Review of Advances in the Utilization of Biochar-Derived Catalysts for Biodiesel Production

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ABSTRACT: Biochar, obtained from the thermal decomposition of different biomass sources, can be used in various scientific technologies by virtue of its distinguishing performance. Recent developments in advanced biochar synthesis methods have led to continuous growth in the literature related to bulk biochar products and synthesized biochar substrates. This review specifically summarizes the current advanced methods for the synthesis of functional biochar catalysts and applications in (trans)esterification. Herein, first the method and design of synthesized biochar substrate catalysts are briefly introduced. Second, the applications of these synthesized biochar substrate catalysts upon (trans)-esterification are comprehensively discussed. Finally, the current research status and the future perspectives of the synthesized biochar substrate catalyst are presented. It is expected that this summary will provide perspectives and instructions for future work on synthesized biochar catalysts for biodiesel products.
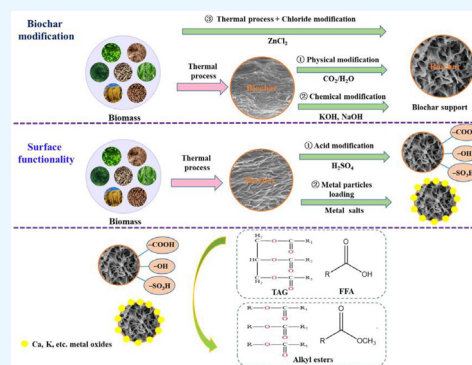
1. INTRODUCTION

Rapid and sustainable development of the economy has created increasingly severe energy and environmental problems, and there is an urgent need for a renewable green energy to replace petrochemical diesel fuel.[1−3] Due to its biodegradability, nontoxicity, low cost, and direct use in internal combustion engines, biodiesel has become one of the most discussed liquid biofuels.[4−6] Transesterification, as well as esterification, is a common chemical reaction for the preparation of biodiesel.[7,8] At present, homogeneous catalysts (NaOH and H_2SO_4) and heterogeneous catalysts (solid acid, solid base, etc.) are used for the preparation of biodiesel by transesterification or esterification.[9−11] Among them, heterogeneous catalysts have been widely studied due to the advantages of high activity, advanced yield, and satisfactory reusability.[12−14] Recently, synthesized biochar substrate catalysts have also been widely applied in the preparation of biodiesel because of their low cost, stability, and other favorable surface characteristics.[15,16]

Generally, biochar is generated from biomass by thermal decomposition under anoxic or anaerobic conditions at mesophilic temperatures of 350−700 °C.[17,18] It largely depends on the internal properties of biomass raw materials and thermochemical processes for the physicochemical properties of biochar.[19,20] As renewable resources, biomass resources of lignocellulose, crops, aquaculture, agricultural waste, urban and rural household waste, and animal fat are natural and abundant and have great potential in the production of thermal energy, electric energy, liquid fuel, hydrogen energy, and other value-added chemicals because of

its wide source and low price.[21−23] During thermochemical decomposition, biomass is converted into biofuels (syngas and bio-oil) by pyrolysis or gasification, leaving behind solid biochar as a residue.[15,24] Biochar is a carbon-rich porous solid, and it has similar properties to activated carbon, such as a large specific surface area, porosity, and the presence of abundant functional groups. Meanwhile, it is also considered in various functionalized biochar substrates due to its surface functional groups (C−O, C=O, −COOH, and −OH).[15,25,26] Therefore, it has been widely applied as catalysts, absorbents, activated carbon products, and soil amendments, etc.[27−29] It is notable that the stability of biochar in pH is negligible, and other profitable physicochemical properties promote its widespread application in the catalyst field, especially as a substrate for metal catalysts.[15,16,30] As catalysts or catalyst carriers, biochar showed excellent activities in transesterification and esterification, catforming, cracking, gasification, pyrolysis, hydrolysis, electrochemistry, photocatalysis, persulfate, persulfate oxidation, and other reactions.[31,32] To date, the synthesis and application of synthesized biochar functional substrates have been frequently reported.[33−36]
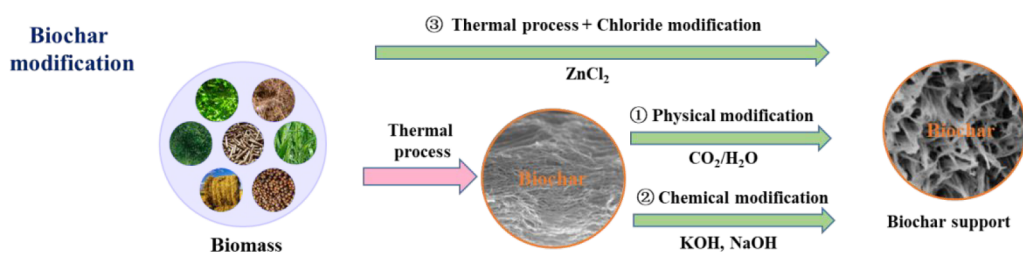
Figure 1. Physical modification of biochar.

Recently, many exciting literature studies have already reviewed renewable material derived catalysts for biodiesel production, and most of them focused on a sole renewable material such as eggshells, nanoporous materials, and so on. Their emphases were also largely placed on the waste materials,[11,12,37,38] and there are few reviews on biochar catalysts for biodiesel preparation. To study the effect of biochar feedstock and the biodiesel preparation process on the catalytic performance of catalysts, a systematic and comprehensive review of the applications of biochar-based catalysts for biodiesel preparation is imperative.

