermediate products are formed. After that, these intermediates are converted to the corresponding esters through rearrangement, dehydration and dehydrogenation processes. Also, to catalyze a transesterification reaction by an acidic homogeneous catalyst, the protons of the catalyst react with TGs and produce ester compounds and glycerol. The mentioned protons are also reused for the next reaction (Figure 7b). Using the homogeneous catalysts in biodiesel production is accompanied by major problems. Acid catalysis is useful, but this process can cause equipment corrosion, high methanol consumption and environmental considerations such as biodiesel washing. Besides, the solubility of the homogeneous catalysts hinders the catalyst recycle process which requires a lot of energy for separation, recycling, and product purification thus increasing the product cost [48]. These challenges highlight the importance of looking for heterogeneous catalysts which would help to solve these problems and make biodiesel production more efficient and sustainable.

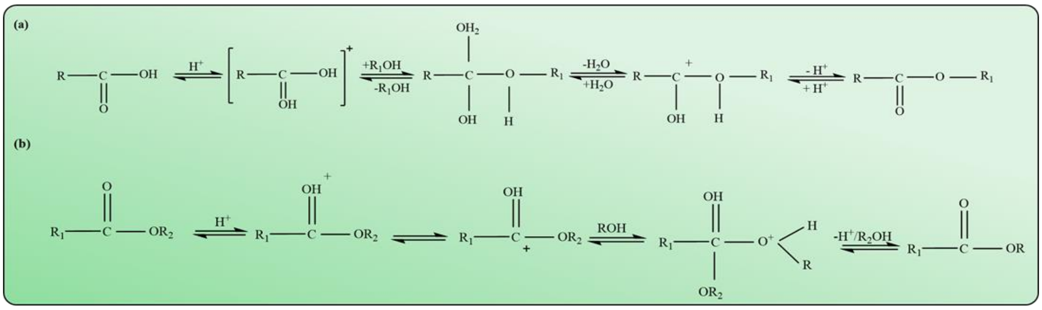

Figure 7. Mechanism of (a) esterification, and (b) transesterification reactions catalyzed by a homogeneous acidic catalyst.

5. Heterogeneous solid acid catalysts: fundamentals and properties

5.1. Definition and Types of Solid Acid Catalysts

Heterogeneous solid acid catalysts, which has gained wide attention recently, generally appear in solid form [49]. In these catalysts, strong acidic groups are anchored on the active sites of solid materials. The solid nature of this catalyst allows it to be easily separated from the liquid mixture after the reaction is complete [50]. Several important characteristics including Brønsted and Lewis

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acidity, number of acidic active sites, and morphology of solid materials are used to classify solid acidic catalysts. Based on this, a variety of acidic solid catalysts including materials with zeolite and zeotype properties, mixed oxides (ion exchange resins, sulfonated materials, etc.), and heteropolysaccharides have been developed to catalyzed biodiesel production reactions from sewage sludge [51].

5.1.1. Zeolites and Zeotype Materials

Zeolites are a type of crystalline inorganic materials made up of TO_4 tetrahedra, where T can be elements like silicon, aluminum, phosphorus, etc. In these structures, each oxygen atom at the tip of the tetrahedron is shared with a neighboring tetrahedron [52,53]. The fundamental characteristics of zeolites have been categorized into two types: intrinsic basicity and additional basicity. Zeolites' intrinsic basic nature is determined by the negatively charged oxygen within the zeolite structure, influenced by both its composition and structure. Moreover, zeolites can exhibit additional basic properties from sources other than framework oxygens, including basic hydroxyls, oxide clusters, supported metals, and more. With this, the production of negative ions in the zeolite structure is increased and as a result, its catalytic activity is improved. AlPO4, MeAPO, and MeAPSO are examples of zeotype with crystalline structure in which the coordinated transition metals such as Si, Al, and P are used [51,54]. Recently, various studies have been conducted on improving the catalytic performance of zeolites and their stability in the reaction environment [55].

5.1.2. Hetero-Polyacid (HPA)

This type of catalyst has a tetrahedral QO4 structure surrounded by metal-oxygen octahedra. Having an ionic structure, these catalysts have acidic properties similar to super-acids in the Bronsted acidity region. The activity of this catalyst in non-polar solvents such as water is much higher than some homogeneous acidic catalysts. Optimizing the conditions for the preparation and synthesis of this catalyst in order to promote biodiesel production is one of the subjects that needs more studies [51].

