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Selective preparation for biofuels and high value chemicals based on biochar catalysts

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Abstract The reuse of biomass wastes is crucial toward today's energy and environmental crisis, among which, biomass-based biochar as catalysts for biofuel and high value chemical production is one of the most clean and economical solutions. In this paper, the recent advances in biofuels and high chemicals for selective production based on biochar catalysts from different biomass wastes are critically summarized. The topics mainly include the modification of biochar catalysts, the preparation of energy products, and the mechanisms of other high-value products. Suitable biochar catalysts can enhance the yield of biofuels and higher-value chemicals. Especially, the feedstock and reaction conditions of biochar catalyst, which affect the efficiency of energy products, have been the focus of recent attentions. Mechanism studies based on biochar catalysts will be helpful to the controlled products. Therefore, the design and advancement of the biochar catalyst based on mechanism research will be beneficial to increase biofuels and the conversion efficiency of chemicals into biomass. The advanced design of biochar catalysts and optimization of operational conditions based

on the biomass properties are vital for the selective production of high-value chemicals and biofuels. This paper identifies the latest preparation for energy products and other high-value chemicals based on biochar catalysts progresses and offers insights into improving the yield of high selectivity for products as well as the high recyclability and low toxicity to the environment in future applications.

Keywords biomass, biochar catalysts, biofuels, high chemicals

1 Introduction

In this era of rapid development, it seems not feasible for humans to use the existing energy sources on earth to supply the demand in the future. In response to the dual challenges of energy depletion and environmental issues, researchers have intensively shifted their focus from traditional energies toward alternative sustainable ones. As a means of renewable energy, biomass energy is the fourth largest energy source worldwide. The thermochemical conversion of biomass produces not only energy products, but also many other high-value chemicals. Therefore, the thermochemical conversion process of biomass has attracted an increasing attention recently from researchers [1].

Thermal conversion processes include gasification, combustion, and pyrolysis, allowing the biomass to be converted into readily usable forms of energy [2]. To maximize the use of biomass, pyrolysis of biomass is a fast and effective method for advancing homogeneity, higher heating valuables, and energy density [3]. Pyrolysis of biomass is the thermal decomposition in the absence or presence of limited oxygen under certain temperature conditions [3]. This process consists of two main decomposition stages, where dehydration, dehydrogenation, and decarboxylation processes occur in the

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primary stage, and macromolecule cracking and solids transformation in the secondary stage [4].

The products of pyrolysis include bio-oil and syngas, which are formed by the thermal decomposition of the three main lignocellulosic biomass components (cellulose, hemicellulose, and lignin), and the chemical composition of the products can be significantly affected by the biomass source, pyrolysis conditions, and process settings (catalyst use, reactor type, etc.) [4].

However, the traditional pyrolysis method produces a lot of by-products, whose selectivity is poor [5]. Therefore, to increase the yield and relative content of the target product, it is of significant importance to selectively control the biomass pyrolysis process [6]. The selectivity of biofuels and high-value chemicals from biomass is influenced by catalysts. Therefore, it is essential to select suitable catalysts to make products rich in specific compounds.

Due to the current environmental situation, researchers prefer green, contamination-free, and facilely-prepared catalysts. Biochar-based catalyst is one of the good choices. Biochar can be prepared from many different waste biomasses, which have a wide range of sources, and are typically inexpensive while waste biomass can be used as feedstock for fertilizers, catalysts, and battery. Kim et al. have discovered that biomass porous as the anode of sodium-ion battery (NIB) has a significantly ultra-stable capacity [7]. Meanwhile, biochar-based catalysts is one of the most widely used catalysts which contain inorganic ions that can be used for tar cracking and other functional groups that contribute to the adsorption of metal precursors [8]. Biochar can hinder the aggregation of metal nanoparticles and provide more accessible active sites by acting as the catalyst supports compared with metal-based catalysts [7,9,10]. This brief review will present different types of biochar-based catalysts, including metal compound modified biochar

catalysts, nitrogen-doped biochar catalysts, and acid/alkali modified biochar catalysts, and provide important insights into the effects of biochar catalyst reaction conditions on selectivity improvement as well as into the preparation of various energy products and high-value products in an attempt to elucidate the mechanisms involved (Fig. 1).

2 Modification of biochar catalysts

Biochar, a solid product by biomass pyrolysis and/or partial gasification, has a variety of functional structures (e.g. oxygen-containing groups and persistent free radicals (PFRs)), making it a good choice as a catalyst [9,11]. Tao et al. have found that PFRs in biochar play an important role in the reducible C=O groups, possibly in aldehydes, aromatic ketones, and quinones, which enhance the catalytic ability [12]. Since the introduction of biochar into the catalysis field, researchers have tried various strategies to enhance the selectivity of biochar for bio-oils and chemicals. However, most of pristine biochar are not considered as sufficient and efficient enough to catalytic conversion for bio-oils and chemicals [9]. The catalytic capacity of biochar can be substantially enhanced by treatments using various physical/chemical activation and modification methods. For example, the pyrolysis and chemical activation could facilitate the catalytic activity on biochar catalyst, and loaded metal and heteroatoms could also enhance it by tuning the inherent properties of catalyst [9,13]. It can be seen that the modified biochar is of significant necessity for improving the selectivity of biochar for bio-oils and chemicals. Consequently, the effects of metal loading, acid-base modification, and heteroatom doping of biochar on product selectivity will be discussed in this section.

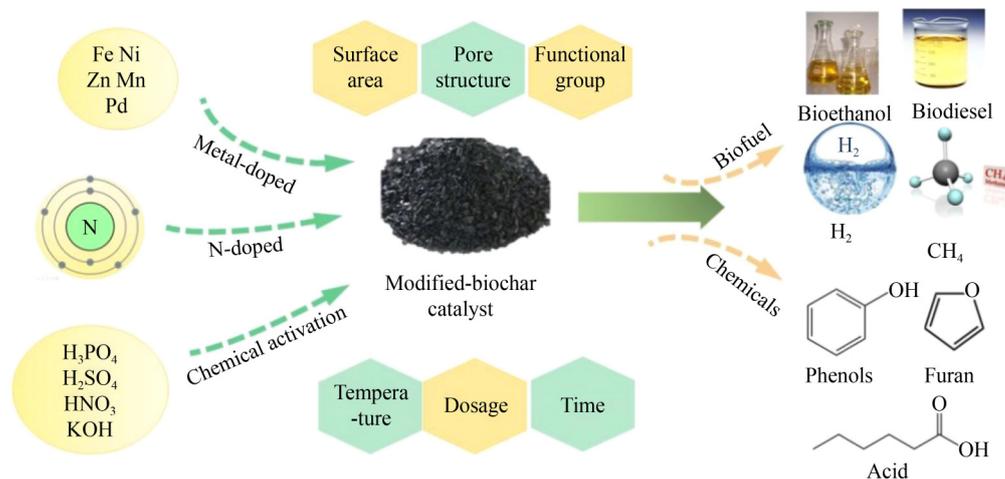


Fig. 1 Selective preparation for biofuels and high value chemicals based on biochar catalysts.

2.1 Metal compound modified biochar catalysts

2.1.1 Ni-doped biochar catalysts

Nickel metal (Ni) can be doped on biochar to improve its catalytic performance due to its strong activity and economic feasibility [14]. One previous study of Ni-based catalysts showed that Al_2O_3 has been the main supports used so far [15]. Nevertheless, the acidity of Al_2O_3 can cause sintering and severe carbon deposition which hinders the activity of the catalyst [16]. The problems of catalyst sintering and carbon deposition can be solved by using biochar as the support of Ni-based catalyst. In addition, the catalytic capacity of the Ni-doped biochar catalyst is increased compared to the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst [16]. Ni-doped biochar catalysts are prepared by impregnation, pyrolysis, and reduction. Generally, different concentrations of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are utilized to impregnate the biomass depending on the required Ni content. The pyrolysis stage is performed at noble gas atmosphere often at $10^\circ\text{C}/\text{min}$ at N_2 atmosphere, and held for 2 to 3 h, with the temperature controlled within $400\text{--}700^\circ\text{C}$. The reduction temperature usually does not exceed the pyrolysis temperature and requires the addition of 5% to 10% of H_2 (Fig. 2) [11,16–19]. In addition, the liquid-phase reduction method can also be used. In this method, sodium borohydride is added dropwise to an ethanol solution for reduction, which avoids the use of H_2 , and thus saves costs [20]. Ni-doped biochar catalysts have been found to improved specific surface area and pore structure to further facilitate their catalytic performance [10,20].