This review focuses on various synthetic methods of synthesized biochar substrate catalysts, highlights the structural properties and profitable biochar materials as catalysts amd catalyst substrates, and provides an effective way to investigate stable and productive catalysts and catalyst substrates. In the end, the current problems of synthesized biochar substrate catalysts are summarized, and the priorities and prospects of future research are predicted.

2. PREPARATION OF BIOCHAR AND BIOCHAR-DERIVED CATALYSTS

Biochar is a product from the pyrolysis process of biomass. Based on the various processes of theremochemical methods, the preparation methods of biochar would be classified by thermal decomposition, torrefaction, and hydrothermal carbonization, etc.[15,39]

2.1. Thermal Preparation of Biochar. Thermal decomposition is a process in which biomass is heated to the temperature of 300−900 °C under an inert atmosphere.[40] During this process, biomass undergoes thermal decomposition, causing its molecular fission, with products including solid, liquid, and gas, known as biochar, biofuel, and syngas, respectively.[6,41] The yield of thermal decomposition products is determined by biomass raw materials and the precise decomposition process, in which heating temperature rate and residence time are key factors.[42] The process of pyrolysis is classified into slow and fast reactions according to different heating rates.[43] In the slow process of pyrolysis, the steam is generated in the range of a 400−600 °C reactor and maintained for a long time.[39] It is mentioned here that unremitting passage of gas increases the product yield of coke. Fast pyrolysis and slow pyrolysis have similar temperature ranges, where fast pyrolysis has a heating rate greater than 200 °C/min, but a shorter residence time than slow pyrolysis, and is often used for bulk bio-oil production and low coke yield.[44] Hydrothermal carbonization is mainly used in the production of high-energy solid fuels from cellulose, hemicellulose, and lignin biomass. Raw biomass, like sewage sludge, municipal waste, and other wastes with high moisture content, requires drying at the first stage to save energy consumption and produce higher-value products simultaneously,[45] and hydro-

thermal carbonization just makes up for this deficiency. Generally, the hydrothermal temperature determines the state of hydrothermal carbonization products. Three hydrothermal reactions are classified based on the different products: the hydrothermal carbonization (HTC) reaction occurs under 250 °C, and the main product is biochar; hydrothermal liquefaction (HTL) requires a temperature range between 250 and 400 °C, which mainly produces bio-oil fuels; and the temperature of hydrothermal gasification (HTG) is higher than 400 °C, of which the most product exists in the gaseous state.[42] Flash vaporization converts biomass to gas at high pressure (about 1−2 MPa), in which the reaction time and temperature are less than 30 min and 300−600 °C.[46] Torrefaction is a process of slowly heating between 250 and 300 °C, with evaporating water and CO_2 to produce solid fuel with a low O/C ratio.[15] Gasification is a process in which solid biomass is converted into a gas phase in the gasification chamber under the conditions of 700−800 °C high temperature and a pressure greater than or equal to atmospheric pressure.[47]

To summarize, the two most effective thermochemical decomposition technologies with a wide range of raw biomass sources and high yields for biochar production are slow pyrolysis and hydrothermal carboniazation. Flash vaporization, torrefaction, and gasification are common methods for the production of bio-oils, solid fuels, and syngas. Biochar prepared by different methods has different physical and chemical properties, which can be directly used as catalysts or catalyst supports and are widely used in various catalytic reactions.

2.2. Modification of Biochar. In general, the decomposition of biomass by direct pyrolysis obtains inadequate biochar, which has the poor surface functionality of the surrounding carbonyl and hydroxyl groups, less porosity, and a small surface area (<150 m²/g), and it is difficult to use widely as a catalyst.[48,49] On the bright side, the surface pores and functional groups of biochar can be modified, thus serving as a substrate for various synthesized carbon materials.[15] The modified biochar has higher porosity and larger surface area, making it easier to load active substances, while its surface functional groups could also provide the active sites for catalytic reaction. Therefore, appropriate modification process selectivity (such as physical and chemical modification methods as shown in Figure 1) is crucial to improve the catalytic performance of synthesized biochar substrate catalysts.

2.2.1. Physical Modification. Raw biochar material undergoes the thermochemical transformation process at a temperature above 700 °C to obtain the physically modified biochar by using the controlled steam, CO_2, or the mixture gas phase explosion.[50] After thermal carbonization, biomass is usually modified by steam activation. Biochar generates initial pores during the general pyrolysis process, which is further activated
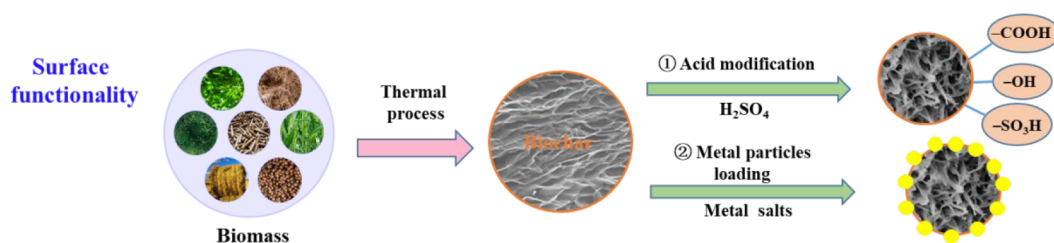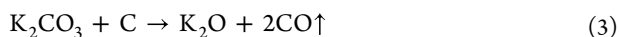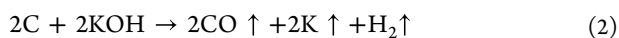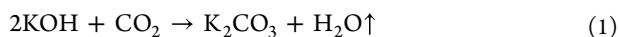
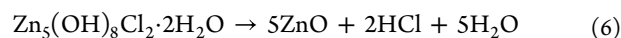**Figure 2.** Surface functional modification of biochar.