5.1.3. Mixed Metal Oxides

Mixed metal oxide catalysts include Lewis (anion) and Bronsted acid sites (cation), which provide the required catalytic sites for the transesterification. To this end, hydrogen cations and methoxide are simultaneously formed with the breaking of the O-H bond, resulting in an increase in the reaction between triglycerides and methoxide anions and producing esterified products or biodiesel [56]. Zinc, zirconium, iron, tungsten and tin oxides have received more attention in industries and research studies due to their high stability, strong acid sites and high porosity [57,58].

5.1.4. Sulphonic Acid Group Catalysts

The basic structure of this type of catalyst is sulfonated cross-linked polystyrene. Even though sulphonic acid group catalysts represent outstanding low corrosion and easy separation from the reaction mixture, they encounter higher costs in preparation compared to homogeneous catalysts. In addition, due to the swelling of the pores in organic environments, these catalysts have a high ability to reduce the mass transfer limitation during lipid esterification reactions [51]. Nafion resins and Amberlysts are commercial examples of these catalysts used in biodiesel production reactions.

5.2. Advantages and Limitations of Solid Acid Catalysts

As solid acid catalysts have significant advantages compared to homogeneous catalysts, they are widely used in biodiesel production. The benefits of solid acid catalysts include increased process efficiency, low corrosive nature, moderate energy requirement, easy separation and reusability for several consecutive cycles, use in continuous flow reactors, and less hazardous wastewater generation by eliminating the washing step [43]. Moreover, with the application of such a catalyst, transesterification and esterification reactions can be carried out at the same time [59]. These benefits

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can help in the reduction of production costs as well as the longevity of the catalyst. Nevertheless, solid acid catalysts are confronted with difficulties, some of which are listed in Table 1.

Table 1. Significant problems, causative reasons, and possible remedies for utilizing solid acid catalysts in biodiesel reactions.

Problem	Causative reason	Possible remedies
Low active sites	Using materials with low specific surface area as catalysts	Providing large interconnected pores in the catalyst
Limited mass transfer	Formation of various phases in the reaction mixture	Using a catalyst with a specific surface area and larger pores
Low reaction rate compared to others	Catalyst pore clogging and diffusion limitation on the catalyst surface	Use of appropriate co-solvents in the reaction
Inactivation in the reaction medium	The presence of impurities in the raw material	Synthesis of catalyst with high water adsorption capability
High reaction temperature required	Blocking of the active sites of the catalyst due to water present in the reaction mixture	Catalyst with high water adsorption capability, using a catalyst with a specific surface area and larger pores
Need for high catalyst loading	Water adsorption on the surface of the catalyst	Synthesis of catalyst with high water adsorption capability
Removal of functional groups due to leaching	Ionic groups hydrolyzed by water	Use an appropriate catalyst preparation technique.

6. Application of Heterogeneous Solid Acid Catalysts in Biodiesel Production from Wastewater-Derived Sludge

6.1. Catalytic Transesterification Reaction

The production of biodiesel typically involves transesterification, where triglycerides are reacted with short-chain alcohols in the presence of a catalyst [60]. However, the availability of both the raw materials (feedstock) and the catalyst can constrain the production of biodiesel [61]. In biodiesel production, heterogeneous solid acid catalysts facilitate the transesterification reaction where triglycerides react with an alcohol (usually methanol) to form biodiesel and glycerol [62]. These catalysts offer benefits such as easy separation from the reaction mixture, potential for reuse, and operational under mild conditions [63]. The efficiency of the reaction depends on factors like the type of catalyst, alcohol-to-oil ratio, temperature, and reaction time [64]. The successful application of these catalysts in the transesterification process can lead to the efficient production of high-quality biodiesel from wastewater-derived sludge [65]. It has been reported that transesterification to convert esters into different esters, when using an alkaline catalyst, the reaction tends to proceed more efficiently. On the other hand, when an acid catalyst is used, the reaction is not as favorable because it takes a longer time to occur and results in lower conversion rates [66]. Wastewater-derived sludges can be involved in the transesterification reaction but most of these matters include soap formation and difficulty in product separation that cause to desirability for biodiesel synthesize in competition with human food in addition to their high cost as they are refined oils [67].

