

Review Article

Efficient Synthesis of Biodiesel Catalyzed by Chitosan-Based Catalysts

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Catalysts play an important role in the preparation of biodiesel. It is of great significance to study catalysts with high efficiency, low cost, and easy preparation. Compared with the homogeneous catalyst system, the heterogeneous catalyst is easy to separate and has a better catalytic effect. In heterogeneous catalysts, supports and preparation methods have important effects on the dispersion of active centers and the overall performance of catalysts. However, the supports of existing solid catalysts have defects in porosity, structural uniformity, stability, and specific surface area, and the preparation methods cannot stabilize covalent bonds or ionic bonds to bind catalytic sites. Considering the activity, preparation method, and cost of the catalyst, biomass-based catalyst is the best choice, but the specific surface area of the biomass-based catalyst is relatively low, the distribution of active centers is uneven, and it is easy to lose. Therefore, the hybrid carrier of biomass-based catalyst and other materials can not only improve the specific surface area but also make the distribution of active centers uniform and the catalytic activity better. Based on this, we summarized the application of chitosan hybrid material catalysts in biodiesel. The preparation, advantages and disadvantages, reaction conditions, and so on of chitosan-based catalysts were mainly concerned. At the same time, exploring the effects of different types of chitosan-based catalysts on the preparation of biodiesel and exploring the process technology with high efficiency and low consumption is the focus of this paper.

1. Introduction

In recent decades, with the accelerated development of industrialization, global fossil fuel consumption and greenhouse gas emissions have increased rapidly. Scientists predict that the total global energy consumption will increase by 28% from 2015 to 2040 [1]. However, traditional energy, which is the main source of global energy supply, is constantly consumed, leading to energy shortage. This problem has attracted the attention of researchers all over the world, who are looking for sustainable and ecofriendly alternative energy [2, 3]. Therefore, scientists try to replace fossil fuels by developing renewable green energy, among which biofuels are the most competitive. Biodiesel is the

most representative liquid biofuel among biofuels. It has the advantages of green, renewable, nontoxic, and environmental protection [4]. Meanwhile, biodiesel is almost free of sulfur and aromatic substances, biodegradable, and belongs to truly renewable “green energy” [5].

First of all, the main raw materials used to prepare biodiesel are rapeseed oil, soybean oil, and other edible oils, but this has an impact on national food safety and there is a problem of competing with people for food. Later, further research showed that nonedible oils are also used as the raw materials for biodiesel production, such as *Jatropha curcas*, *Euphorbia lathyris* [6], *Xanthium sibiricum* [7], *Firmiana platanifolia* [8], and *Koeleruteria integrifoliola* [9]. This expands the raw material source of biodiesel and greatly

reduces the cost. After that, to further reduce the cost, biodiesel was prepared from waste cooking oil and animal fat with high acid value [10]. In addition, microalgae are also used as biodiesel raw materials, which is effective to reduce the cost of biodiesel, but the cultivation of microalgae also requires additional costs. In short, the new raw materials of biodiesel are of great significance for alleviating the energy crisis, protecting the ecological environment and adjusting the agricultural structure [11–13].

Biodiesel is generally a mixture of fatty acid methyl ester or ethyl ester, mainly because the raw materials for its synthesis contain many types of triglycerides [5]. The conventional method of synthesizing biodiesel are esterification and transesterification. Generally, acids [14], bases [15], and enzymes [16] are used as catalysts for biodiesel synthesis. Heterogeneous catalysts have gradually replaced homogeneous catalysts, which is mainly because heterogeneous catalysts can be reused many times, which can effectively reduce the cost [11]. Nowadays, different kinds of heterogeneous catalysts have been used to prepare biodiesel, including carbon materials [17], SiO₂ materials [18], oxides [19], ion exchange resins [20], magnetic materials [21], and supported enzymes [22]. However, the traditional solid catalyst has the disadvantages of easy loss of active sites and poor reusability. Therefore, looking for a green, efficient, and stable heterogeneous catalyst to prepare biodiesel has become one of the research hotspots for the preparation of high-performance heterogeneous catalysts [1].

Nowadays, people realize that the development of renewable and biodegradable biomass-based catalysts is more conducive to green environmental protection [23]. The excellent performance of functionalized biomass-based catalysts has attracted much attention [24]. In terms of biomass, chitosan prepared from shrimp shells and crab shells is a high molecular polymer biomass-based material. Chitosan has a large number of active –OH and –NH₂ groups and has strong modification ability. At the same time, chitosan is a cheap polymer material, which has natural advantages as a catalyst material in industrial production. Chitin, the raw material of chitosan, is a natural polymer compound second only to cellulose in nature. It is not only rich in resources but also widely used in medicine, food, chemical industry, cosmetics, water treatment, and other fields because of its biological function, compatibility, safety, and biodegradability [25–29].

This paper focuses on the research progress of chitosan-based catalysts in biodiesel. The synthesis method, physicochemical properties, catalytic efficiency, and reaction conditions of chitosan-based catalysts were also discussed. We hope that through this paper, we can provide new ideas for the preparation of biomass-based catalysts and obtain more efficient, green, and environmentally friendly new catalysts for the industrial synthesis of biodiesel.

2. Chitosan Derivatives

Because chitosan is easy to be modified, there are many derivatives of chitosan, which makes it possible to prepare a variety of chitosan-based catalysts, with more and more applications for the production of biodiesel.