by steam to generate activated biochar with high porosity. Meanwhile, CO_2 gas is used as the common active gas for biochar physical modification. It has been shown that CO_2 as a medium can promote the generation of surface defects and carbonyl and hydroxyl functional groups. With the increasing temperature and pyrolysis time, the surface area and pore volume of activated biochar also increase,[25] resulting in the improvement of catalytic performance due to the increased active sites of biochar materials.[51]

2.2.2. Chemical Modification. The raw biochar surface can be modified with alkaline solutions such as NaOH and KOH under an inert gas flow at 500−1000 °C after impregnation. It has shown that the porosity of activated carbon can be adjusted by the amount of alkali and impregnation time.[15] Generally higher base dosages result in higher porosity with concomitant increases in surface area and pore volume.[52] The mechanism of advanced surface area and porosity for alkaline-modified biochar is as follows (eqs 1−4):

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O\uparrow \tag{1}$$

$$2C + 2KOH \rightarrow 2CO \uparrow + 2K \uparrow + H_2\uparrow \tag{2}$$

$$K_2CO_3 + C \rightarrow K_2O + 2CO\uparrow \tag{3}$$

$$K_2O + C \rightarrow 2K \uparrow + CO\uparrow \tag{4}$$

Under high temperature, some volatile substances such as water and carbon compounds in biochar could evaporate and react with KOH to form K_2CO_3 (eq 1); subsequently, carbon oxide and hydrogen were released to the atmosphere (eq 2), where the gas escapes to form porous structures. Once the temperature is further increased, the product K_2CO_3 would react with the carbon to release more gaseous species (such as CO and K), thereby forming larger pores (eqs 3 and 4).[53,54]

Another modification method is the utilization of a chemical such as zinc chloride that can modulate the biochar pore structure by in situ catalysis of the pores during biomass pyrolysis.[55] It is found that the main reason for the activation of $ZnCl_2$ was that after heat treatment the $ZnCl_2$ had a strong dehydration ability, which significantly promotes the formation of pores.[56] Specifically, pyrolysis of lignin under low-temperature conditions (e.g., <200 °C) swells wood fibers, and the addition of zinc chloride ($ZnCl_2$) invades the interior of biomass until depolymerization occurs, eventually facilitating the generation of a molten mixture. Based on the significant temperature points of zinc chloride ($ZnCl_2$) pyrolysis with melting and boiling points of 263 and 732 °C, respectively, it is in the liquid phase at approximately 700 °C.[15] After modification, $ZnCl_2$ is removed, and an abundant microporous structure was generated with the interior sites of biomass, which greatly increased the specific surface area and porosity. The potential pyrolytic process of $ZnCl_2$ in the mixture may be summarized as (eq 5−7):

$$5ZnCl_2 + 10H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot 2H_2O + 8HCl \tag{5}$$

$$Zn_5(OH)_8Cl_2 \cdot 2H_2O \rightarrow 5ZnO + 2HCl + 5H_2O \tag{6}$$

$$3ZnO + 2C \rightarrow 3Zn \uparrow + CO \uparrow + CO_2\uparrow \tag{7}$$

2.3. Surface Functional Modification of Biochar.
2.3.1. Acid Modification. The sulfonic acid group ($-SO_3H$) is one of the most common substances for functional groups of biomass insertion in the solid acidic phase. The most common method for preparing biochar-based solid acids is biochar immersion with concentrated sulfuric acid or other derivatives such as $H_2SO_4 \cdot xSO_3$ and $ClHSO_3$, which generates sulfides on the surface of biochar.[57] Biochar with $-SO_3H$ groups is one of the classic solid Brønsted acids with acid site densities up to 2.5 mmol H^+/g.[58] The high density of acidic sites on the surface of the modified catalysts ($-OH$, $-SO_3H$, and $-COOH$ functional groups as shown in Figure 2) can enhance their catalytic performance and stability, which can further promote various acidic catalytic reactions, especially for esterification and hydrolysis reactions.[59,60]

2.3.2. Metal Oxide Doping. Most biochar catalysts loaded with metal oxides can be prepared by biomass pyrolysis. Normally, the doping method of metal oxide is carried out by soaking biochar in the metal salt solution, and then the metal ions are adsorbed on the pores and surface of the biochar. After thermochemical processes, metal ions loaded on the surface of biochar are transformed into oxides. The most commonly used active substances are Ca, K, etc. (as shown in Figure 2).[61] When the biomass is immersed in the metal salt solution, based on the mechanism of electrostatic reaction, metal cations would be adsorbed on the surface or enter the pores of the biomass. In the subsequent pyrolysis process, metal ions loaded on the surface of biomass are converted into nanoscale metal oxides or metal elements. The biochar prepared by this method has been widely used as a biochar-based nanocomposite.[62] In addition, magnetic media (such as Fe_2O_3 or Fe_3O_4) are combined with biochar by pyrolysis activation or chemical coprecipitation to form magnetic materials, which are convenient for recycling and reuse.[63,64] It is notable that many biomass materials (such as walnut shells, potato peels, banana peels, etc.) that are rich in Ca, K compounds could be directly used as catalysts for biodiesel production after simple calcination.[65−67] These catalysts exhibited excellent catalytic performance even at room temperature.