Several studies have focused on esterquats precursor through heterogeneous catalyzed-transesterification. Abdul Aziz et al. used calcium oxide (CaO)-based catalysts for production of N-methyldiethanolamine di-ester. Their results indicated that high di-ester yield using ZnO/CaO catalyst, showing durability and reusability benefits over pure CaO catalyst in multiple reaction cycles [68]. Another study explored the catalytic performance of biochar derived from woodchips for biodiesel production. The catalyst which synthesized via transesterification, showed highest biodiesel yield (74.66%) and good reusability (≥5 cycles) under specific reaction conditions [69]. Using waste eggshells, a nanocatalyst (CaO/Au) was developed by Liu et al. for transesterification in biodiesel production. The catalyst showed high activity, with optimal performance at a 12:1

methanol-oil ratio and 1.0 wt% catalyst content at 70°C for 3 hours. The CaO/Au nanocatalyst maintained catalytic activity over 5 recycling cycles, yielding 88.9% biodiesel [70]. Researchers have utilized CaO derived from organic ash supported on titanium dioxide nanoparticles in the catalytic transesterification process. The CaO–TiO_2 catalyst exhibited both basic and acidic properties, crucial for facilitating transesterification of dairy scum oil feedstock. They achieved a peak biodiesel yield of 97.2% under specific conditions: 3 wt.% catalyst concentration, 1:20 oil to methanol molar ratio, 70 °C reaction temperature, 120 minutes reaction time at 300 kPa pressure [71].

6.2. Mechanisms of Biodiesel Production with Solid Acid Catalysts

The catalytic mechanism of the solid acidic catalysts is originated from Bronsted-Lewis's acid theory (Figures 8 and 9). Accordingly, in an esterification reaction initially the active components of the catalyst surface convert the carbonyl groups of FFAs into intermediate products. Then, the hydroxyl groups of methanol combine with these products and produce ester products (Figure 8 (a) and (b)) [72].

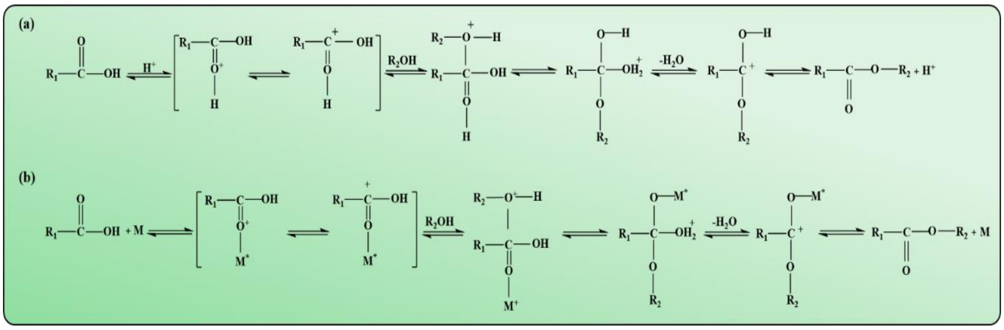

Figure 8. Mechanism of esterification reactions catalyzed by (a) Bronsted's acid theory (b) Lewis's acid theory.

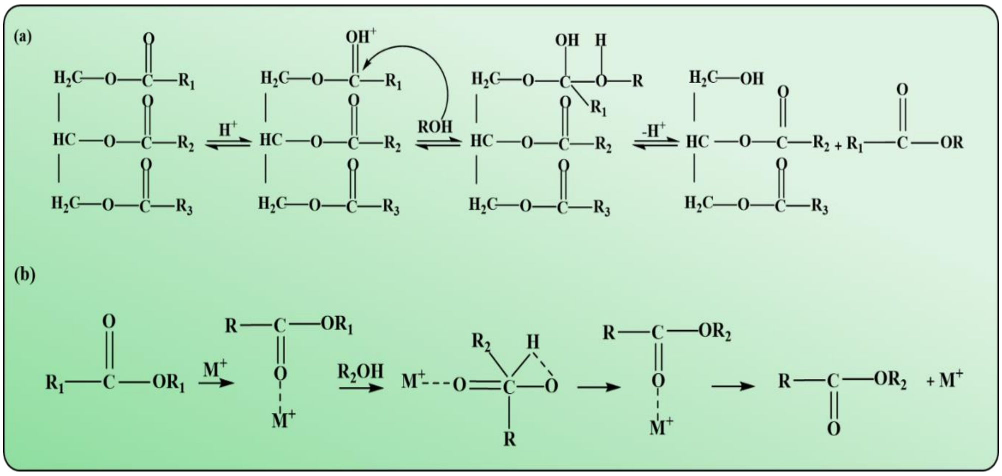

Figure 9. Mechanism of transesterification reactions catalyzed by (a) Bronsted's acid theory (b) Lewis's acid theory.