Zhao et al. [30] prepared CoFe₂O₄-CS-SO₃H chitosan solid magnetic sulfonic acid catalyst for the synthesis of compounds. The preparation process of the catalyst is simple, and the obtained catalyst has strong magnetism (Figure 1).

Chitosan is a kind of polysaccharide that is easy to graft. Some researchers have tried to graft sulfonic groups onto chitosan monomers and synthesized several chitosan sulfate membranes. This makes the catalyst contain the sulfonic group and amino functional group, which further improves the activity of the catalyst [31]. Gu et al. [32] prepared chitosan-doped polyvinyl alcohol films by the blending heating method. The surfaces of these membranes are usually wrinkled and have excellent separation performance. They can be used for pervaporation to separate methanol-biodiesel mixtures. Gupta and Jabrail [33] used the glutaraldehyde crosslinking method to prepare chitosan microspheres (in Figure 2). Usually, glutaraldehyde condenses with the amino group of chitosan ammonia to form a network polymer, and the formed chemical bond crosslinks and solidifies the microspheres. In this process, the loaded particles can be wrapped in the microspheres or adsorbed on the surface of the microspheres. This is conducive to the encapsulation of internal magnetic particles and the adsorption of external catalyst particles.

Liu et al. [34] introduced a simple method for preparing magnetic chitosan Fe₃O₄ nanoparticles. Immobilized lipase was prepared by a glutaraldehyde crosslinking reaction under a 0.45 T static magnetic field. The results show that there is no significant difference in the structure of nanoparticles, the morphology of nanoparticles changes from spherical to a rod, and the magnetic properties change significantly.

Li et al. [35] prepared a series of chitosan hybrids based on polyoxometalates by anion exchange of a novel cross-linked chitosan ionic polymer with H₃PW₁₂O₄₀. Bodmeier et al. [36] first proposed the preparation of chitosan microspheres by the ionic gel method (in Figure 3). The polyanion of sodium tripolyphosphate is used as a cross-linking agent, which is combined with the positively charged amino group after the protonation of the chitosan molecular chain. Through the electrostatic interaction, the physical crosslinking of the molecules can be reversible, intramolecular or intramolecular, so that the chitosan can be gelled into spherical particles.

Huang et al. [37] prepared N-doped carbon prepared by chitosan with a large specific surface area. Chitosan is dissolved in acetic acid and carbonized to form porous carbon. After KOH activation, its specific surface area can reach 3532 m²/g. The carbon-based catalyst is relatively stable and has a large specific surface area.

A new type of sustainable catalytic material was prepared from biological waste (chitosan) and rare earth-rich cobalt salt (in Figure 4). Through the chelation of chitosan with Co, the carbonized catalyst has a carbon shell containing N and encapsulates Co and Co₃O₄, which can improve the performance of the catalyst and effectively reduce the loss of active components. The catalyst has been reused many times, and the efficiency has not changed significantly [38].

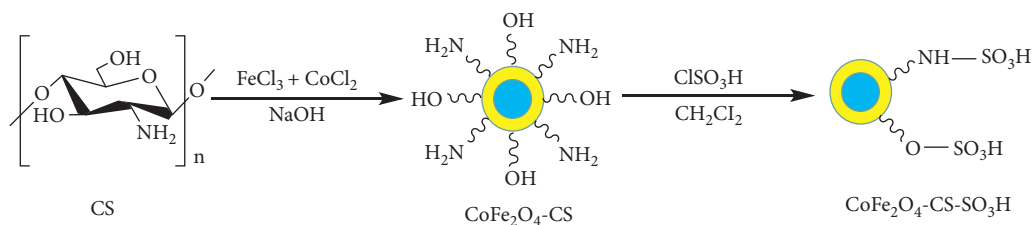


FIGURE 1: The preparation process of $\text{CoFe}_2\text{O}_4\text{-CS-SO}_3\text{H}$ catalyst [30].

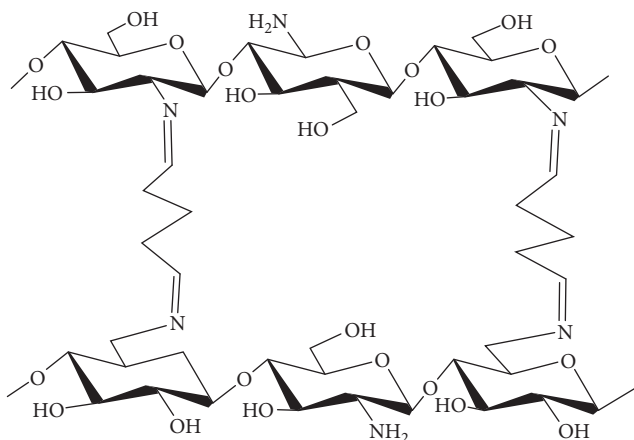


FIGURE 2: The microsphere formed by crosslinking chitosan and glutaraldehyde [33].