The characteristics of biochar after modification are improved by using different methods. The specific surface area and the porosity of biochar are adjusted by physical modification, alkali modification, and chloride modification. The acidic sites of biochar through acidic modification increase by introducing acidic functional groups, and the properties of biochar are altered by adding metal sites through metal-loaded

modification. Therefore, one or more modification methods are selected to prepare biochar, so that biochar materials can be more widely used.

3. APPLICATION OF SYNTHESIZED BIOCHAR SUBSTRATE CATALYSTS IN CATALYTIC TRANSESTERIFICATION

In this section, the latest research results of biochar materials in transesterification/esterification are discussed.

3.1. Esterification. Esterification is a typical catalytic reaction that uses acid substances to catalyze the synthesis of fatty acid methyl esters (biodiesel) from inexpensive free fatty acids (FFAs) such as inedible vegetable oil, waste edible oil, and short-chain alcohols.[68,69] The equation of the esterification reaction is shown in Figure 3.
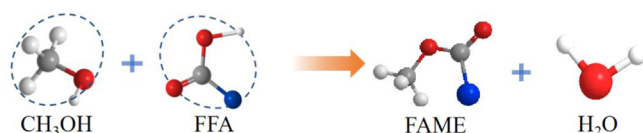

Figure 3. Esterification reaction between FA and alcohol. Reproduced with permission from refs 68 and 69. Copyright 2018 Elsevier Ltd. and Copyright 2016 Elsevier Ltd.

Aiming to enhance the industrial production of biodiesel, the preparation of solid acid catalysts from biochar has attracted extensive attention.[70] Several biomass solid acid catalysts for esterification are summarized in Table 1. Generally speaking, the acid catalyst for the preparation of biodiesel needs to be sulfonated by a strong acid such as concentrated sulfuric acid or oleum to obtain a strong acid site for esterification. Among them, raw materials of biochar generally originate from agricultural and forestry wastes such as pine chips, coconut shells, and sawdust, which are sulfonated by concentrated sulfuric acid though a pyrolysis process at 400–600 °C, and the products could be collected and used as a solid acid catalyst for esterification.[71] The sulfonated solid acid catalyst contains the $-SO_3H$ group, which has good catalytic performance, high reaction rate, and a biodiesel yield of 97%. Similarly, sulfonated carbon can be prepared from palm kernels, coconut shells, cauliflower seeds, and Douglas firs, while biodiesel can also be prepared from free fatty acids.[72−74] In addition, it has been shown that solid acid catalyst derived from peanut shell biochar has stronger acid sites (such as HZSM-5) and better activity than those of traditional solid acid catalysts, which can be used in the esterification of fatty acids and also catalyze the further conversion of glycerol as a byproduct into high value-added chemicals.[75,76] Corrêa et al.[77] prepared a series of sulfonated biochar from the fruit shell of Magnolia and applied it to the esterification with oleic acid and methanol. The results presented that under the optimum esterification conditions the substrate conversion reached 97.2%. Meanwhile, by comparison of the performance of catalysts with different raw materials such as palmitic acid, distillated soybean fatty acid, palm fatty acid, and coconut fatty acid, it was found that carbonized materials from different sources had different acid group binding capacities. Xia et al.[78] used biomass-based reed as raw material to prepare sulfonated biochar and applied it to catalyze the reaction of pyrolysis oil. The results showed that the sulfonated solid acid catalyst promoted the substitution of esters for its organic acids,

increased the calorific value and pH of the pyrolysis oil, significantly reduced the viscosity of the pyrolysis oil, and improved the quality of the pyrolysis oil. Reed biochar as a substrate was conducive to obtaining more active solid acid catalysts because of its large specific surface area, unique aromatic structure, abundant electron donor functional groups on the surface, and low inorganic salt content. Bora et al.[79] used sulfonated clematis seed catalysts for FFA conversion, and they found that temperature was the most significant parameter influencing the FFA conversion followed by reaction time and catalyst amount.

Aiming to enhance the performance of synthesized biochar substrate catalysts, Ayadi et al.[80] used olive pomace as raw materials to prepare synthesized biochar substrate catalysts by pyrolysis, steam activation, and sulfuric acid sulfonation. The results showed that the number of micropores increased after the thermal steam activation of the pyrolyzed biochar, which was the result of sulfonation removing the residual tar in the pores and expanding the micropore structure. Therefore, the surface area and porosity of sulfonated olive fruit residue biochar increased significantly. In addition, the reutilization of the catalyst is also a crucial indicator for evaluating the catalyst in the environment. Jenie et al.[81] prepared magnetic biochar by the pyrolysis−carbonization method, with the pretreatment of the oil palm hollow fruit string biomass by $FeCl_3$, and further sulfonation to obtain the magnetic solid acid catalyst with a high content of acid sites. The study showed that the performance of biochar substrate catalysts was determined by the concentration of modified hydrogen ions ($-SO_3H$, $-COOH$, and $-OH$) on the surface of the catalyst, and the recycling activity was greatly enhanced because of the presence of magnetic Fe_3O_4 on the catalyst surface.