Wang et al. showed that the Ni-doped biochar catalysts obtained from rice husks using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with thermal treatment, a type of waste biomass, was upgraded through HNO_3 oxidation to facilitate the overall hydro-

phobicity [17]. Consequently, the catalyst was reduced for 2 h at 600°C at a mixed N_2/H_2 gas atmosphere [17]. Hydrophilicity/hydrophobicity was a critical step for the adsorption of less polar functional groups in heterogeneous catalysts [17]. Specifically, the co-presence of the hydrophobic and hydrophilic sites in the Ni-biochar treated by HNO_3 showed a superior activity for adsorption of the reaction intermediates with the C–O–C aliphatic structures [21]. Furthermore, the selective preparation of tar-free methane-rich gas with pyrolysis volatile of reed biomass over the biochar-loaded Ni catalyst using $\text{Ni}(\text{NO}_3)_2$ impregnation was investigated by Yue et al. [16]. Figure 3 showed the scanning electron micrography (SEM) images of the biochar-doped Ni catalysts. It was found that the pyrolysis temperature also had a significant impact on the yield of products, where the methane production of the selectively prepared tar-free gas products at atmospheric pressure and 600°C was as high as 188 L/kg and active sites of the Ni-doped biochar catalyst were enhanced by the aggregation mode of NiO particles. Particularly, this type of NiO particles at 600°C presented the optimal active sites as it might hardly be agglomerated or sintered during catalytic conversion [16].

Moreover, Quan et al. found that the activated Ni-doped biochar catalyst derived from pine sawdust had an excellent selectivity for the reforming of toluene carbon conversion (86.2%) and production of H_2 (64.3%) [19]. As the size of the activated Ni particle is reduced, the dispersion of nickel particles on Ni-doped biochar is considerably enhanced, and the specific surface area is increased [19]. However, excessively high Ni content (more than 10%Ni loading) in catalyst may have a negative influence on nickel accumulation and blockage of catalyst pores, which may decrease the catalytic active sites [19]. Furthermore, one kind of Ni-doped biochar with a honeycomb-like structure and morphology by

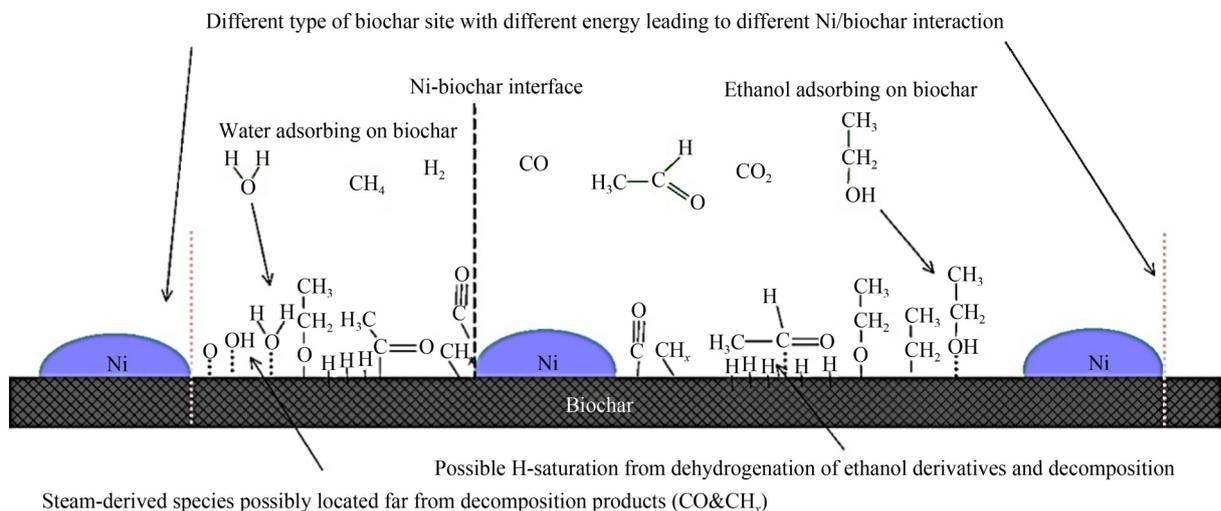


Fig. 2 Ethanol and steam process on Ni/biochar derived species on various active sites in reforming reaction (adapted with permission from Ref. [11]).

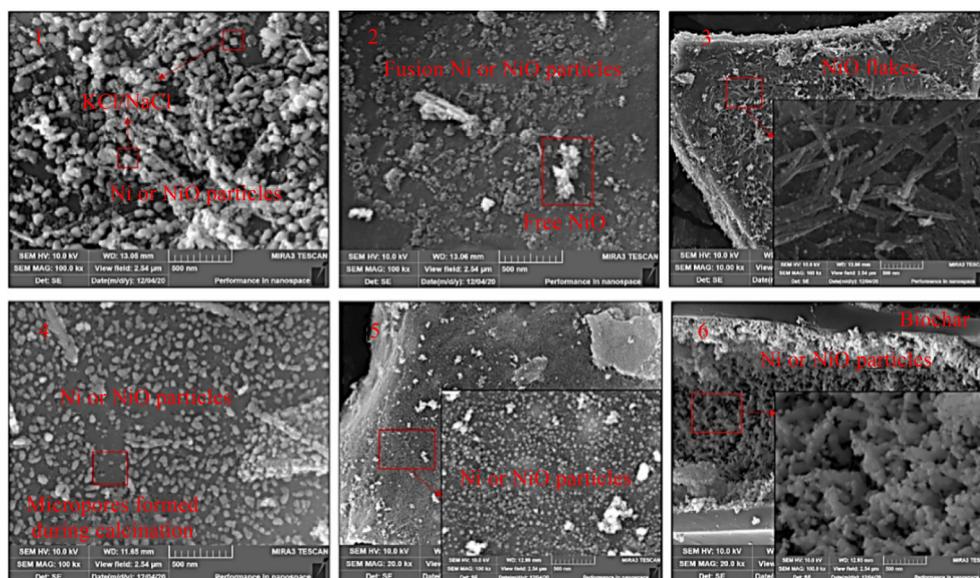


Fig. 3 SEM images of Ni-doped biochar catalysts (adapted with permission from Ref. [16]).

microwave pyrolysis can promote mass transfer around the catalytic active sites [22], which leads to a remarkable increase in the selectivity for H_2 in gas mixtures [22]. Additionally, Ido et al. found that the upgrading of liquid-phase biofuel from the *Scenedesmus obliquus* oil using 20% (mass fraction) nickel nitrate hexahydrate-impregnated biochar catalyst was extremely realized [23]. A kind of high-quality liquid-phase biofuel was obtained under the optimal conditions (246 °C, 3.72 (w/w) dodecane-to-oil mass ratio and 3.84 MPa hydrogen pressure), which consisted of 100% green liquid hydrocarbons with 94% alkanes, 6% olefins and no sulfur [23]. Analogously, Ren & Liu synthesized Ni-doped biochar catalyst by impregnation using 20% (mass fraction) $Ni(NO_3)_2 \cdot 6H_2O$ at 600 °C and toluene conversion (90.2%), and gas production (261.4 mmol/g) were facilitated due to its lower activation energy and small Ni crystallite dimension [14].

Therefore, Ni-doped biochar catalyst by impregnation using $Ni(NO_3)_2 \cdot 6H_2O$ has significant prospects for methane-rich gas, hydrogen production, and the upgrading of biofuel. The dispersion of nickel particles on Ni/biochar is remarkably enhanced and the specific surface area is increased. However, there are some limitations. For example, Ni-doped biochar catalysts are less selective for turn-over frequencies (TOFs) due to the lack of basic sites on the surface of Ni-doped biochar catalysts [18]

2.1.2 Fe-doped biochar catalysts

Ni-doped biochar catalyst has a poor selectivity to TOFs due to the lack of alkaline sites on its surface. The introduction of Fe can improve the selectivity of TOFs. The Fe-modified catalysts have a high activity, and can

achieve efficient fracture of C–C and C–O bonds [24]. The preparation of Fe-doped biochar catalysts is summarized into two major steps: impregnation and calcination [25–27]. Generally, reagents such as $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3$, and $Fe_2(SO_4)_3$ are used to impregnate the biomass. The impregnation process requires mechanical stirring, ultrasonic treatment, and drying and dehydration, which are done to allow a better mixture of Fe with the biomass for the next calcination step. Subsequently, Fe-doped biochar catalyst is obtained by calcination at 300–900 °C in N_2 atmosphere with a flow rate of 100–200 mL/min. In addition, the performance of Fe-doped biochar catalyst can be improved by a variety of methods, including microwave pyrolysis, introduction of dual carriers, and bimetallic catalysis [10,28–30].