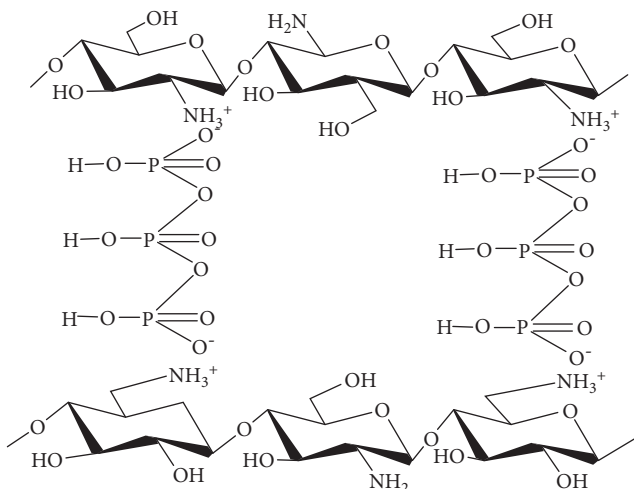


FIGURE 3: Structure of microspheres crosslinked by chitosan and sodium triphosphate [36].

Roosen et al. [39] prepared SiO_2 chitosan composite mesoporous material with a specific surface area of $219 \text{ m}^2/\text{g}$, pore volume of $1.036 \text{ cm}^3/\text{g}$, and pore size of 9.5 nm , which belongs to mesoporous structure and is more suitable as a catalyst support material. Sana et al. [40] prepared chitosan microspheres supported a Pd catalyst, including the direct complexation of Pd^{2+} with the amino group on chitosan and the complexation of chitosan modified by glutaraldehyde with Pd^{2+} , and the complexation of chitosan modified by glutaraldehyde with Pd^{2+} . γ -Thiobutyrolactone-modified

chitosan has three kinds of catalysts: sulfhydryl group and Pd^{2+} . The specific surface areas of the three catalysts are 239, 239, and $302 \text{ m}^2/\text{g}$, respectively. γ -Thiobutyrolactone-modified chitosan microspheres have a higher specific surface area. Also, the catalyst is used in the mixed solution of water and ethanol, so it has strong hydrophobicity. It is expected that the modified biodiesel can be used in the preparation of water-containing biodiesel.

3. Chitosan Gel and Chelating Metal Catalysts

3.1. Chitosan Gel. To reduce the production cost of biodiesel, more and more kitchen waste oil, non-edible vegetable oil, and microalgae oil are used as raw materials of biodiesel. However, these raw materials contain a large amount of free fatty acids (FFA). The key to the synthesis of biodiesel is to find heterogeneous catalysts that can simultaneously catalyze esterification and transesterification. Kayser and Pienkoß [41] evaluated the transesterification with chitosan and frozen gel as catalysts for different oils and methanol. As a green waste and a catalyst for biofuel production, chitosan can increase new possibilities for local value. Chitosan freeze-gel successfully catalyzed transesterification of three oleic glycerin and soybean oil with methanol and achieved a yield of 90% of biodiesel at 8 to 32 hours at $100\text{--}150^\circ\text{C}$. The chitosan beads were washed with tertbutyl alcohol and methanol, and the fat and glycerin were desorbed. To achieve practical use, further research and development opportunities can be identified at the catalyst design level, and new catalysts based on chitosan, such as aerogels, layers, and chitosan derivatives can be used to achieve more efficient catalytic activity and will show a greater degree of recyclable results.

3.2. Chitosan Chelating Metal Catalysts. Da Silva et al. [42] used chitosan-adsorbed Cu (II) and Co (II) catalysts for transesterification of soybean and babassu oil. The maximum adsorption capacities of copper and cobalt ions were 1.584 and 1.260 mg, respectively, while the oil conversion of biodiesel was higher when using chitosan-adsorbed Co (II) as a catalyst.

4. Acidic Modified Chitosan Catalysts

4.1. Sulfonic Acid. Based on the fact that chitosan is easy to crosslink, a new type of acidic chitosan membrane (ACM) was formed by crosslinking chitosan with sulfosuccinic acid (SSA). The esterification reaction of oleic acid and methanol was carried out to test the catalytic effect (in Figure 5). The acid

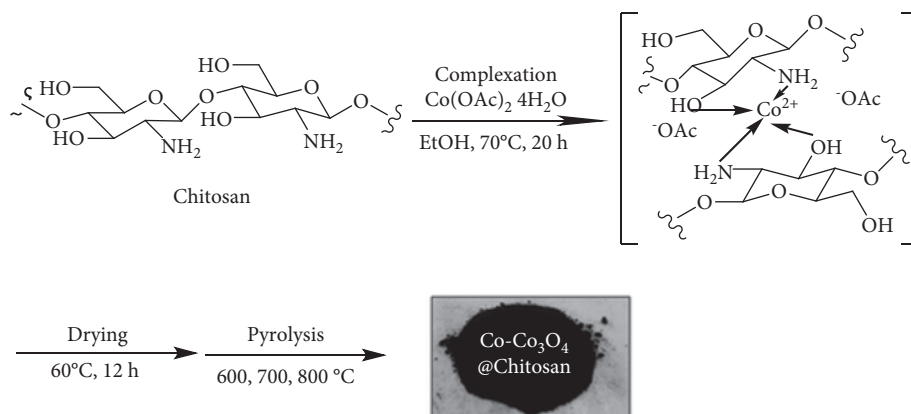


FIGURE 4: Synthesis of Co-Co₃O₄@chitosan materials. [38].

density of ACM was 4.62 mmol/g, which was only slightly lower than that of Amberlyst-15 (4.76 mmol/g). Under the same conditions, the catalytic efficiency of Amberlyst-15 was only 44.30%, while that of ACM was 98.76%. The reaction conditions were optimized by combining a single factor test with the response surface method. The catalytic activity of ACM for esterification of fatty acids with alcohols was studied. In addition, the reusability of ACM is also studied [43]. In conclusion, the active sites are more exposed after chitosan crosslinking, which is beneficial to the catalytic reaction, which is also the reason why ACM has higher catalytic efficiency.