Based on the above research, it is concluded that the strong acid site ($-SO_3H$) after acidification is the key for esterification of a biochar-based solid acid catalyst. In addition, $-COOH$ and $-OH$ (weak acid site) in biochar catalysts also have a certain catalytic effect. Taking sulfonated biochar as an example, the catalytic reaction mechanism of methanol and oleic acid is as follows: In the first step of the reaction, methanol is coordinated with oleic acid through hydroxyl oxygen and carbonyl oxygen to form a carbocation under the action of a Brønsted acid site on the surface of magnetic sulfonated biochar. Subsequently, the nucleophilic substances are produced during the deprotonation of hydroxyl groups attack carbocation ions and finally form water and methyl oleate.[77] Cao et al.[82] studied the effect of hemicellulose extraction on the catalytic performance of sulfonated biochar in biodiesel. They treated a corncob with aqueous sulfuric acid for extract hemicellulose, optimized its preparation conditions of the catalyst by acid density titration, and compared the effect of hemicellulose on the catalytic performance in the esterification of oleic acid and methanol. The results showed that hemicellulose extraction could realize multistage utilization of biomass and significantly increase the service life of sulfonated biochar.

Based on the previous research results, the present research on the esterification of biochar-based solid acid catalysts mainly focuses on (1) the selection of biomass-based raw materials for preparing biochar, (2) the selection of biodiesel raw oil, and (3) the sulfonation mode of biochar. Basically, the catalytic activity improved due to the enhancement of the specific surface area, porosity, and surface acidic sites such as $-SO_3H$, $-COOH$, and $-OH$ groups.

Table 1. Biochar Catalyst for Biodiesel Production

raw material	crude oil	preparation method	reaction type	parameters				yield (%)	ref
				time (h)	catalyst amount (%)	molar ratio of alcohol to oil	temperature (°C)		
Pine chips	soybean oil	pyrolysis at 400 °C, 100 °C, concentrated sulfuric acid sulfonation	Esterification	6	5	6:1	65	97	71
Coconut shell	palm oil fatty acid	150 °C, concentrated sulfuric acid sulfonation	Esterification	4	7	12:1	60	87	72
Begonia seeds	begonia seed oil	pyrolysis at 400 °C, concentrated sulfuric acid and PTSA sulfonation	Esterification	4	7.5	30:1	180	99	73
Douglas fir	microalgae oil	pyrolysis at 600 °C, sulfonation of concentrated sulfuric acid at 150 °C	Esterification	1	5	20:1	120	99	74
Broadleaf tree	vegetable oil	sulfonation with concentrated sulfuric acid at 100 °C for 24 h	Esterification	3	5	18:1	65	92	54
Astrocaryum murumuru shell	oleic acid, etc.	pyrolysis at 600 °C for 1 h and sulfonation with concentrated sulfuric acid at 200 °C for 4 h	Esterification	1.5	5	10:1	90	97.2	77
Freshwater reed	bio-oil	pyrolysis at 700 °C for 1 h and sulfonation with concentrated sulfuric acid at 135 °C for 2 h	Esterification	2	10	2:1	70	/	78
Clematis seeds	clematis seed oil	pyrolysis at 500 °C for 1.5 h, activation of superheated steam at 350 °C for 1.5 h with 15 kg/cm² (pressure), concentrated sulfuric acid sulfonation	Esterification	2	10	6:1	55	95.57	79
Olive pomace	olive residue	pyrolysis at 900 °C in a N_2 atmosphere, sulfuric acid sulfonation at 100 °C, and storage for 18 h	Esterification	5	20	9:1	60	97	80
Oil palm empty fruit bunch	oleic acid	$FeCl_3$ solution stirred for 5 h, activated by superheated steam at 500 °C for 20 min, and pyrolyzed at 500 °C for 1 h	Esterification	1.5	5	8:1	150	97.6	81
Remaining corncob residue	oleic acid	after hemicellulose extraction, pyrolysis at 300 °C for 3 h and sulfonation with concentrated sulfuric acid	Esterification	2	10	12:1	90	98.5	82
Avocado seeds	sunflower oil	pyrolysis at 900 °C for 2 h, precipitation with NaOH at 70 °C for 1 h, and activated at 900 °C for 2 h	Transesterification	5	7.3	15.6:1	99.5	96	4
Palm kernel shell	cooking oil	mixed with iron(III) chloride solution and pyrolysis, sulfonation with concentrated sulfuric acid at 120 °C for 12 h, and activated at 110 °C for 24 h	Transesterification	1.7	3.66	13:1	65	90.2	91
Polymerization of lignin-derived monomers	Jatropha oil	(1) Preparation of lignin-derived monomers: 4-methylphenol, 4-ethylphenol, and 4-propylphenol dissolved with 1,2-dichloroethane and then added with formaldehyde and anhydrous ferric chloride; (2) Carbonization: preheat the mixture at 45 °C for 5 h and keep it at 80 °C for 20 h and subsequent carbonization with 1,2-dichloroethane and H_2SO_4 at 80 °C for 4 h	(Trans) esterification	5	4.37	15.22:1	130.68	97.66	92
Potato peel	cooking oil	calcined at 700 °C for 3 h	Transesterification	2	3	9:1	60	97.5	65
Banana peel	soybean waste cooking oil	pyrolysis at 500–600 °C for 30 min	Transesterification	2	1.5	9:1	60	98	98
Sweet potato leaves	Scenedesmus obliquus oil	calcinated at 600–900 °C for 3 h with the ramping rate of 10 °C/min	Transesterification	1.5	7	15:1	60	99.5	66
	waste cooking oil		Transesterification	2	5	9:1	60	98.0	
Citron (Citrus medica) peel	Oil extraction from food waste	calcinated at 300 °C for 4 h in an ambient atmosphere	Transesterification	0.87	4	10:1	55	96.3	99