Specially, as suggested by Zeng et al., Fe-doped biochar catalysts for phenol-rich bio-oil were synthesized through impregnating waste corn cobs with $Fe(NO_3)_3$ over microwave pyrolysis [28], among which, the biochar of impregnating 0.4 mol/L $Fe(NO_3)_3$ had the best selectivity to phenol, which was enhanced by 16.45% [28]. Notably, Zhao et al. found that the bio-oil yield could be significantly increased and the degree of hydrodeoxygenation of bio-oil products could be facilitated by the addition of metallic Fe during biomass liquefaction [31]. Furthermore, Sun et al. prepared a Fe-doped catalyst using iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) impregnated and discovered that Fe could tremendously increase the yields of monocyclic aromatic hydrocarbons (MAHs) [30]. This was the reason why Fe could vastly advance the oxygen removal rate during catalytic deoxygenation and hydrogenation. Meanwhile, Fe-doped catalyst inhibited the production of polycyclic aromatic hydrocarbons (PAHs). Because the polymerization reactions primarily occurred on position of B acid, the modification of Fe

decreased the B/L acid center ratio, which ultimately inhibited the yield and selectivity of PAHs [32].

Moreover, Fe-Mo₂C catalysis can enhance the selectivity for hydrogen-rich syngas using hardwood biomass as feedstock, where the optimal reaction conditions were > 60% H₂ concentration and H₂:CO ratio as 2:4. The Fe-Fe₃C active site is responsible for the activation of methane while Mo₂C is responsible for the activation of π -ring of oxygenated aromatic species in biomass. In particular, the Mo₂C active site can contribute to hydrogen deoxygenation with Fe, which made it easier to release H₂ and CO from the syngas [33]. Furthermore, Xue et al. performed pyrolysis with pine wood, using Fe₂O₃ as the oxygen carrier, which could result in a higher gas yield and a significant selectivity of CO [29]. Nevertheless, compared with CaFe₂O₄, Fe₂O₃ as the oxygen carrier, had less selectivity for CO. The site where the oxygen carrier (Ca₂Fe₂O₅) was formed when the ratio of iron to calcium was 1:1 produced the highest hydrogen yield (23.07 mmol/g biomass) at 800 °C [34].

Fe-doped biochar catalyst is strongly active, simple in preparation, and stable in performance. It has a good selectivity to high-value products such as phenolic compounds, monocyclic aromatic hydrocarbons, and gas fuels such as H₂ and CH₄. It provides a favorable pathway for sustainable energy substitution and the preparation of high-value energy products. In addition, the introduction of other elements in appropriate amounts on Fe-doped biochar catalyst can advance the location of active sites in the catalyst, and thus significantly increase the activity and selectivity of the catalyst.

2.1.3 Other metals-modified biochar catalysts

Transition metals can modify the redox activity of biochar by acting on functional groups and persistent free radicals [35]. Interestingly, Mn-modified catalysts have a crucial advantage in catalytic applications because of their ability to resist oxidative deactivation [36]. The loading of Mn on biochar is featured by its stability, adjustable specific surface area, and rich porosity [37]. Pierri et al. found that the Mn(II) loading on biochar promoted the efficiency of the oxidation of H₂O₂ and significantly enhanced the selectivity for cyclohexene, which accelerated the evolution of Mn^{II} to Mn^{IV}, and promoted its coordination with metals when H₂O₂ was present [36]. Similarly, Zn, as a transition metal, can effectively upgrade bio-oil to hydrocarbon fuel through compound aromatization [38]. For instance, Nikkhah et al. found that Zn-loaded biochar catalysts were effective in reducing the acid and oxygen content of bio-oil, raising the selectivity of bio-oil for aromatic content, and improving the conversion of hydrogen [38]. Especially, the introduction of Zn particles in the biochar facilitated the formation of Lewis acidic when impregnated by ZnCl₂ [38]. These Lewis acidic sites remarkably

benefited the production of subsequent reactions.

In addition, the concentratedly-loaded monoprecious metal catalysts are usually based on Pt, Pd, and Au, among which Pd has a superior activity and stability. However, the selection of a suitable carrier is an essential factor affecting the state and mass transfer process of Pd [39]. In particular, the rich porous structure and surface-active centers of biochar can be an ideal carrier for Pd loading. The process of preparing Pd-doped biochar is also relatively effortless, which mainly includes pyrolysis, impregnation, and reduction. Notably, before the pyrolysis process, the mineral content is removed by nitric acid treatment, and the Pd-doped biochar catalyst is produced by a 1:1 reduction of H₂ and N₂. Furthermore, Santos et al. [39] ameliorated the structural properties of Pd-doped biochar that derived from grape stems by adding different ratios of ZnCl₂. This was due to the fact that ZnCl₂ could significantly increase the porosity and volume of the biochar with a selectivity of 100% for the dehydrogenation reaction, and that the hydrogen production rate increased with the growing of the meso-macropore surface [39], among which, the rising of the surface pore area was beneficial to the stabilization of Pd. Table 1 showed the catalytic performance of different modification of catalysts with biomass. The use of carriers with large interconnected pores helps the reactants to diffuse into the active center, thus boosting the catalytic activity [39].

2.2 Acid and alkali modified biochar catalysts

Many researchers have studied the effects of acid treatment of catalysts on the product. For instance, Nikkhah et al. found that the pretreatment of Zn-doped biochar with acid improved the selectivity for bio-oil due to the fact that acid treatment can remove inorganic substances in biochar and reduce the interference of inorganic matter [38]. In addition, acid with oxidizing properties (HNO₃) is beneficial to the oxidation of oxygen-containing species on the catalyst surface [17]. Similarly, Wang et al. found that the overall catalytic activity of the catalyst with HNO₃ pretreatment was significantly advanced via the oxidation while the one without HNO₃ treatment had a slightly lower catalytic activity [21]. As the concentration of HNO₃ increased (from 0.02 to 2 mol), the pore structure on the surface of biochar was improved, and the formation of carbonyl was facilitated [21]. Furthermore, Cao et al. discovered that H₃PO₄-activated biochar had an excellent selectivity for hydroxymethylfurfural (HMF) (30.2 C % (mole fraction) at 180 °C, 20 min) and glucose (86.5 C % (mole fraction) at 150 °C, 20 min) [40]. The formation of acidic C-O-PO₃ and C-PO₃ surface groups on the biochar surface were promoted by activated with H₃PO₄. These surface groups became beneficial to the yields of HMF and glucose [40]. Analogously, Zeng et al. showed that

Table 1 Catalytic performance of different modification of catalysts with biomass

Catalytic performance	Feedstock	Preparation for product	Synthesis condition	Reagent and dosage	Catalytic performance	Ref.
Metal compound modified biochar catalysts	Reed straws	Methane-rich gas	Pyrolyzed at 500–700 °C with 10 °C/min	1.23 g/g Ni(NO ₃) ₂ ·6H ₂ O	188.38 L/kg	[14]
	Corn cobs	Phenol-rich bio-oil	Microwave pyrolysis was performed at 600 °C for 1 h	0.4 mol/L Fe(NO ₃) ₃	16.45%	[25]
	Vine shoot and crystalline cellulose	Hydrogen production from formic acid	Pyrolyzed at 800 °C in CO ₂ flow (200 mL/min) for 2 h and reduced at 300 °C for 2 h in N ₂ /H ₂ (1:1) flow (300 mL/min)	Pd (II) acetate (purity = 47.14%) dissolved in 0.001 mol/L acetone	100% in 150 min	[37]
	Cladophora glomerata macroalgae	Aromatic compounds of bio-oil	Carbonized at 600 °C for 120 min in 30 mL/min	ZnCl ₂ with impregnation ratios of 1.5	47.86% in 120 min	[36]
Acid and alkali modified biochar catalysts	Pinewood sawdust	Glucose and 5-hydroxymethylfurfural	Pyrolyzed at 600 °C and 10 °C/min for 2 h	Impregnation ratios (2 mass ratios of 85% (w/w) H ₃ PO ₄)	Glucose (86.5 C mol% at 150 °C, for 20 min) HMF (30.2 C mol% at 180 °C, for 20 min)	[38]
	Peanut shell	Algal biodiesel production	Pyrolyzed at 400 °C	1 g BC with 10 mL 98% H ₂ SO ₄	94.91% in 4h	[41]
	Sargassum tenerrimum	Phenol conversion to cyclohexanol	Pyrolyzed at 700 °C for 2 h	1:2 KOH impregnation ratio	≥ 99.9% in 4h	[42]
Nitrogen-doped biochar catalysts	Bamboo wastes	Phenols products (mainly 4-vinyl phenol and 4-ethyl phenol)	Pyrolyzed at 600 °C for 30 min with mixture atmosphere of Ar (99.999%) and NH ₃ (99.999%)	NH ₃ concentrations (30%, volume fraction)	Phenols (82%) including 31% 4-vinyl phenol and 16% 4-ethyl phenol	[52]
	Pinus sylvestris	CO ₂ methanation	Pyrolyzed at 600 °C for 1 h (400 mL/min) with 5 °C/min	Pinus sylvestris powder, urea and NaHCO ₃ were mixed according to the mass ratio of 1:4:3	99.7%	[46]