A typical transesterification reaction is also initiated with a Bronsted acid catalyst by protonating the carbonyl groups of the TGs in oils or fats. This short-chain alcohol immediately starts to attack the carbon proton at the active site, which forms the reactive center and produces a tetrahedral intermediate. Ultimately, it is the protonation that migrates, and then bond breaking takes place through intermediate steps, producing the final ester product (Figure 9 (a)) [72]. When the transesterification reaction is catalyzed by the Lewis acid, the oxygen atoms of the carbonyl group of ester compounds combination with Lewis's acid, result in the formation of strong electrophilic compounds. The electrophilic compounds are subsequently united with alcohols creating

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nucleophilic bonds. At last ester compounds formed with a new generation and the Lewis acid was separated from carbonyl oxygen (Figure 8 (b)) [72].

6.3. Effects of Catalyst Loading on Biodiesel Yield

The catalytic conversion of TGs into biodiesel is a reaction that requires a catalyst to lower the activation energy and speed up the reaction. Accordingly, biodiesel production relies on the catalyst usage amount. At the beginning of the reaction, the catalyst loading decreases, then the biodiesel yield is measured. The next catalyst loading at constant reaction conditions will be increased until the optima for biodiesel content from the feedstock is observed [73]. For example, in the study of Qi et al., by increasing the catalyst loading from 1 to 5%, the biodiesel efficiency increased to 16.7%, and with a further increase in the amount of catalyst, no change in biodiesel efficiency was observed [74].

6.4. Performance Metrics and Catalyst Evaluation

Evaluation of heterogeneous catalyst application for biodiesel production is related to criteria such as catalyst effectiveness and suitability for industrial use. Here, by reviewing the research literature according to Table 2, some of the main performance criteria and evaluation criteria have been introduced.

Table 2.

Authors	**Year**	**Catalyst**	**Catalytic activity biodiesel yield (%B.Y.) OR FAME yield (%FAME)**	**Optimal condition**	**Recyclability**	**Cost-effectiveness**	**Environmental Impact**	**Ref.**
Hatami et al.	2023	SBGAC-$PhSO_3H$[a]	17.34% B.Y.	Reaction time of 14 h, reaction temperature of 70 °C, methanol-to-lipid relative content of 40 mL/g, and catalyst loading of 20 wt %.	Density decreased by 62.6% after the fifth reaction cycle	N.M.	N.M.	[75]
Siddiquee et al.	2011	as-synthesized SBA-15	30.14% B.Y.	Temperature of 135 °C and a pressure of 135 psi for 3 h reaction time	N.M.	N.M.	N.M.	[59]
Melero et al.	2015	Zr-SBA-15	15.5% FAME	209 °C, 2000 rpm, 50:1 methanol to saponifiable matter molar ratio, 12.5 wt% catalyst based on lipids mass	N.M.	N.M.	N.M.	[76]
Sangaletti-Gerhard	2015	Sulfuric acid	36% FAME	Temperature of 55 °C, 7 h reaction time, methanol-to- sludge ratio of 20 mL/g	N.M.	11.27 US$ /kg_{FAME}	N.M.	[77]
		Novozym435	52% FAME	Temperature of 55 °C, 7 h reaction time, methanol-to- sludge ratio of 20 mL/g	For 5 times reaches an energy efficiency of 66%, while after 17 times reused 100% energy efficiency	1143.14 US$ /kg_{FAME}	low	

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Booramurthy et al.	2022	Fe3O4/BaO	97.6% B.Y.	18:1 molar ratio of methanol/oil, 8 wt% of catalyst loading, Temperature of 65 °C, 5 h reaction time,	There was not reduction in yield of biodiesel until the seventh cycle and 86 wt% recovery of catalyst was recovered	N.M.	N.M.	[78]
Zhang et al.	2020	SO_4/Al_2O_3-SnO_2	73.3% B.Y.	0.8 g catalyst loading, Temperature of 130 °C, 4 h reaction time,	N.M.	N.M.	N.M.	[79]
Saravanan et al.	2022	$Ca/Fe_3O_4/Cs_2O$	98.6% FAME	20:1 molar ratio of methanol/oil, 9 wt % of catalyst loading, Temperature of 65 °C, 5 h reaction time,	up to five cycles, the yield of biodiesel was above 90 wt %	N.M.	N.M.	[80]
Nabgan et al.	2022	3CaO–TiO_2	97.2% B.Y.	20:1 molar ratio of methanol/oil, 9 wt % of catalyst loading, Temperature of 70 °C, 2 h reaction time,	up to five runs with negligible activity loss	N.M.	environmentally friendly	[71]
Patino et al.	2021	Amberlyst IR120	32.9% FAME	33:1 MeOH/sludge ratio, 1:2 catalyst/sludge ratio, Temperature of 120 °C, 21 h reaction time,	six times with negligible catalytic activity loss	N.M.	N.M.	[81]
Hashmi et al.	2022	Amberlyst A21	95.52% B.Y.	20:1 molar ratio of FFAs to ethanol, acidic resin weight of 6%, Temperature of 70 °C, 8 h reaction time,	N.M.	annual net profit gain of Pakistani rupees Rs 54.89 and Rs 93.32 million	N.M.	[82]
I. Ngoie et al.	2019	CMSG/ZVINPs,	88% B.Y.	6:1 molar ratio of methanol/oil, catalyst dosages of 8 wt.% , Temperature of 75 °C, 2 h reaction time,	27% decrease in biodiesel yield after four reaction cycles	N.M.	N.M.	[83]