Caetano et al. [44] studied the esterification of palmitic acid with methanol at 60°C. The sulfonic group was introduced into chitosan (CT) by crosslinking with sulfosuccinic acid (SSA). With the increase of sulfonic group content in chitosan, the catalytic activity increased. However, with the increase of sulfonic group content, the catalytic activity decreased. This kind of behavior can be explained by the factors of limiting diffusion. The catalytic stability of CT4 (2.08 mmol sulfonic group/g) was evaluated by using the same catalyst samples for continuous batch operation. After the second batch reaction, the catalytic activity tends to be stable. CT4 catalyst is also used for esterification of oleic acid and stearic acid with methanol. CT4 has good catalytic activity for different substrates used in esterification. It is confirmed that chitosan is a kind of biopolymer rich in the sulfonic group, and it is an efficient and environmentally friendly heterogeneous catalyst.

Wang et al. [45] prepared a chitosan sulfonic acid catalyst by a relatively simple method. The specific method is to disperse chitosan with dichloromethane as the solvent and then sulfonate chitosan with chlorosulfonic acid to obtain a biomass-based catalyst with an acid density up to 3.81 mmol/g. SEM results show that CS-SO₃H is spherical with a diameter of about 10 μm. After four times of reuse, the yield of the catalyst can still reach 85.7%, which indicates that this kind of sulfonic acid catalyst has a good application prospect.

4.2. Heteropoly Acid. Tong et al. [46] used H₃PW₁₂O₄₀, chitosan, and Ti⁴⁺ as carriers to prepare water-insoluble multifunctional active sites and H₃PW₁₂O₄₀/Ti/chitosan

hybrid materials (in Figure 6). Due to the presence of B acid from H₃PW₁₂O₄₀, Lewis acid from Ti⁴⁺, and base from -NH₂ group of chitosan, the catalyst showed high activity in the esterification reaction, all of which was due to the pore formation in chitosan by introducing Ti ions. Moreover, H₃PW₁₂O₄₀/Ti/chitosan can be reused at least 6 times as a heterogeneous catalyst; the activity reduction is not obvious, and only a small amount of Ti⁴⁺ and H₃PW₁₂O₄₀ are leached from the carrier chitosan.

Han et al. [47] prepared organic-inorganic hybrid catalysts by glycine (Gly) and phosphotungstic acid (TPA), namely [GlyH]_xH_{3-x}PW₁₂O₄₀ (x = 1.0–3.0), and studied the catalytic performance of various Gly-TPA catalysts in the esterification of palmitic acid with methanol to produce methyl palmitate. Under the optimum conditions, the yield of biodiesel can reach 93.3%.

4.3. Chitosan Magnetic Acid. Wang and his colleagues [48] synthesized a new magnetic mesoporous solid acid catalyst (FCHC-SO₃H) (in Figure 7). The catalyst was prepared from biodegradable chitosan with a double-shell hollow structure, which increased the active sites, and the synthesis process was mild and environmentally friendly. More importantly, the catalyst has good catalytic performance for the esterification of oleic acid and methanol to biodiesel, which can be reused 5 times without a significant decrease in activity and can be easily separated by an external magnetic field.

5. Basic-Modified Chitosan Catalysts

5.1. Inorganic Base. Used waste cooking oil (WCO) or frying oil is considered to be a rich source of economic raw materials for biodiesel production. Zeolite/chitosan/KOH composite was used as a solid heterogeneous catalyst for transesterification of WCO to methyl ester (biodiesel) (in Figure 8). The results show that the treatment of natural zeolite (clinoptilolite) with KOH can significantly reduce the silicon content and increase its K⁺. The content is determined by the formation of hydroxy calcium carbonate. Electrolysis (EM) is used as a suitable technology for energy and resource recovery in waste treatment. In theory, EM can