H₃PO₄ could improve the catalyst activity by enhancing the specific surface area of biochar [28]. However, Xiong et al. sulfonated the metal-free loaded biochar with 30% (w/v) H₂SO₄ [41], and discovered that H₂SO₄ changed the morphology of the biochar, and boosted the catalytic activity of the biochar compared with the unsulfonated biochar. In addition, the use of diluted sulfuric acid (30%, w/v) is preferable to concentrated sulfuric acid (98%, w/v) in terms of safety issues and environmental compatibility [42], and the selectivity of maltose hydrolysis to glucose was significantly improved at 140–160 °C (maximum glucose yield of 85%) (Fig. 4) [41]. Similarly, Behera et al. treated pure biochar with sulfuric acid, and increased the selectivity for biodiesel (94.91%) [43].

Additionally, biochar with a high specific surface area was produced by chemically activating the by-products from the pyrolysis process with KOH [19]. Kumar et al. found that KOH-activated biochar catalyst derived from *Sargassum tenerrimum* dry seaweed (SDSW) demonstrated a remarkable selectivity for phenol conversion (≥ 99.9%) to cyclohexanol (≥ 99.9%) at 5 MPa, 100 °C, and 4 h in isopropanol [45]. Similarly, Wang et al. also proved that KOH could significantly increase the specific surface area and the pore volume of biochar (from 80.25 m²/g and 105.36 mm³/g to 230.86 m²/g and 296.23 mm³/g, respectively), and consequently improve the stability of the catalyst (reused for 10 cycles, the biodiesel yields still above 81.6% of selectivity) [46]. Similarly, Kim et al. proved that KOH activation could increase the porosity and surface area of biochar catalyst [13]. Moreover, Fan et al. found that KOH could significantly improve the electron exchange capacity (EEC) with biochar catalyst by increasing O-containing

functional groups to facilitate the aromatization of biochar [47]. As the concentration of KOH rose, the redox activity of biochar gained. Therefore, it can be seen that the appropriate amount of KOH has a considerable effect on ameliorating the activity of biochar, which exhibits an effective way to upgrade the redox activity of biochar.

In general, both acids and alkalis can improve the catalytic activity of biochar by improving its pore structure and specific surface area. Respectively, dilute acid can reduce the ionic interference by depressing the inorganic composition of biomass in pretreatment, whereas HNO₃ with oxidizing property can adjust the hydrophilicity of biochar and thus change the pore structure of catalyst to improve the catalytic activity. H₃PO₄ and KOH can activate biochar and then advance the catalytic performance on catalyst, while H₂SO₄ can directly sulfonate biochar and enhance the catalytic activity by changing its morphology.

2.3 Nitrogen-doped biochar catalysts

Nitrogen-doped biochar is considered as a promising, stable, efficient, and widely available catalyst. A large number of acid intermediates and pyrolysis species are produced during biochar pyrolysis. The nitrogen-doping methods of biochar include direct synthesis and post treatment. Particularly, the direct synthesis is achieved through a carbonization reaction of carbon precursors mixed with nitrogen dopants, while the post treatment is typically completed by reactions with nitrogen-containing reagents [48]. Compared with direct synthesis methods which only required one step, post treatment is more

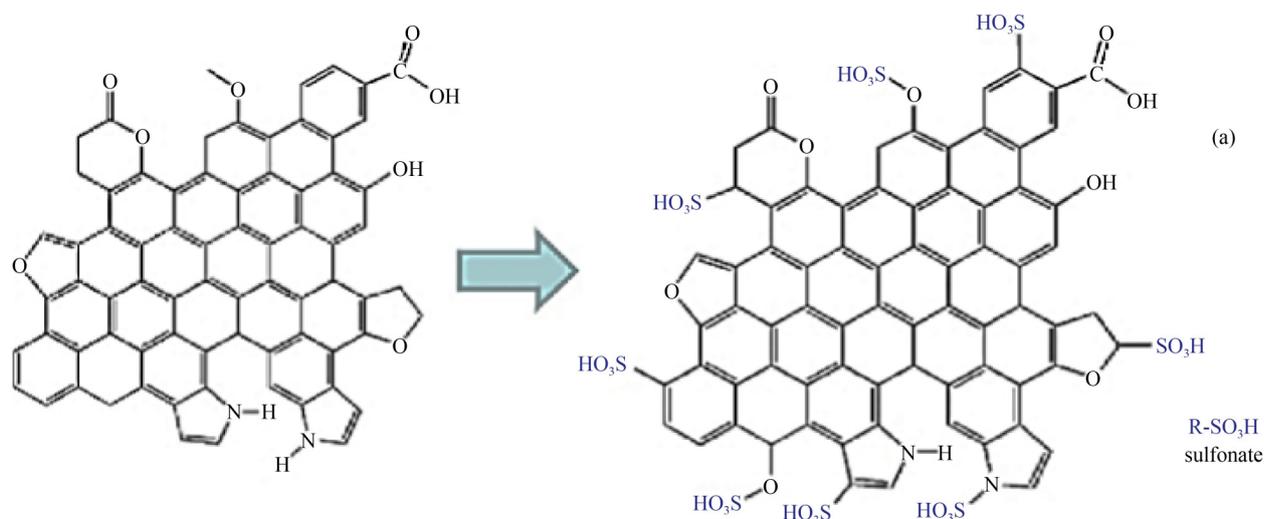


Fig. 4 Sulfonation reaction (adapted with permission from Ref. [44]).

complicated, requiring more than two synthetic steps to prepare the targeted materials [48]. Doping with nitrogen sources are achieved by urea [49], melamine [50], $\text{NH}_3\text{-H}_2\text{O}$ [51], and diverse nitrogenous groups including pyridine-N, pyrrole-N, and graphite-N are generated during different pyrolysis temperature (500–700 °C) [49], among which pyridinic-N and graphitic-N made significant contribution to providing active sites and reducing mass transfer resistances in the catalytic process [49]. Furthermore, the characteristic of the ion centers and coordinative environment are modulated through the nitrogen doping biochar catalyst, further enhancing catalytic oxidation activities [52,53]. Interestingly, Sekhon et al. showed that the biochar derived from the pyrolysis of coconut shells with nitrogen-doped had a unique cellular structure, which enhanced its porosity and catalytic activity [53]. Wang et al. introduced pyridine-N into biochar by using urea as nitrogen precursor and NaHCO_3 as activator [49], and discovered that when the pyridine-N content was at the highest rate (37.7%), the nitrogen-doped biochar catalyst was extremely selective for CO_2 methanation, where the CO_2 conversion and CH_4 selectivity was 93.8% and 99% [49]. Besides, the pyridinic-N and graphitic-N had a remarkable performance in providing active sites and reducing mass transfer resistances [49]. The hydrogenation of CO_2 to CH_4 could be facilitated through increased active sites [49]. In summary, the high pyridinic-N and graphitic-N content on the surface of catalyst played an important role in enhancing performance of CO_2 methanation [49]. Moreover, Song et al. prepared nitrogen-doped mesoporous carbon with a cylindrical pore structure using dicyandiamide as nitrogen source for thermosetting, resulting in a superior selectivity for synthesizing ethanol from CO_2 [54]. Interestingly, it was a critical initial step for CO_2 electroreduction to the dimerization of the adsorbed intermediates COOH^* or CO^* by the proton-electron

transfer reaction (Fig. 5) [54]. During the formation of key COOH^* and CO^* intermediates, the subsequent proton–electron transfers could be significantly impacted by pyridinic/pyrrolic N sites that initiated the adsorption/activation of aqueous CO_2 [54]. In summary, the cylindrical structures with their pyridinic/pyrrolic N sites may be the main reasons for a better catalytic performance of nitrogen-doped catalyst in CO_2 electroreduction, as demonstrated by the density functional theory calculations.