Table 2 shows various biodiesel or FAME (Fatty Acid Methyl Ester) production experiments. Based on the biodiesel yield (%B.Y.) or FAME yield (%FAME) in the table, the most effective catalysts for biodiesel production are $Ca/Fe_3O_4/Cs_2O$ used by Saravanan et al., which achieved a FAME yield of 98.6%. Fe_3O_4/BaO used by Booramurthy et al. (biodiesel yield of 97.6%), and 3CaO–TiO_2 used by Nabgan et al. with a biodiesel yield of 97.2%. However, the effectiveness of a catalyst can also depends on other factors such as cost-effectiveness, environmental impact, and recyclability, which are not fully detailed in the table for all studies. The recyclability of a catalyst is an important factor in its overall effectiveness, as it can significantly impact the cost and environmental footprint of the biodiesel production process. In this table, the details about the recyclability of the most effective catalysts based on the biodiesel or FAME yield included $Ca/Fe_3O_4/Cs_2O$ with a biodiesel yield of above 90 wt % up to five cycles. Also, Fe_3O_4/BaO, which there was no reduction in the yield of biodiesel until the seventh cycle. And up to five runs with negligible activity loss was reported for 3CaO–TiO_2.

6.4.1. Catalytic Activity

Catalytic activity describes the catalyst's ability to speed up the conversion of TGs into biodiesel during transesterification. It is usually determined by monitoring the conversion of TGs into biodiesel in a particular reaction setup. Greater catalytic activity is a characteristic of a more powerful catalyst [84].

FAME

6.4.2. Stability

Catalyst stability is of utmost importance as it ensures that the catalytic performance remains stable and constant within reaction times and multiple cycles. Stability testing entails determining the catalyst's deactivation, leaching, and structural alterations resistance under reaction conditions [85].

6.4.3. Recyclability

Overcome with the cost-effectiveness as well as the sustainability being dependent on the reusability of the catalyst and the catalyst's activity/selectivity minimized loss is vital. Recycling catalysts need the evaluation of the catalyst separation from the reaction mixture, and their performance in the next cycles [47].

6.4.4. Cost-Effectiveness

The cost of catalyst materials, synthesis, and disposal greatly influences the entire economic system of biodiesel production costs. Cost-effectiveness analysis will be carried out by the consideration of both catalyst efficiency and cost to determine the most economical catalyst option for large scale production [43].

6.4.5. Environmental Impact

Assessment of the environmental impact of heterogeneous catalysts covers issues relative to how much resources, emissions, and energy are consumed during catalyst manufacture, operation, and disposal. Catalysts that are environmentally compatible with a low ecological footprint are the best choice for opting for sustainable biodiesel production [59].

Assessment of heterogeneous catalysts for biodiesel production generally starts with lab experiments and the scale-up procedure. The comparison studies of diverse catalysts during identical conditions provide a comparative evaluation of them in terms of performance and prospects of commercialization. Ongoing research focuses on developing novel catalyst formulations, optimizing reaction conditions, and enhancing catalyst performance to improve the efficiency and sustainability of biodiesel production processes.

7. Synthesis and Characterization Techniques of Heterogeneous Solid Acid Catalysts

Synthesis and the characterization of heterogeneous solid acid catalysts involve several preparation approaches and characterization techniques which are meant to change the catalyst properties and determine the structure-activity relationships. The principal methods of synthesis and characterization of heterogeneous solid acid catalysts are described.