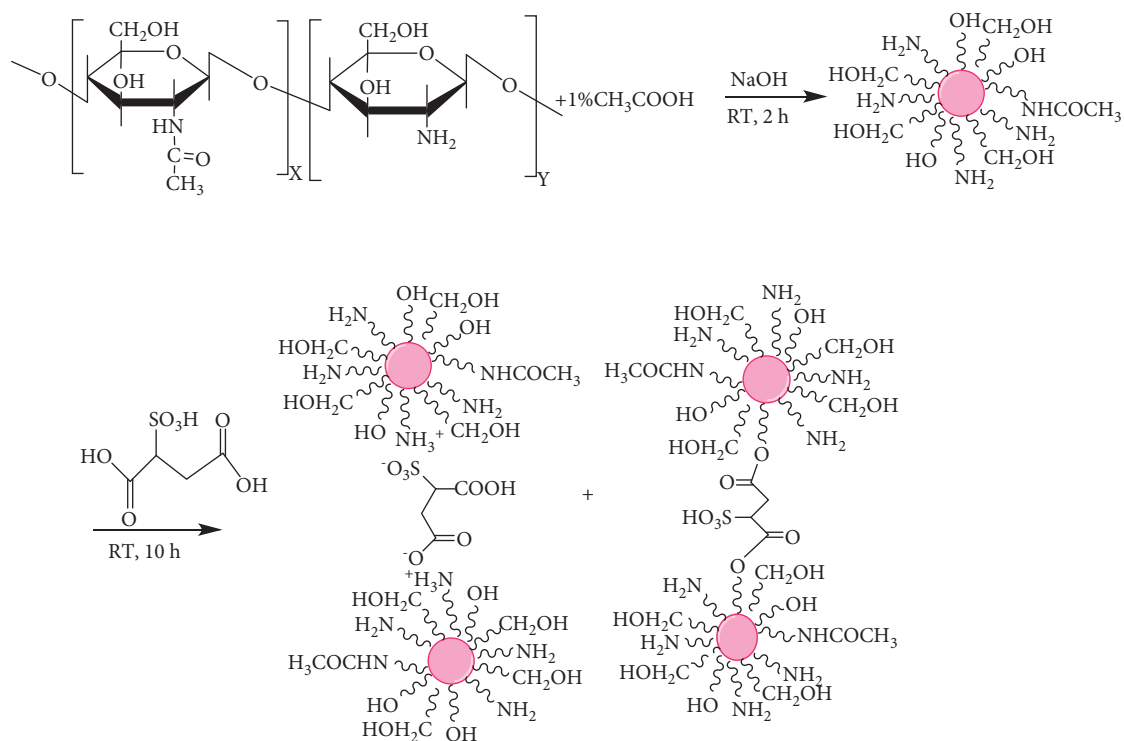


FIGURE 5: Synthesis of CSA catalyst. Reproduced with permission from [43] copyright 2019, Elsevier.

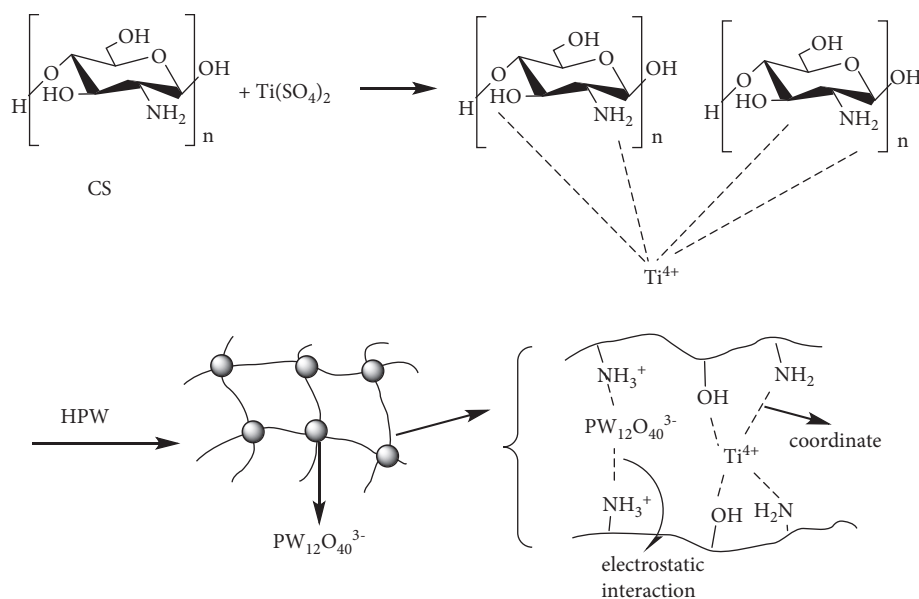


FIGURE 6: The preparation of HPW/Ti/chitosan hybrids. Reproduced from [46] under creative commons license (CC BY 3.0) copyright 2017, Royal Society of Chemistry.

convert any biodegradable waste into H_2 , O_2 , biofuel, glycerol, and other byproducts. However, the effectiveness of the system may vary greatly in different situations. In the presence of water, the conversion of biodiesel from WCO was obtained with 93% yield within 3 hours with 1% catalyst concentration and 1:70 alcohol/oil ratio (at 40 V) and 2% of the total solution. The best conversion process can be achieved by using acetone as the cosolvent [49].

Correia et al. [50] think that chitosan can be used as a structural agent by inserting calcium oxide and as a catalyst in transesterification. These calcium-doped chitosan spheres were calcined to obtain porous calcium catalyst without organic matter. The materials were characterized by X-ray diffraction, thermogravimetric analysis, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, temperature-programmed CO_2 desorption, scanning

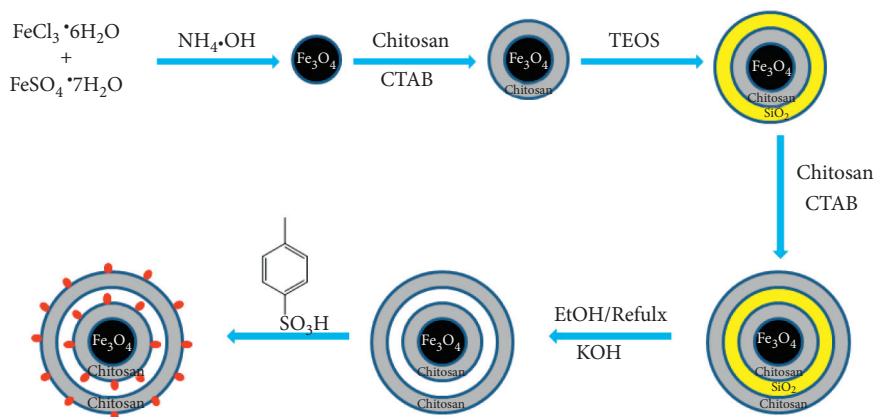


FIGURE 7: Synthesis of the FCHC-SO₃H catalyst. Reproduced with permission from [48] copyright 2018, Elsevier.