Except for methanation and electroreduction of CO_2 , N-doped biochar can also advance the quality of bio-oil and boost the selectivity for a certain type of high-value product. Chen et al. prepared nitrogen-doped biochar with fast pyrolysis bamboo wastes at 600 °C using NH_3 , which remarkably increased the selectivity (by up to 82%) for phenol products, especially the higher-value 4-vinyl phenol (at 31%) [55]. The nitrogen-doped biochar had a significant impact on catalytic conversion of the pyrolytic intermediates to active N- and O-containing groups, among which pyrrolic-N took effect on providing hydrogen for H-acceptors and $\text{C}=\text{O}$, and $-\text{OH}$ groups could facilitate O-species intermediates for the formation of phenols [55]. Besides, a dehydration reaction was found between the two, which improved the selectivity for phenols and enhanced the quality of bio-oil [55].

Heteroatomic N-doping biochar is considered as an effective method to enhance the catalytic activity. However, Wang et al. found that N-doping was inefficient for (E)-1,2-bis(4-chloro-phenyl) diazene, while Fe and N co-doped biochar boosted a unique active site for the selectivity of nitroarenes to (E)-1,2-bis(4-chloro-phenyl) diazene (within 40 min, up to 96%) using melamine and potassium ferrocyanide as nitrogen and iron sources [56]. When a 1:1:1 mass ratio of mixtures (carbon support: melamine: potassium ferrocyanide) was subjected to pyrolysis at 800 °C for 1 h, a higher amount

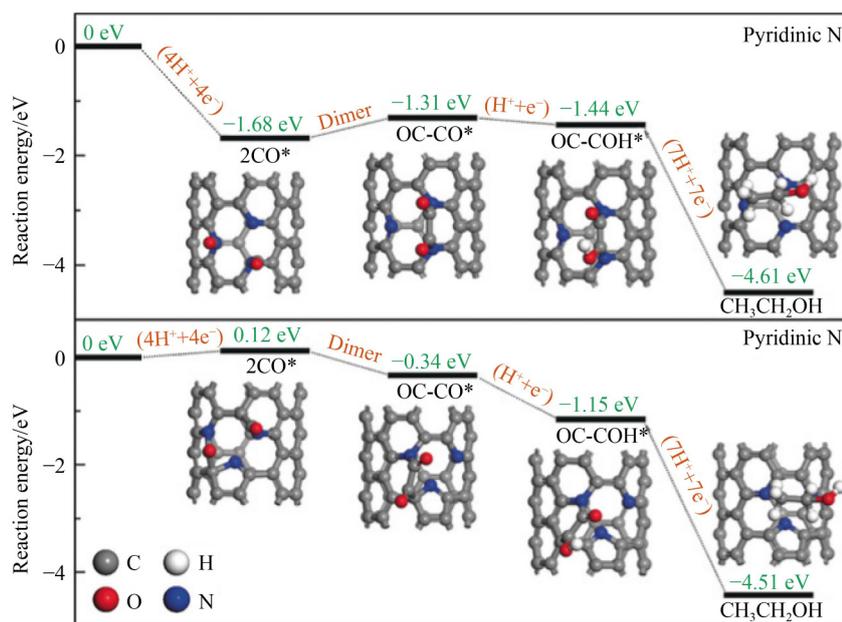


Fig. 5 Calculated reaction energy for the electroreduction of CO₂ to ethanol over pyridinic and pyrrolic N sites (adapted with permission from Ref. [54]).

of pyrrolic N was converted to pyridinic N during this process. Furthermore, compared with the raw carbon catalyst, the vacancies and defect sites of the carbon nanosheets were occupied by Fe and N doping catalyst [56]. As the Fe-active center, the electron-absorbing substrate during Fe/N co-doping could better stabilize the transition. It thus converted nitroarenes to the corresponding azo compounds with a high selectivity in the coprolysis process [56]. Moreover, Cao et al. discovered that nitrogen-doped carbon-supported iron catalysts had significant performances in the reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS acid) to 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD acid) [57]. In general, N-doped treatment does advance the active sites and catalytic performance of biochar, and it can be concluded that pyridinic and pyrrolic N in N-doped biochar play a critical role in facilitating the produce yield for certain types of high-value products such as phenol and methane.

To summarize, as mentioned in this paper, metal loading, acid-base activation, and heteroatom-doped biochar, which are novel, efficient in action, and stable, might take effect to the activity of biochar catalysts. The preparation of biochar catalyst not only offers an attractive route for waste resource utilization, but also provides a novel high-efficiency catalyst for preparing valuable chemicals or alternative liquid fuels. Table 2 exhibited the selectivity for product using different catalysts. To be specific, metal-loaded biochar such as Ni, Fe, Mn, and Zn were converted to the liquid phase fuels with a high selectivity, and had a significant potential for enhancing bio-oil quality. These metals can modify the redox activity of biochar by improving the

specific surface area and pore structure [20], as well as acting on functional groups and persistent free radicals [35]. Furthermore, the metal-modified biochar catalysts are superior to hinder the aggregation of metal nanoparticles and to produce more accessible active sites than pristine biochar [9]. Furthermore, the metal-modified biochar catalysts are superior to hinder the aggregation of metal nanoparticles and produce more accessible active sites than pristine biochar [9]. Meanwhile, Fe and N co-doped porous carbon has a superior oxygen reduction reaction (ORR) [10]. However, extra alkali metals may inhibit the production of H₂ owing to their easy migration and coverage of the Ni-active sites [19]. Besides, N-doped biochar has remarkable effects on CO₂ methanation and electroreduction, and thus has a good performance in the preparation of high-value products such as phenol. Generally, compared with raw carbon supports, the N-doped and metal-modified biochar has the advantages of wide source, simple preparation, large specific surface area, rich porosity, and functional groups. Furthermore, Kim et al. reported MOF-derived nanoporous carbons with rich porosities, excellent thermal, and chemical stabilities had a beneficial effect on versatile applications [58]. Therefore, biochar catalysts have become a hot topic in recent years, and have a significant potential for future catalytic applications.

3 Selective preparation of energy products

Reliable efficient and green alternatives need to be found as soon as possible due to the shortage of non-renewable

Table 2 Selectivity for product using different catalysts

	Modification of biochar catalysts	Selectivity for product	Ref.
Metal compound modified biochar catalysts	Ni-modified biochar	Methane	[16]
	Ni-modified biochar	H ₂ production, 64.3%	[19]
	Ni-modified biochar	Alkanes, 94%	[23]
	Pd-modified biochar	Hydrogen production, 100%	[39]
	Zn-modified biochar	Aromatic compounds of bio-oil, 47.86%	[38]
	Fe-modified biochar	Phenol, 16.45 area%	[25]
	Fe-modified biochar	CO, 23.07 mmol/g	[34]
Acid and alkali modified biochar catalysts	H ₃ PO ₄ -activated biochar	HMF, 30.2 C mol%, glucose (86.5 C mol%)	[40]
	H ₂ SO ₄ (30% w/v)-activated biochar	Glucose, 85%	[41]
	H ₂ SO ₄ -activated biochar	Biodiesel, 94.91%	[43]
	KOH activated biochar	Cyclohexanol, 99.9%	[45]
	KOH activated biochar	Biodiesel, 81.6%	[46]
Nitrogen-doped biochar catalysts	Nitrogen-doped biochar	CH ₄ , 99%	[49]
	Nitrogen-doped biochar	Phenol, 82%	[55]
	Nitrogen-doped biochar	(E)-1,2-bis (4-chlorophenyl) diazene, 96%	[56]

energy. Biofuels, including both liquid and gaseous fuels, are expected to replace liquid fossil fuels in the future. Numerous researchers have tried various methods to upgrade biofuels, including pyrolysis and ester exchange, and it has been discovered that biochar catalysts have a great potential in the upgrading of biofuels.