7.1. Preparation Methods

Synthesis procedures by different methods would be employed to prepare solid acid catalysts, of which every method could have the privileges of zoning catalyst qualities. Hence, the impregnation approach involves the infusion of the support of choice, be it silica or alumina, by an acid precursor like sulfuric acid or phosphoric acid. The support is soaked with precursors and then buzzing to form acid sites on the surface of the support material, enhancing the catalytic efficiency [86]. Furthermore, this process would entail the co-precipitation of metal oxides or hydroxides along with an acid component, which can be sulfuric acid that is drawn from a mixed solution. The after-processing comes down to filtering, washing, drying, and calcinating the precipitate to obtain the solid acid catalyst with the optimized composition and structure [87].

Template-oxidative generates the pores structure and morphology of the catalysts using templates like surfactants or organic molecules. The acid moiety is added into a tangled template structure. After the template is removed, a well-structured specifically modified catalyst with tailored properties can be obtained [88]. Concurrently, the sol-gel method makes use of hydrolysis and condensation of substances in a solution to form a sol which undergoes gelation to yield a solid network. An acidic component is added to the wonder of what the gel contains, and then after drying and burning, a solid acid catalyst is obtained with the desired characteristics [89]. At last, the ion exchange uses support materials with ion exchange capacity example of which could be zeolite or ion-exchange resins that are reversed to acidic ions such as H+ or NH_4^+ through ion exchange reactions. The washed and dried catalyst is now exchanged instead, enabling the user a high degree of control and adjustability over catalyst acidity [90]. These synthesis processes allow the manufacture of various solid acid catalysts, which can be tuned to desired properties, making them outstanding for acid-catalyzed processes, including biodiesel production.

7.2. Characterization Techniques

Characterization procedures are quintessential in providing an understanding of the operations and properties of the heterogeneous solid acid catalysts. Employing surface area and pore size techniques such as BET analysis and BJH pore size distribution method can figure out the structural characteristic of a catalyst. These types of analysis determine the specific surface area and pore size distribution type, which are the factors that impact the catalyst's activity and selectivity [47]. Through X-ray Diffraction (XRD) analysis, the crystalline structure and the phase composition of the catalyst can be determined, thus it is possible to specify the particular phases of crystallinity as well as to estimate their levels [84].

Fourier Transform Infrared Spectroscopy (FTIR) stand for Functional Group Characterization involved in the Acidic Sites Act, especially -OH and -COOH, which is great for catalytic activity. The determination of the size, the shape and the forms' dispersion of the nano-catalysts are realized by the methods of SEM and TEM imaging in the morphological analysis stage. It appears that this technique enables determining where the active sites are on the surface of the catalyst as a result of these sites structure. Solid-state NMR gives equivalent data about the immediate vicinity of acidic species as well as the reaction chemistry at the bonds of the catalyst surface and helps discovering acid sites and also explaining their reactivity. Next, the Tunneling Temperature Programmed Desorption (TPD) technique is applied at the nanoscale to carry out the desorption of probe molecules from the catalyst surface to obtain the number, strength, and density of the acid sites [84]. In a combined mode, these characterization techniques depict the whole picture of heterogeneously solid acid catalysts. That is how their adjustment for different catalytic functions is facilitated, for example biodiesel production.

8. Recent Advances in the Development of Heterogeneous Solid Acid Catalysts

Heterogeneous solid acid catalysts that have lately been proven to be superior solution to solve problems concerning biodiesel from sludge-derived lipids have been demonstrated by several recent studies leading to improved conversion and better catalytic performance. Zhang et al. obtained a significant biodiesel yield of 73% (based on dried extracted crude fat) using the $SO_4^{2-}/Al_2O_3-SnO_2$ catalyst [79]. Great innovative discovery in this sense consists of the production of new catalyst structure from the right synthesis methods and the use of nanotechnology. Template synthesis ensures that the reprecipitation of the catalysts is precisely by controlling the morphology and porosity of the catalysts which results in an enhanced accessibility to the active sites. In this regard, the development of nanoscale engineering tools has led to the creation of catalysts that have been designed for micro-level particle size and dispersion, which consequently boosts the activity and selectivity of lipid conversion from the digested sludge. Nabgan et al. reported a CaO-TiO_2 nano-catalyst with bifunctional properties to produce biodiesel from dairy scum. The maximum biodiesel yield (97.2%) was obtained using 3Ca-3Ti nano-catalyst under optimized conditions, i.e., at the reaction time of 120 min, catalyst loading of 3 wt.%, and lipid to methanol molar ratio of 1:20 [71].