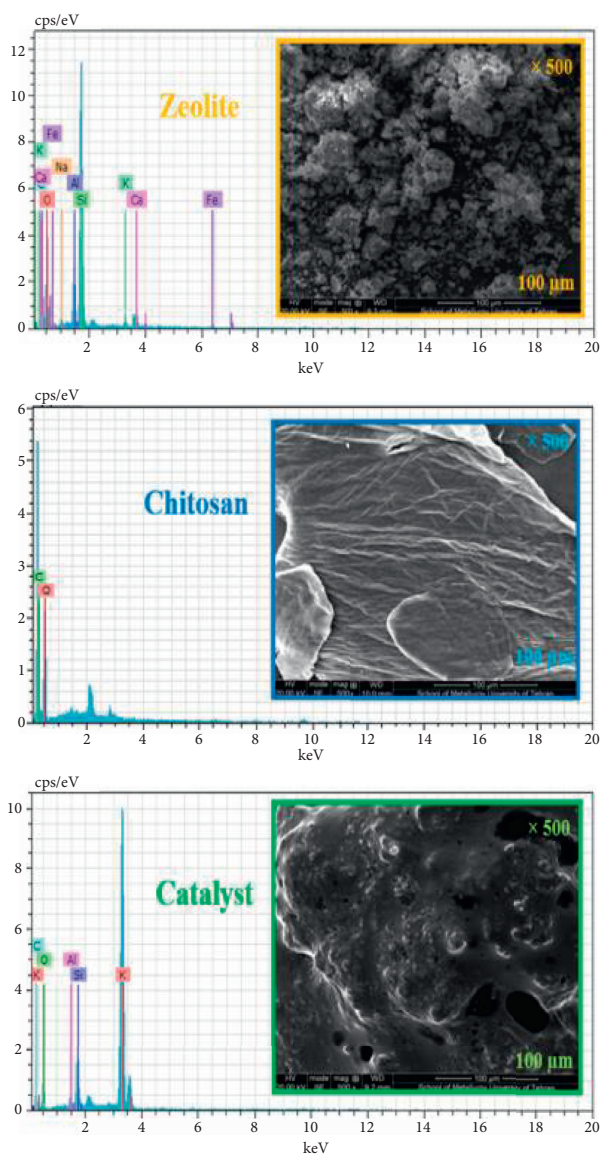


FIGURE 8: SEM micrographs and EDX spectra of raw zeolite, pure chitosan, and modified zeolite/chitosan/KOH catalyst. Reproduced with permission from [49] copyright 2017, Elsevier.

electron microscopy, and specific surface area analysis. Then, the calcined calcium/chitosan spheres were used for the transesterification of sunflower oil with methanol. Sunflower seed oil was converted to methyl ester (FAME) under the optimal reaction conditions: 3 wt%; time, 4 h; temperature, 60°C; magnetic stirring (1000 rpm) was $56.12 \pm 32\%$ by weight. These results indicate that chitosan can be used as a precursor for the formation of calcium/chitosan spheres to produce porous calcium oxide (with a high surface area) which can be used as an alkaline catalyst for biodiesel production.

Liang et al. [51] prepared a new polymer-based alkaline biodiesel catalyst from epichlorohydrin (ECH)-crosslinked n-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTCC) and sodium silicate (Na_2SiO_3). The structure and properties of the catalyst were studied by Fourier-transform infrared spectroscopy, thermogravimetry-mass spectrometry, and transmission electron microscopy. The effects of various factors on the preparation of biodiesel by transesterification of soybean oil were studied. The results show that Na_2SiO_3 is bridged on the HTCC chain by ECH and dispersed in the HTCC matrix in nanoscale. Under the optimum reaction conditions (6/1 methanol/oil mole ratio and 4 wt% catalyst dosage at 55°C for 1 h), a high biodiesel yield of 97.0% was obtained. After the second reaction, the catalyst activity remained stable, which was conducive to the stability and dispersion of Na_2SiO_3 in the catalyst.

Fu et al. [52] used chitosan as a new substrate for immobilization of CaO. Biodiesel was produced by transesterification of soybean oil with methanol, and CaO immobilized on chitosan beads was used as a heterogeneous catalyst. To obtain a stable immobilized catalyst, chitosan beads with immobilized CaO were crosslinked with glutaraldehyde. Two crosslinking parameters, crosslinking time and glutaraldehyde concentration were studied to reveal the optimal immobilization conditions, which were 30 min and 0.22 mol/L^{-1} , respectively. Under those conditions, the immobilized catalyst with a very low CaO leaching rate can be obtained. The immobilized CaO catalyst was prepared by transesterification of soybean oil with methanol. The transesterification rate was studied by response surface

methodology, which was affected by catalyst loading, methanol-oil molar ratio, and temperature. The maximum reaction rate was 0.6 H^{-1} , the molar ratio of methanol to oil was 13.4 at 60°C , and the catalyst loading was 13.78 wt%. Under these conditions, the equilibrium conversion of soybean oil was 97% after 3 hours. In addition, the fixed catalyst can be reused at least five times. This study developed a simple and energy-saving method to prepare chitosan-based immobilized CaO catalyst, which is expected to be used in potential applications including biodiesel production.