3.1 Liquid fuels

3.1.1 Biodiesel

Biodiesel, mainly derived from vegetable oils, animal fats, or other materials composed of triacylglycerols, is used as an alternative to traditional petroleum energy [59,60]. As one of the most promising renewable and sustainable fuels, biodiesel has the advantages of low- or no content of sulfur, no aromatic content, and biodegradability [59]. In the process of biodiesel production, catalysts play an extremely important role. Recently, biochar catalysts have been widely and effectively applied in biodiesel production, as they are considered as green and stable catalysts that make a great contribution to advancing the quality of biodiesel. Specifically, sulfonation is viewed as one of the most effective methods to treat biochar, which increases the activity by introducing a covalent bond of sulfonic acid group (SO₂-OH) on the surface of biochar. Quah et al. found that the biochar catalyst obtained by sulfonation with concentrated sulfuric acid could remarkably increase the overall biodiesel selectivity of edible waste oil [61]. By contrast, the use of 4-benzenediazonium sulfonate (4-BDS) is much milder and the sulfonation process is more stable than the direct use of sulfuric acid. Based on 4-benzene diazonium sulfonate (4-BDS), Lim et al.

reported that biochar derived from oil palm empty fruit bunch managed to significantly increase biodiesel selectivity by 98.1% at 200 °C pyrolysis with 15:1 sulfanilic acid [62]. Generally, a period of 7 h was regarded as the optimum period for transesterification reaction, because the yield of biodiesel increased gradually with the increase of esterification duration, while it had only a slight increment after 7 h. It can be seen that the esterification duration is also a key factor affecting the transesterification reaction. Besides, palm fatty acid distillate (PFAD) was used in biodiesel production, which could fulfill the recycling of the product and the production of high-value biodiesel at the same time. However, the reaction was easily affected by the pyrolysis temperature, and a higher pyrolysis temperature will destroy the catalyst structure, thus affecting the adhesion of the sulfonic acid group [62,63]. Moreover, CO₂ is considered to be an effective means to manipulate carbon distributions, which could crack and expand pyrogenic products during pyrolysis, and further react with them [64]. Yoon et al. found that the use of CO₂ as the reaction medium in the co-pyrolysis of lipid waste and red mud could control the carbon distribution between pyrolysis products, and consequently obtain a biodiesel yield of 92% [65]. In addition, biodiesel could be produced with a low energy consumption through the catalytic transesterification reaction. Aside from waste fruit shells and peat, the pseudo-catalytic transesterification reaction using biochar that is derived from livestock manure (chicken manure, pig manure) has been investigated. It can be a promising candidate as a catalyst as it realizes energy recovery (biodiesel, pyrolysis oil, H₂ and C1-2HCs). Jung et al. found that the existence of the Ca species in chicken manure could provide alkalinity for

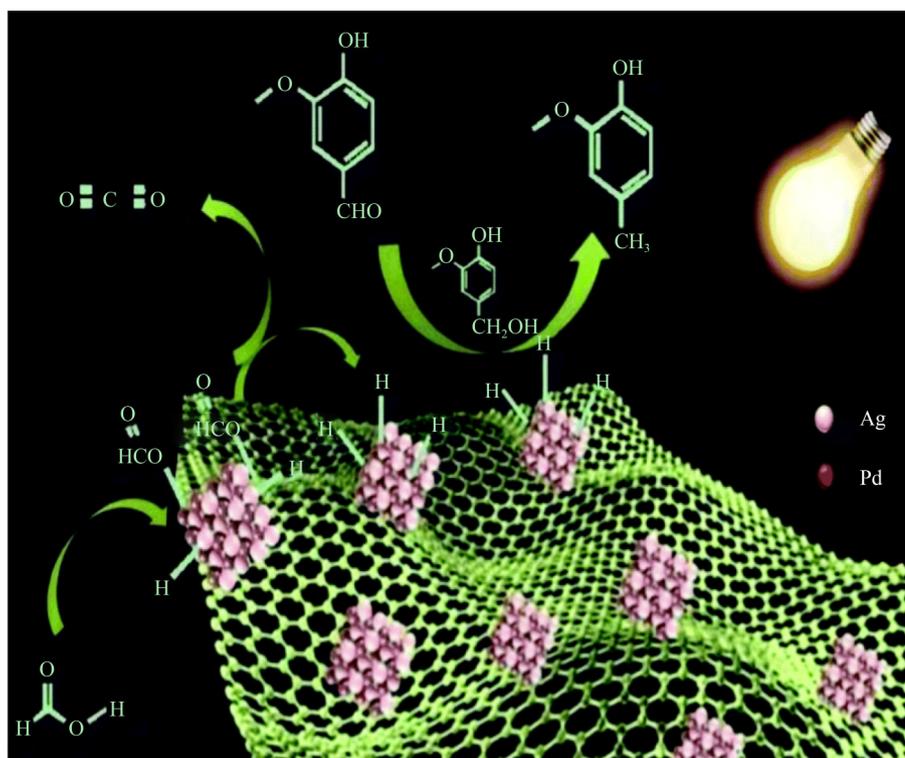


Fig. 6 Hydrodeoxygenation of vanillin depicting a plausible mechanism (adapted with permission from Ref. [72]).

transesterification, thus significantly enhancing its catalytic capacity, in which chicken manure biochar at 350 °C exhibited the best performance (95.6%) for biodiesel [66]. However, biochar that was derived from high content Ca species in chicken manure could impact the catalytic activity and decrease the selectivity for biodiesel by accelerating the thermal cracking. Furthermore, Jung et al. suggested that metal components in pig manure could be an effective catalyst for biodiesel synthesis, resulting in a biodiesel yield of 96% [67]. Interestingly, biochar that was derived from the pyrolysis of pig manure contained a substantial amount of high value-added gas products (H_2 , CO, and CH_4) and pyrolysis oil [67]. It was also found that pig manure biochar had better reaction kinetics than chicken manure biochar due to the imparted catalytic capability. Therefore, pig manure biochar is believed as an effective and novel means for facilitating reaction kinetics and enhancing the catalytic activity to use of livestock and poultry. Moreover, the algae catalyst with a crystalline structure was modified by Foroutan et al. and was applied for the biodiesel production from edible waste oil [68]. Among those, a catalyst loading of 4% (mass fraction) was reported as the optimum esterification condition which provided the highest biodiesel yield at 98.83% [68]. However, prior to the transesterification reaction, high free fatty acid (FFA) was removed from the waste cooking oil to less than 1%, because biodiesel yield was affected by FFA to create some by-products. Further-

more, both biomass reaction temperature and methanol/oil ratio were the key factors that influenced the transesterification reaction. Consequently, both parameters must be well controlled to facilitate the attachment of the biodiesel selectivity. When the reaction temperature was extremely high (over 65 °C), the transesterification reaction experienced methanol evaporates partially and reduced the mass transfer rate between methanol and catalyst [69]. Additionally, at an extreme excessive methanol/oil ratio, the selectivity for biodiesel of catalyst would also be impacted by the accelerated transesterification reaction which reduced the catalytic activity [70]. Besides, the production of algal oil derived from cellulosic seaweed has been focused as an effective measure for alternative resources [71]. Behera et al. showed its excellent catalytic behavior as a heterogeneous catalyst in biodiesel production from algal oil [43]. In terms of the temperature, catalyst dosage and methanol-oil ratio were the key parameters affecting the transesterification of microalgae oil. When the catalyst dosage was extremely high, it would increase the resistance of mass transfer instead of reducing the production efficiency [43].

In general, reaction temperature is the key factor in determining the transesterification reaction. A rise in temperature can increase the reaction rate and consequently increase the output of biodiesel with the increase in reaction kinetic energy. However, an excessively high temperature can result in the inhibition of the reactivity.

In addition, the esterification time, the addition of catalyst, and the ratio of methanol/oil may also affect the process of transesterification, while pressure can adjust the rate of transesterification. From the perspective of biochar catalysts, choosing biomass with a higher lignin content to prepare biochar is more conducive to the selective production of biodiesel.

3.1.2 Fuel ethanol

Fuel ethanol is one of the most common types of liquid fuel extracted from biomass recently. It is believed to be an energy-saving alternative to the conventional energy. It has a higher heat of vaporization, flame speed, and octane number, and is thus considered as a sustainable product which can reduce crude oil consumption and environmental pollution [73]. The traditional methods of preparing ethanol are inefficient. Emerging distillation techniques related to green and efficient energy mainly includes ohmic-assisted hydrodistillation, membrane-assisted distillation, and heat-integrated techniques [73].