On the other hand, the late-breaking advancements in this direction aim at the various development of catalysts consonance with the purpose of the enhancement of biodiesel produced from lipid which originated from sludge. A broad range of coordinating sites with different acid characteristics, those being Bronsted and Lewis, have been used as a tool to modify catalysts' composition. Here, the objective is to obtain maximum efficiency by improving the acid sites' density, strength, and distribution. Methods like cation exchange and surface adsorption allow for a high level of acid site control and good refining of biodiesel quality and yield. Like the study of Patino et al., who used Amberlyst IR120 as a catalyst and achieved a favorable biodiesel efficiency [81]. Moreover, multifunctional catalysts that are capable of undertaking tandem or cascade reactions have recently attracted researchers' attention, which represents a novel direction in biodiesel synthesis with the dual benefit of simplification and a more sustainable approach. Bimetallic catalysts [91], zeolite-based catalysts, Metal-Organic Frameworks (MOFs) [92,93], and supported nanoparticle catalysts [94], are some of the multifunctional catalysts that have been used in recent studies.

However, the recent progress in heterogeneous solid acid catalysts have got noteworthy relevance for greener biodiesel production from sludge-derived lipids. Together with the increasing demand of renewable energy sources, these catalysts take an extremely important place for providing biodiesel production by an efficient and environmentally-friendly means. Additionally, compliance with these raw sludge lipid base feedstocks, their durability and the possibility of reuse are all essential features that make them popular in large-scale biodiesel production facilities. Ongoing studies focus on the efficiency of the catalysts, the catalytic curb, and the resolution of issues relating to scale up, and this assists in optimizing the biodiesel production processes that are both sustainable and pro-economics.

9. Environmental and Economic Implications of Biodiesel Production Using Solid Acid Catalysts

9.1. Sustainability Assessment

The usage of solid acid catalysts in the process of biodiesel production brings about both environmental and economic issues that should be properly assessed for sustainability. An environmental advantage is that a solid acid catalyst has a possible benefit of reduced environmental impact in relation to that of a traditional homogeneous catalyst. Solid catalysts provide ease with separation and recycling which in turn cause less waste generation and minimize the energy consumption required to extract catalysts [41]. Besides, the practice of using heterogeneous catalysts also enables feedstocks such as those from sludge-derived lipid to be of low cost and renewable which in turn reduce reliance on fossil fuels as well as mitigating the associated environmental pollution and greenhouse gas emissions.

Economically, the fact that solid acid catalysts may enable cost-cutting compared to the current catalysts is one of the benefits of the alternative catalysts. With the sizable capital investment required for long-lived solid catalysts and associated infrastructure at a start, improved catalyst stability, higher catalytic activity, and reduced operating costs enable this disbursement to pay off in the long run. Finally, the benefit arising from the capability of inexpensively using feedstocks for such low reaction conditions may actually give a chance for overall cost reduction in the biodiesel refining process. In addition, the utilization of the locally available feedstocks not only enhances the economic development of the region but also reduce the environment impact [95]. Nevertheless, it is important to perform a comprehensive economic analysis based not only on catalyst life span and costs of regeneration of the spent catalyst but also on taking into account the market behavior of the feedstock costs factors to arrive at the most economically viable and sustainable method of biodiesel production [96].

9.2. Economic Viability and Techno-Economic Analysis

The economic feasibility of such a manufacturing method primarily depends on the way how we conduct techno-economic analysis. The application of solid acid catalysts instead of homogeneous ones offers the possibility to decrease the costs thanks to the increase of its stability, activity (of the catalyst), and the reduction of operating costs. Yet, in this case of initial expenses for high-quality catalysts and their infrastructure, start-up financing may be an issue. Therefore, this techno-economic analysis (as well as an overall cost-effectiveness assessment) is needed to assess the use of solid acid catalysts for producing biodiesel. This study should have in mind variables like catalyst durability,

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catalyst regeneration expenses, feedstock availability and costs, energy emission, labor costs, and the market demand for biodiesel.

From an economical point of view production of biodiesel by using solid acid catalysts in various scenarios includes the consideration of risks such as unstable feedstock prices and regulations changes. Cost-benefit analyses (CBAs), sensitivity analysis (SA), and scenario modeling are applied in the identification of key cost drivers, assessment of risk values, as well as optimization of process parameters that ensure big returns. Moreover, the results of techno-economic analysis do not only offer valuable insights into the competitiveness of biodiesel production using solid acid catalysts compared to the other methods of production of biodiesel but also contribute towards educated choices and strategic planning for the creation of sustainable and economically profitable businesses meant to produce biodiesel [97].