5.2. Organic Base. He et al. [53] synthesized guanidine chitosan (GCS) as the heterogeneous basic catalyst for transesterification of soybean oil with methanol using amino methylene sulfonic acid as a graft (in Figure 9). The structure and properties of GCS films were studied by Fourier-transform infrared spectroscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy. Under the conditions of catalyst dosage of 20%, methanol-oil ratio of 2.5 : 1, reaction temperature of 60°C , and reaction time of 6 h, the conversion of soybean oil reached 98.8% for the first time, and 96.6% for the fifth time. The results showed that the transesterification mainly occurred on the surface of the catalytic membrane. The kinetics of transesterification was studied by a pseudohomogeneous model. The reaction was a first-order reaction with an activation energy of 76.95 kJ/mol and a pre-exponential factor of $7.94 \times 10^9 \text{ min}^{-1}$.

6. Modified Chitosan/Enzyme Catalysts

The unique structure of chitosan is not considered an excellent carrier for immobilized lipase, which promotes the production of a variety of chitosan-loaded lipases. Its advantages include low reaction temperature, repeated use, and high reaction activity. This makes chitosan-loaded lipase widely used in the production of biodiesel.

Rhizopus lipase was immobilized on magnetic chitosan microspheres (MCMs), and biodiesel was prepared from soybean oil and methanol. The maximum content of methyl ester in the reaction mixture reached 91.3 (w/v) at the flow rate of 25 mL/min and the magnetic field strength of 150 Oe . In addition, MCMs-immobilized lipase in the reactor has excellent reusability, and it still maintains 82% productivity even after 6 batches, which is far better than that in a traditional fluidized bed reactor. These results show that MCMs-immobilized lipase is a promising biodiesel production method [54].

The preparation of biodiesel from rapeseed soap residue methanol catalyzed by chitosan-immobilized *Candida* lipase (CRL) was studied by response surface methodology (RSM). Methanol-substrate molar ratio, enzyme dosage, water content, and reaction temperature are four important parameters. RSM analysis shows that the experimental values are in good agreement with the predicted values. The results show that the most effective parameter is water content, which is in good agreement with the experimental values. The coefficient of determination (R^2) of the model is 92.86%,

with a probability value of $P < 0.0001$. The optimal conditions for biodiesel production by immobilized lipase were as follows: the molar ratio of methanol to the substrate was 4 : 1, the amount of lipase was 8%, the water content was 6%, and the reaction temperature was 45°C . After molecular distillation, the content of methyl ester is more than 95% [55].

Magnetic whole-cell biocatalyst (MWCB) was prepared using chitosan Fe_3O_4 microspheres as a carrier (in Figure 10). The yield of biodiesel was 87.32% after 48 h. After 10 cycles, the yield of biodiesel was 83.57%, which was higher than that of whole-cell biocatalyst without Fe_3O_4 (74.06%). It can be seen that the introduction of magnetic particles not only makes the catalyst easy to separate but also effectively immobilizes the active enzyme to avoid the loss of yield. Interestingly, in previous studies, it was not realized that the introduction of magnetic particles can also increase the yield [56].

Cubides-Roman et al. [57] used magnetic chitosan-immobilized *Pseudomonas fluorescens* lipase as a biocatalyst to study the enzymatic synthesis of ethyl ester from coconut oil and ethanol in an electromagnetic field-assisted bioreactor. The results show that under the conditions of 30°C , 45°C , and 60°C , oil alcohol molar ratios of 1 : 6, 1 : 9, and 1 : 12, and magnetic induction intensity of 6.5, the maximum conversion is about 12%. In the differential reactor, the molar ratio of oil to alcohol was 1 : 11.25, and the reaction time was 12 h. In this unconventional bioreactor, under the assistance of a magnetic field, the synthesis of esters is positively affected by the molar ratio and temperature, and magnetic induction is very important for the establishment of a magnetically stabilized bed. In addition, magnetic biocatalysts are retained/separated for further use. Although this interesting device did not obtain a large yield, the application of the new device proved that this model can be used for transesterification to synthesize biodiesel, which added a new method for the preparation of biodiesel.

At present, the efficiency of biomass-based materials is further improved, and the application of immobilized enzymes in biodiesel synthesis is expanded. Batista et al. [58] reported a new biodegradable membrane catalyst, which is composed of chitosan, lipase, and polyvinyl alcohol. The thicknesses of PVA/chitosan and PVA/chitosan/lipase membranes were 70.4 and $79 \mu\text{m}$, respectively. The SEM images showed the formation of continuous films without holes or cracks. It is estimated that the lipase rejection efficiency is 92%. The membrane can be reused for 25 hydrolysis cycles and can maintain 62% of the initial activity. These results show that PVA/chitosan/lipase is a promising material for biodiesel production. Similarly, Xie and Wang [25] used magnetic chitosan microspheres to immobilize lipase to study the transesterification of soybean oil. Using glutaraldehyde as a crosslinking agent, magnetic chitosan microspheres lipase was prepared by the chemical coprecipitation method. Using immobilized lipase, the yield of converted soybean oil fatty acid methyl ester reached 87% at an alcohol-oil ratio of 4 : 1, 35°C , and 30 h. the catalyst was reused 4 times without significant reduction in activity.