Unfortunately, the high cellulosic crystallinity and lignin content of biomass, especially woody biomass have negative impacts on ethanol yields. To overcome the negative influence of high-fiber structure and thus improve the bioconversion efficiency of bioethanol, many researchers have studied the effects of biomass pretreatment [74]. Table 3 showed the active sites and mechanisms of different biochar in selective preparation of biofuels and high chemicals. Pretreatment can be divided into three categories: physical (mechanical crushing and ultrasonic), chemical (acid-base, oxidation and ionic liquid pretreatment), and biological (enzyme pretreatment and microbial/fungal pretreatment), or a combination of those [75,76]. Moreover, biochar has emerged as important catalysts for conversion of bioethanol due to its inclusion of functional groups, pH buffering capacity, and cation exchange capacity (CEC). Sun et al. examined that the treatment of biochar made from waste woody biomass and poultry litter could remarkably increase the yield of overall ethanol [77]. They explored the potential of biochar in enhancing the

Table 3 Active sites and mechanisms of different biochar in selective preparation of biofuels and high chemicals

Catalyst	Feedstock	Product	Catalyst/% (mass fraction)	Reported active sites	Mechanism	Ref.
BC	Chicken manure	Biodiesel	4.71	Ca species in catalyst imparts a strong basicity	Pseudo-catalytic transesterification	[61]
CaO/K ₂ CO ₃ BC	Brown algae of <i>Sargassum oligocystum</i>	Biodiesel	4	CaO and K	Transesterification process	[63]
Solid acid BC	Oil palm empty fruit bunch	Biodiesel	20	S-O and S-O ₃ H sulfonic groups	Esterification	[57]
Magnetic BC	Palm kernel shell	Biodiesel	3.66	Comparable magnetisation saturation of 8.458 emu/g and high acid density of 1.92 mmol/g	Transesterification process	[56]
Ni BC	Mallee wood	Ethanol steam reforming		Alkali and alkaline earth metallic species and the O-containing functional groups	C ₂ H ₆ species associatively desorb with available hydrogen dehydrogenation and decomposition steps	[11]
Poultry litter biochar (PLBC)	Poultry litter	Ethanol and butanol	10	Highest pH buffering capacity, CEC and total amount of cations	Clostridium carboxidivorans syngas fermentation	[71]
BC	Rice straw (RB) and manure (MB)	Methanogenesis		Redox-active properties or charging and discharging capacities, quinones	Quantitative polymerase chain reaction, electron transfer	[75]
BC	Corn straw	Methane	1	-CH ₃ , -CH ₂ , C=C bonds or C=O bonds, higher porosity, surface biological phosphorus content	Hydrogenotrophic methanogens biocarrier	[80]
Fe-rich BC	Corn stalk	Methane (95%)	10	Less <i>in situ</i> carbon consumption and a minor change of porous structure	Microwave methane reforming	[81]
Pd BC	Vine shoot and crystalline cellulose	Hydrogen	10	Pd size and dispersion and its interaction, chars and textural properties	Deoxygenation	[37]
Ni-BC	Wheat straw	Hydrogen	15	Interaction between Ni, biochar and volatiles	Steam gasification	[88]
BC	Sugarcane bagasse	Hydrogen	15	At low temperature with redox activity, at high temperature via cell growth enhancement	Ethanol-type fermentation	[92]
BC	Bamboo wastes and microalgae	Bio-oil (aromatics and phenols)	-	Long-chain fatty acids and O-species	Deoxygenation	[94]
BC	Nanocellulose	Phenolic monomers and hydrogen	3	Free, bound, or produced water, cellulose	Demethoxylation, the transalkylation reaction	[95]
Pd-Al ₂ O ₃ -BC	Plastic and biomass	C9 monomeric phenol	5	Hydrogenation of C α = C β or dehydroxylation of C γ , dehydroxylation at C γ -OH	Lignin hydrogenolysis, decarboxylation and demethoxylation	[96]
BC	Pine	Caproate production	20	Extracellular polymer substances (EPS), methanogens	Chain elongation, electron efficiency process	[97]
BC	Hardwood (80%, mass fraction) and coniferous wood (20%, mass fraction)	Ethanol and caproic acid	10	Cell retention, decouple the growth of <i>C. kluyveri</i> and its caproic acid production	Secondary fermentation of syngas fermentation effluent, energy intensive distillation	[98]

selectivity of ethanol via syngas fermentation [77]. The conclusion was that biochar could act as a nutrient supplement by the nutrients available, and that it was expected to reduce medium cost and enhance ethanol production in syngas fermentation processes [78]. Furthermore, Kyriakou et al. studied the potential use of biochar derived from biowaste (olive kernels, vineyard prunings, sewage sludge and seagrass residues) as a microbial cell carrier to facilitate the yield of alcoholic [79]. They concluded that the quantity and type of electron accepting and donating units within biochar may play a dominant role in enhancing ethanol production [79].

3.2 Gas fuel

3.2.1 Biomethane

The synthesis of methane consists of two stages, the first stage being promoting tar cracking and the second stage being reducing the high syngas concentrations in the produced gases of the first stage [16]. Biomethane plays an important role in the carbon circular processes, presumably as a sustainable fuel, and the vigorous development of biomethane production is in line with the current carbon neutral era [80]. The methods of methanogenesis mainly include hydrogenotrophic, acetoclastic and electromethanogenesis [81,82]. Biochar has good redox active properties because of its rich surface porosity and functional groups, which could directly facilitate methane yield in anaerobic fermentation by functioning as an electron shuttle [81,83]. Qin et al. evaluated the effect that the biochar derived from different biomasses (anoxic, 500 °C temperature conditions) had on methane production during anaerobic digestion (AD) and found that the biochar enhanced the methane production performance mainly by reducing the lag phases during AD [84]. Furthermore, the biochar prepared from woody biomass has a higher methanation performance than the herbal one [84]. Similarly, Paranhos et al. found that the highest methane yield was obtained from corn cob and poultry manure, depending on high hemicellulose and low lignin content in corn [85]. Additionally, the approach of carbonization was a significant parameter affecting the functional structures of biochar. Xu et al. proved that the remarkably enhanced methane production in digesters with hydrothermal biochar derived from swine manure could be attributed to the more abundant surface functional groups of hydrothermal biochar (hydrochar) as compared to pyrolysis biochar [86]. The massive oxygen-containing groups on hydrochar could accelerate the electron transfer capacity between microorganisms and reach the target of the growing methane yield [87]. Moreover, the Fe-rich biochar with Fe₂O₃ addition of 10% prepared by Li et al.

exhibited a significant performance for CH₄ conversion using microwave pyrolysis [88]. A less *in situ* carbon consumption and a minor change of porous within Fe-rich biochar was significantly favorable for a stable syngas production [88].

3.2.2 Hydrogen production

Hydrogen has a fairly high energy density and no pollution during combustion, and therefore, it is undoubtedly a major alternative of renewable and sustainable energy [89,90]. Hydrogen also has the highest gravimetric heating value of combustion (142 MJ/kg) that makes itself increasingly significant in the energy production compared with other fuels [91,92]. Therefore, hydrogen is deemed as a practical and effective way to utilize efficient and selective hydrogen production for wide biomass. The waste vine shoots and cellulose activated with ZnCl₂ (carbonized at 800 °C and at CO₂ atmosphere) was applied by Santos et al. [39] for selective hydrogen production from formic acid. The porosity and volume of the catalyst were significantly improved after the treatment with ZnCl₂, and the increased activity of meso-macroporous surface contributed to the hydrogen production [39]. In addition to the large pore volume, it was discovered that the fact that the catalytic surfaces were close to neutral pH was favorable for facilitating remarkably selective dehydrogenation with the increased group surface adsorption [93]. Moreover, Han et al. found that gasification could further promote hydrogen production compared to pyrolysis. For instance, H₂-rich syngas and magnetic-activated carbon was performed through the pyrolysis of FeSO₄ impregnated lignin and biomass steam gasification [94]. Furthermore, the addition of an iron catalyst was beneficial for the water-gas shift reaction so as to significantly facilitate hydrogen generation. The increase in pyrolysis temperature and iron loading exhibited a notable impact on promoting the effect of char on gasification process [95]. Analogously, Tran et al. discovered that the additions of FeCl₃ to the water hyacinth provided more channeled magnetic biochar and produced rich pore to enhance the conversion of hydrogen from synthesis gas [96]. Moreover, Yao et al. found that the Ni-loaded biochar with a high external surface area could facilitate hydrogen production from biomass steam gasification through a two-stage fixed bed reactor [97]. Further, cotton-char supported Ni exhibited a higher activity of H₂ production (64.02% (volume fraction), 92.08 mg/g biomass) from biomass gasification compared to rice-char due to the higher content of alkali and alkaline earth metals (AAEMs) found in cotton-char [97].