10. Challenges and Future Perspectives

10.1. Current Challenges and Limitations

Heterogeneous solid acid catalysts seem to be able to deliver green biodiesel production from sludge wastewater, but this type of catalyst has also several limits and issues which need to be worked out. The one difficult problem has been the variability of sludge composition that can affect the efficacy of a catalyst and product quality. The wastewater sludge is derived from organic and inorganic substances as well as heavy metals and moisture that may decrease the catalyst's efficiency. This will in turn reduce its activity and stability too. For instance, the hazardous efficiencies are likely to require that some preliminary treatments be undertaken in order to get rid of or reduce the effect of the pollutants and this adds to the process complexity and cost. Moreover, the very dense acid ester-stocks are usually difficult to mix well and mass transfer and may only give a low concentration and yield of biodiesel fuel.

Further, the work on heterogeneous solid acid catalysts specially designed for that purpose has both technical and economic problems. Although progress has been made over the years in terms of catalyst design and synthesis technologies and optimization has been achieved, the optimization of catalyst performance is still complicated for feedstocks, including the sludge. Catalyst stability in an array of products containing some impurities and reaction conditions can be challenging, as well as regeneration and recycling of the catalysts, are the technical areas that need proper research and development progress. Lastly, the economic sustainability of biodiesel production from sludge-derived lipid with this type of solid acid catalyst needs to be carefully considered by taking into account factors such as the cost of the catalyst, the availability of feedstock, and the market demand for the fuel storage riot of biodiesel products. Adhering to those obstacles and constraints to the point where they would not define heterogeneous solid acid catalysts' potential fully in creating sustainable biodiesel from wastewater-based sludge will play a key role.

10.2. Future Research Directions and Opportunities

Research on the different solid acid catalysts that can be used in environmentally friendly biodiesel production from sewage sludge will bring new prospects for future progress in this area and solving the current problems. Another field that should be investigated is the discovery of new catalyst materials that are more effective for the purpose of converting sludge-based lipids to something useful. Through catalyst composition, structure, and active site arrangement optimization, researchers can improve both catalyst performance and stability in the presence of sludge feedstocks of varying complexity. In addition, finding other feedstock pretreatment methods and conditions of the reaction can reduce the effect of sludge impurities and boost the efficiency of the process.

Also, these heterogeneous solid acid catalysts have the prospect to be used for integrated biorefinery options of wastewater treatment and biofuel production. Employing biodiesel production and other extra value-added processes, including biogas generation and nutrient recovery, enables researchers to build up synergistic systems that maximize resource utilization and minimize waste production. Along with that, innovation of catalyst recycling and regeneration technologies, looking

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into novel reactor designs and process intensification strategies, can make this method even more sustainable and economical. Thus, future research in this area gives rise to adventurous designs for addressing the world's problems related to wastewater treatment and clean energy production.

11. Conclusion

The review emphasizes the potential of solid acid catalysts in biodiesel production from sludge, promoting sustainability and innovation. Challenges include variable composition, contaminants, and cost. Success hinges on research, technology, and collaboration. Progress in catalyst design boosts biodiesel yield. Customizing materials and exploring pretreatment methods enhance efficiency. Integrating solid acid catalysts in biorefinery methods boosts resource use and reduces waste. Standardized reporting is crucial for comparison and progress in biodiesel research. Catalyst efficiency, recyclability, and cost-effectiveness are vital for sustainable production. Research on catalysts for biodiesel production highlights performance metrics, optimal conditions, and environmental impact. Catalyst selection and optimization are key for sustainability. The evaluation of solid acid catalysts involves factors like activity, stability, recyclability, cost, and environmental impact. Effective catalysts show high yields and recyclability. Catalyst synthesis methods and characterization techniques are essential for tailored properties. Recent advances in catalysts improve biodiesel yield and performance through innovative methods. Controlled morphology and acid site types optimize efficiency. Multifunctional catalysts enhance sustainable biodiesel synthesis. Solid acid catalysts offer environmental benefits through recycling and reduced waste. Economically, they offer long-term cost savings and regional development. A techno-economic analysis is crucial for evaluating viability. Solid acid catalysts hold promise for sustainable and economically viable biodiesel production. Challenges like sludge variability and technical issues require further research. Innovations in catalyst materials, recycling, and reactor design can enhance sustainability and economic viability in biodiesel production. Continued exploration of solid acid catalysts is essential for a greener future.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figure S1: The PRISMA chart of study;

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