3.2. Transesterification. Biodiesel prepared by the transesterification method refers to the reaction between fatty acid triglyceride (TAG) and short-chain alcohol, with the methoxy group replacing the glycerol group on a long-chain fatty acid to produce fatty acid methyl ester (FAME) with small relative molecular weight.[83] The reaction equation is shown in Figure 4.
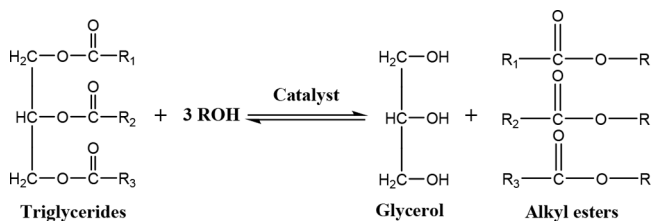

Figure 4. Transesterification reaction between triglycerides and alcohol.

Homogeneous (NaOH, KOH, etc.) and heterogeneous catalysts (solid acid and solid base) are used for transesterification, and the latter has become a research hotspot due to its easy separation and reusability.[84] The heterogeneous solid acids and alkaline catalysts are the common substances for the production of biodiesel. The catalysts modified by the solid acid would be applied in the reaction of esterification and transesterification. For example, Bhatia et al.[60] prepared solid acid catalysts by pyrolysis of cork at 600 °C; optimized various reaction conditions such as the different concentrations of alcohol to oil, doping catalyst, reaction temperature, and catalyst reusability in the process of biodiesel preparation; ensured maximum conversion of waste oil into biodiesel; and analyzed fatty acid alkyl ester components in biodiesel produced from waste cooking oil. The conversion rate of 98.58% was achieved under optimal conditions for 6 h, and the catalyst was reused 5 times without deactivation. In addition, biochar containing sulfonate substances such as peanut shells, and lignin and lignose was investigated to be applied in the transesterification.[59,60,85] The acidic sites ($-OH$, $-SO_3H$, and $-COOH$) on the surface group helped to improve the performance and stability of catalysts which were obtained from biomass. Acid catalysts can be used to catalyze the transesterification of feedstock oils with higher acid values.[12] Many studies have shown that simultaneous transesterification and esterification of acidic oils (containing more free fatty acids) are also effective methods for producing biodiesel. Dehkhoda et al. reported that through sulfonated pyrolysis of woody biomass with concentrated sulfuric acid or oleum, the synthesized biochar solid acid catalyst could simultaneously catalyze the transesterification and esterification of a rapeseed oil and oleic acid mixture.[54,86] The results also showed that the sulfonated biochar exhibited excellent catalytic activity in biodiesel synthesis, especially in the removal of free fatty acids. Similar studies were also carried out on the synthesis of acid catalysts using cassava peel, wood chips, coconut shells, peanut shells, and vegetable oil pitch as raw materials.[85,87−89] Bastos et al.[90] studied the activity of the *Astrocaryum murumuru* husk sulfonated biochar catalyst for esterification and transesterification reactions and further explored the reusability of catalysts on oil-derived chlorophyll. The results showed that the deactivation of the catalyst after repeated use was related to the leaching of acid sites, and the oil-derived chlorophyll had a negative impact on the regeneration and utilization of the

catalyst. The prepared solid acid catalyst derived from *Astrocaryum murumuru* was capable of adsorbing chlorophyll effectively in an oil source, so it could be used as a dual function material for removing chlorophyll from vegetable oil and producing biodiesel. Quah et al.[91] introduced a novel synthesis method of a catalyst by a palm kernel shell using sulfonated and magnetic modification for biodiesel production. The catalyst presented high surface area, remarkable thermostability, and abundant active sites and showed desirable activity of catalytic efficiency and recyclability. Huang et al.[92] prepared acid catalysts with 3D structure and laminar structure by calcining lignin monomer polymers at low temperatures, and its acidity could be controlled by changing the monomer composition. The 3D layered biochar derived from lignin was effective to promote the transesterification reaction of nonedible Jatropha oil, mainly due to the 3D structure of the catalyst that maximizes the exposure of the active site, increasing the contact between the acidic sites of the catalyst and the reactants. In addition, the kinetics of esterification for the catalyst was calculated in this study, and the activation energy of the reaction was lower than that of previous studies, which further indicated that the catalyst had an excellent catalytic performance.