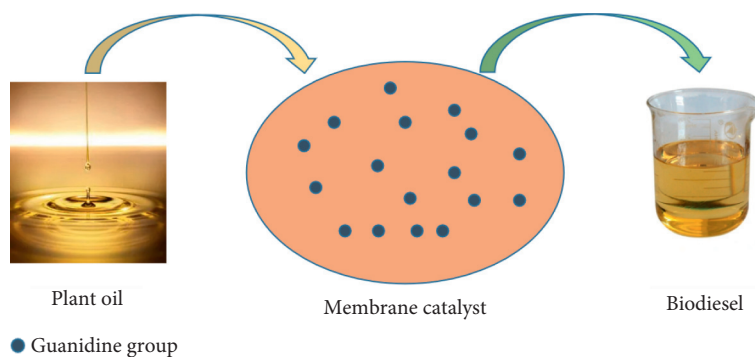


FIGURE 9: The chitosan-based membrane catalyst. Reproduced with permission from [53] copyright 2015, Elsevier.

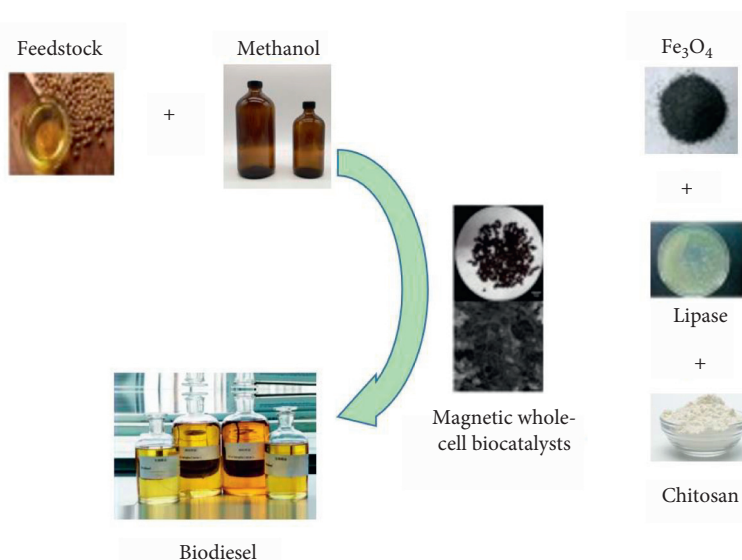


FIGURE 10: The magnetic chitosan biocatalysts. Reproduced with permission from [56] copyright 2016, Elsevier.

Undoubtedly, lipase can efficiently catalyze transesterification at low temperatures, which is considered to be the greatest advantage of lipase in biodiesel synthesis. However, the high cost of lipase is considered to be the main obstacle to the commercialization of enzymatic transesterification. Karimi synthesized superparamagnetic iron oxide nanoparticles (SPIONs), coated them on silica, and then grafted aldehyde groups to immobilize *Bacillus* capacity lipase, which is a promising method to improve the economy of enzymatic transesterification. The results show that the average particle size of SPIONs is about 20 nm. The nanoparticles linked to lipase showed almost superparamagnetism. Under the conditions of methanol to oil molar ratio of 6 : 1, immobilized lipase concentration of 25%, n-hexane content of 10%, the water content of 10%, reaction temperature at 35°C, and reaction time of 35 h, the conversion rate of WCO to biodiesel reached 91%. The immobilized lipase is easy to recover and reuse, and the enzyme activity has hardly decreased [59].

Chitosan was tried to be used as a perfect carrier for lipase immobilization by adsorption and crosslinking. The

immobilization efficiency of the crosslinking method was 99.1%, and the reusability was 12 cycles. The esterification of oleic acid and transesterification of olive oil showed that the partially purified enzyme proved its ability to catalyze the formation of methyl oleate. The partially purified and immobilized lipase of *Rhizopus oryzae* R1 has excellent efficiency and reusability and plays an important role in biodiesel production [60].

7. Conclusions

This paper reviews the application of heterogeneous catalysts supported on biomass-based chitosan in the synthesis of biodiesel. Chitosan has the greatest advantage of having a large number of active amino and hydroxyl groups, easy to modify and graft, and easy to chelate metal ions. At the same time, it can be compounded with a variety of materials to obtain multifunctional catalytic materials, which will undoubtedly improve the catalytic efficiency. At present, it is common to prepare chitosan-based catalysts rich in acid, alkali, metal ions, or enzyme active sites. However, these

catalysts with different forms still have the problems of low catalyst surface area, easy loss of active centers, and difficult separation, and there is still a need for further improvement.

Therefore, we need to further develop new chitosan-based materials to make this kind of catalyst not only to have good catalytic efficiency but also biodegradable, green, and nontoxic and can be used many times. At present, the number of chitosan-based biodiesel synthesis materials reported is limited. It is hoped that more chitosan-based catalysts with excellent performance can be developed and applied to the large-scale production of biodiesel based on laboratory research.

Data Availability

No data were used in the study.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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