Sythesized biochar substrates modified by solid base susbtances are also used as catalysts for transesterification reactions, especially for the reaction of high-purity oils and fats with low free fatty acids.[37,93] According to the structure of biomass materials, sythesized biochar substrate catalysts are classified into two categories, including single biochar catalysts and metal-loaded biochar catalysts. Since biomass contains a large number of anisotropic substances such as calcium and potassium, the biochar treated by pyrolysis acts as a catalyst alone. Counting on the easier pyrolysis treatment or calcination processes, those anisotropic substances serve as active sites, thus endowing biochar with high catalytic activity. For example, biochar synthesized from the gasification of palm shell could be directly applied as a catalyst in the methanol cracking reaction of sunflower seed oil.[94] The main component of the biochar was CaO, which effectively catalyzed the reaction, and the FAME yield was up to 99%. Likewise, biochar prepared from $CaCO_3$-enriched chicken manure also achieved higher FAME yields.[95,96] Miladinović et al.[67] found that biochar prepared by carbonization of walnut shells contained abundant active substances such as CaO and K_2O and thus had strong reactivity. Jung et al.[97] also confirmed that the biochar would be obtained from direct pyrolysis of pig manure and had strong activity. It contained a large amount of metal oxides (CaO, etc.), which greatly promoted the occurrence of transesterification, and the yield of biodiesel prepared by pig manure biochar reached 96.65% using waste oil as raw material. Daimary et al.[65] followed cost-effective processing methods to convert potato peels as one of the reliable resources for conversion into bio-oil and green heterogeneous catalysts. The synthesized catalyst presented great oxides and carbonates sites on its surface because of high potassium content (36.54%) doping, achieving a conversion of 97.50% under the optimal parameters of transesterification. In subsequent studies, Daimary et al.[98] pyrolyzed banana peels to obtain biochar with a high level of alkali ions and alkaline metals, which was highly effective and comparable in the soybean waste biochar catalyst transesterification of cooking oil to biodiesel. A heterogeneous catalyst was synthesized by using sweet potato waste leaves as raw material and employed in the

production of biodiesel from slanted Sedum mycorrhizae oil and soybean cooking oil by Eldiehy et al.[66] The sweet potato waste leaf-based catalyst provided sufficient alkaline adsorption sites for the transesterification reaction to effectively promote biodiesel production, and the high concentration of potassium was the main reason for the high activity of the catalyst in the transesterification reaction. Rajendran et al.[99] used a citrus peel biochar catalyst for the transesterification reaction of food oil and used SuperPro Designer and Simapro software to perform an economic analysis and environmental impact investigation of the process. The results showed that the use of waste citrus peels as feedstock reduced the cost of catalyst synthesis. The feedstock and byproducts played an important role in developing an economically sustainable process. The life-cycle assessment also showed that this biodiesel production process had a low greenhouse impact compared to traditional petroleum production options but presented negative impacts on terrestrial acidification, fine particulate matter formation, and fossil resource scarcity.

Nowadays, more and more attention of researchers has focused on the preparation of biodiesel by transesterification. The further development and application of biochar-based catalysts should follow the following aspects: (1) the acid and basic sites of the biochar-based catalyst are flexibly regulated to improve the selectivity and catalytic activity. (2) One or more modification methods are used to enhance the specific surface area and pore structure to obtain higher dispersibility and reaction activity. From the perspective of catalysts, it is of great significance to develop a series of heterogeneous biochar-based catalysts with low cost, convenient preparation, and good catalytic performance to improve the effectiveness of transesterification.

In addition to being directly used as a catalyst, biochar can commonly be used in the preparation of biodiesel as an inexpensive alkaline carbonaceous catalytic support because of its easily tunable porous structure, and potassium and calcium ions are often loaded on biochar as active substances. In order to display its own superiority, the surface of biochar is generally modified (Section 2 for details). Wang et al.[100,101] successfully prepared K_2CO_3-loaded biochar from solid waste (peat and bone) and used them as catalysts to produce biodiesel. The increased surface basic sites were very helpful to improve the catalytic activity. Zhao et al.[102] investigated that the pyrolyzed pomelo peel biochar reacted with KOH as a carrier for K_2CO_3. Bitonto et al.[4] prepared biochar by pyrolysis of avocado seeds, which was loaded with nanostructured calcium oxide as a catalyst to produce biodiesel from waste oil. The biochar carrier enhances esterification and transesterification reactions, such as oil esterizes methanol, but it differs significantly from metal-doped catalysts in that there is no active site loss even if it then demonstrates triple reproducibility. Wang et al.[103] also investigated a biochar substrate catalyst, which followed the method of spray dehydrating, and accelerated carbonization in the fluidized bed reactor, impregnating the papermaking black liquor with KOH. Under the optimal reaction conditions, the conversion rate reached 91.5%. At the same time, this experiment indicates that spray drying–fluidized bed carbonization can significantly shorten the time of high-temperature carbonization, which is of great significance for the preparation of catalysts with low energy consumption. Maria et al.[104] produced biochar from waste malt, a byproduct of the brewing industry, which was treated by NaOH, H_2SO_4, and H_2O, respectively. Next, the transesterification of triacetin, a probe

molecule of triglyceride, was tested, with the results showing that the activity was similar to that of the homogeneous catalyst, and the deposition of alkaline minerals on the surface was the main reason for the improvement in the activity of the catalyst. Biochar modified by NaOH showed high reactivity in transesterification, while a negligible change of biochar modified by H_2SO_4 or H_2O could be attributed to its high acidity and low alkalinity. Foroutan et al.[105] prepared a novel heterogeneous biochar/calcium oxide/potassium carbonate catalyst by using biomass-based Sargassum and brown algae as raw materials. In order to reduce the cost, the eggshells were dried and calcined for 4 h to prepare CaO, which was mixed with a K_2CO_3 aqueous solution containing biochar at 80−90 °C for stirring, and its solid after evaporation was continuously calcified at 500 °C for 3 h. The resulting biochar/calcium oxide/potassium carbonate catalyst effectively promoted the reaction, and the final utilization rate of biodiesel reached 98.83%. The recovery of the catalyst was also investigated, and the results showed that the leaching of active sites and the excessive adsorption of acidic substances would reduce the catalytic efficiency. Bitonto et al.[4] used the pyrolytic carbon from avocado seeds as the carrier and the coprecipitation method to load nanostructured CaO to study the effects of loading contents of calcium on the structure, morphology, and activity of biodiesel. Under optimal conditions, the yield of transesterification using sunflower oil was as high as 99.5%. The increased content of nano-CaO could enhance the basicity of the catalyst, thus affecting the catalytic activity of glycerol transesterification. Besides, the catalyst loaded with nano-CaO was easier to recycle than CaO. Although the catalyst loaded with potassium salt and calcium salt showed high catalytic activity in the transesterification, there was still a huge leaching problem during the reaction. Attaching Si compounds in the rice husk could form a new Ca−O−Si bond on the surface of sludge-derived biomass substrates, which has been shown to control the loss of Ca^{2+} within a certain range.[106,107] Kim et al.[108] investigated the potential of krill oil for biodiesel production. The results showed that the biodiesel exhibited low yields through conventional acid-catalyzed (trans)-esterification in the presence of impurities and free fatty acids in krill oil. However, the thermally induced noncatalytic transesterification reaction showed 94.7 % biodiesel yield.

Anak Erison et al.[109] conducted a life cycle assessment (LCA) of palm-based edible oil using the Simapro impact assessment method for two cases: choosing to purchase refined palm-based edible oil and synthesizing palm-based edible oil from raw materials. The results showed that the end point eco-indicator of the former (6.64×10^2 Pt) was lower than the latter (1.83×10^3 Pt), indicating that the purchase of refined palm oil for biodiesel production can reduce the environmental impact by 64% compared to biodiesel production from raw fruit bunches. In addition, the esterification process released chemicals into the ocean that had a significant impact on marine aquatic ecotoxicity in the midpoint assessment. This study determined the feasibility of impregnated magnetic biochar catalysts from spent palm kernel shells in the transesterification reaction, but the recycling performance of the catalysts was not considered in the process of conducting the environmental assessment.

In conclusion, the types of biodiesel synthesized by biochar substrate catalysts mainly depend on the different biochars. For sour oil feedstocks, a common method is to sulfonate various biomasses for esterification/transesterification of high-purity

oils. In recent years, waste edible oils and nonedible vegetable oils which are economical petroleum feedstocks have received extensive attention and are expected to be the most promising resources for biodiesel synthesis,[16] although they have high moisture content and variable FFA content. The existing solid acid catalysts have low efficiency and cannot meet the demand of biodiesel to a certain extent, so finding a highly efficient method to synthesize biodiesel with an economical feedstock is a quite challenge.

4. CONCLUSION AND PROSPECT

To summarize, biochar has become an outstanding carbon material because of its low cost, easy surface modification, and multicomponent and mature method of preparing catalysts from biochar. This paper mainly summarizes the preparation and synthesis methods of biochar. Despite the rapid development of biochar substrates for catalyst applications, it is still a great challenge for further catalytic applications: (1) its selectivity and stability are still limited due to the complexity and heterogeneity of its surface chemistry and (2) how to design precise catalyst structures at the multiscale level, accurately identify the synergistic interaction between metals and biochars, and explore the catalytic mechanism of catalysts. Therefore, in future research, the following aspects should be focused on.

(1) In-depth study on the surface functional groups of biochar related to catalytic activity, the synergistic interaction between metals and supports, and the mechanism of synthesizing catalysts would have certain roles in promoting the further development of industrial catalysis, particularly waste biomass catalytic production in the biofuel field. (2) To prepare a cost-effective biochar-based catalyst that replaces precious metals. The key for research is to enhance the performance of catalyst recycling and reuse and develop a scalable production scheme so that biochar can be used more widely in practice. (3) Develop more modification methods of biochar, surface functionalization of introducing carboxyl and hydroxyl groups, and heteroatom materials, graphene materials, and carbon nanotubes could be loaded on the surface of biochar, combining the beneficial characteristics of biochar substrates and functional materials. (4) The feature of biochar is determined by the type of biomass. In the future, it is necessary to carefully investigate the synergistic mechanism of the biomass in the catalyst reaction, so that it can be used more widely. (5) In order to decrease the cost of biodiesel production, nonedible oils have been commonly used as feedstocks for biodiesel synthesis. Therefore, the prepared catalyst is required to be more suitable for highly contained water and free fatty acids in raw oil.

In a word, the related research is expected to provide a reference for the advanced synthesis method of biochar substrate catalysts in the field of biodiesel preparation.

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Notes

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