Hydrothermal liquefaction (HTL) is generally regarded as one of the most efficient thermochemical conversion techniques to be applied in producing high-quality fuel

systems [98]. Ibrahim et al. prepared biochar derived from microalgae *Galdieriasulphuraria* (Algal biomass) by HTL, in which H₂ was selectively separated from the membrane reactor [98]. Moreover, the hydrogen in the permeate stream were recovered and the conversion of biochar to gaseous fuels were further facilitated due to the involvement of Pd₇₇Ag₂₃ membrane in the reactor [98]. Aside from participating in the HTL system, biochar can improve hydrogen production by shortening the lag phases [99]. The biochar plays a role in providing temporary substrates to support microbial metabolism. Bu et al. proved that biochar could facilitate bacterial growth, enhance critical enzymatic activities, and stimulate electron transfer efficiency via fermentation system to remarkably boost biohydrogen yield (317.1%) [100]. Additionally, Li et al. proved that the feedstock of biochar had a significant influence on the ethanol-type fermentative hydrogen production [101]. The rich mineral nutrients, porous structure and the high abundance of O-containing function groups of biochar benefited hydrogen production [101]. The pyrolysis temperature had an influence on the physicochemical properties of biochar. When the pyrolysis temperature was too high (more than 700 °C), it may cause the loss of surface functional groups, particularly the O-containing functions to affect fermentative hydrogen production [101]. In short, choosing the biomass with a high lignin content and metal component to prepare biochar is more conducive to the high selectivity for biodiesel. Furthermore, catalysts with O-containing functional groups, strong CEC, and buffering capacity can facilitate the conversion of bioethanol. Similarly, the high abundance of O-containing function groups of biochar benefits hydrogen production. The selectivity for the methane can be enhanced in the presence of C=C bonds or C=O bonds, higher porosity and surface biological phosphorus content.

4 Selective preparation of other high-value products

4.1 Phenols

Generally, phenols could be used for the production of phenolic resins, bisphenol A, caprolactam, as well as pharmaceutical products, which are all regarded as significant platform compounds [55]. Phenolic compounds are formed by cracking the phenyl-propane units derived from macromolecular lattice of lignocellulosic biomass [102]. Besides, Chen et al. found that the generation of non-methoxyl phenols could be facilitated by active O-containing groups in biochar [55]. Catalytic deoxygenation co-pyrolysis of bamboo wastes and microalgae with biochar catalyst was also investigated in a fixed bed reactor to promote the formation of phenols

[103]. Additionally, the nanocellulose-derived biochar in a fixed bed quartz tube furnace reactor were prepared (Wang et al.), and the water appeared in the pyrolysis biochar system played an important role in enhancing the formation of phenols (53.77 mg/mL) [104]. The hydrogen evolution indicated an upward tendency as the temperature and ratio of biochar to Douglas fir increased, but the higher temperature was not beneficial to the formation of phenolic monomers.

In addition, Zeng et al. concluded that the Fe-modified biochar catalyst impregnated by Fe(NO₃)₃ was effective in converting microwave pyrolysis of corn cobs into phenol-rich bio-oil, thereby significantly increasing the content of phenolic compounds [28]. For example, the biochar of impregnated 0.4 mol/L Fe(NO₃)₃ had the conversion of biomass to phenol-rich bio-oil at the best electivity [28]. Besides, Gurralla et al. reported that the biochar catalyst activated by Pd-Al₂O₃ greatly promoted valuable monomeric phenols yields at lignin hydrogenolysis [105]. For instance, nearly 45% of lignin conversion was obtained with only Al-activated catalyst, while the conversion of lignin increased by 65.3% with Pd-Al interactions. Furthermore, the addition of Pd played a substantial role in activating the hydrogenation activity. This can be attributed to the fact that interactions of Pd-Al could alter its electronic structure and activate dehydroxylation at C_γ-OH [28].

4.2 Acids

Caproate is considered as a versatile and high-value chemical as it includes an antimicrobial agent and a plant growth promoter. There are usually two types of synthesis from syngas to hexanoic acid, one being the direct fermentation of syngas through acetone to produce hexanoic acid, and the other being the secondary fermentation method (fermentation first to separate ethanol and acetic acid and then enhance the chain extension to hexanoic acid) [106]. Liu et al. found that the biochar prepared at 800–1000 °C made the microbial community structure more stable in the chain elongation system and enhanced the bioproduction of caproate and caprylate [106]. A higher conductivity induced by biochar could contribute to the reinforcement effect in chain elongation [106]. Similarly, Ghysels et al. also discovered that the addition of biochar decreased the lag phase and consequently the selectivity for the caproic acid was improved (92%) [107].

4.3 Furans

Furans are often considered as significant intermediate products in converting biomass into high-value products [108], especially because it is a product of the depolymerization reaction of the D-glucose unit in cellulose. Saynik & Moholkar investigated the influence of

chemical pretreatment on the compositional and structural properties of pyrolysis of *Arundo donax* [108] and discovered that the water retention of biomass was also related to the concentration of acid, which increased and then decreased as acid concentration increased.

Enhanced thermal stability with acid (H_2SO_4) treatment and alkali (NaOH) treatment effectively increased the amount of lignin up to 87.3%, while weak acids (H_3PO_4) are more favorable for the reduction of lignin in biomass and thus for the improvement of furan conversion compared to strong acids [108]. Similarly, Zheng et al. found that the yield of furans and levoglucosan (LG) could be facilitated via chemical pretreatment [109]. It was attributed to different chemical pretreatment removed of lignin fraction, the interaction of which could inhibit the formation of LG. Meanwhile, the interaction of lignin and cellulose can inhibit the formation of LG due to the inherent covalent linkages between cellulose and lignin. Hence, the increase in LG production could be attributed to the removal of lignin fraction during different chemical pretreatments [109]. Furthermore, furans could catalytically be reconverted into the more valuable tetrahydrofuran (THF). Lee et al. achieved the conversion of furan to tetrahydrofuran (THF) using a straw biochar catalyst, accompanied by the production of high-value 1,4-butanediol (1,4-BD) [110]. The Ru-Re catalyst was treated by wet impregnation, and the dried sample was reduced at 300 °C for 2 h. The reaction was conducted in a high-pressure batch reactor to ensure that the reactor was filled with H_2 . Interestingly, the furan fixation activity of Ru-Re/biochar was found to be three times higher than that of Ru-Re/activated carbon [111]. It can be seen that biochar has far-reaching prospects for the preparation of high-value products. Figure 7 shows the process for furan production from lignocellulosic biomass [111].

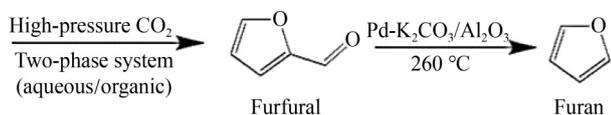


Fig. 7 Process for furan production from lignocellulosic biomass (adapted with permission from Ref. [111]).

Furan contains numerous derivatives, including furfural, 5-hydroxymethylfurfural (HMF), tetrahydrofuran (THF), maleic anhydride (MA) and 2-methyltetrahydrofuran (MTHF) [112]. The aldehyde furan ring contained in furfural can be used as a raw material for value-added chemicals due to its high selectivity for aromatic and unsaturated compounds in organic solvents [113]. Among those listed above, furfural (FUR) and 5-hydroxymethyl furfural (HMF) are widely used in the treatment of value-added chemicals and liquid fuels because of their special chemical structures [114]. Especially, Li et al. prepared a

sulfonated carbon microsphere catalyst by using hydrothermal carbonization with a selectivity of up to 75.12% for furfural at 170 °C [115]. Particularly, it was found that the catalyst dosage, biomass feedstock, and reaction temperature played critical roles in furfural yield. When the biochar catalyst dosage increased from 10 to 90 mg, the yield of furfural reached the peak at 50 mg and then decreased, probably because the excessive catalyst dosage would result in condensation and other reactions which further lead to the degradation of furfural [115]. The reaction temperature also affected the yield of furfural to some extent. At the same amount of catalyst, the yield of furfural increased with the rise in the temperature. In contrast, the Pd catalyst prepared by Guo et al. was highly selective for lignin fiber biomass to aromatics, 5-hydroxymethylfurfural (HMF) and furfural [116]. The process included depolymerization of lignocellulosic biomass, separation of lignin oil, separation of methylated C_5 sugars, hydrodeoxygenation of lignin oil, and dehydration reaction of methylated C_5 sugars [116]. Therefore, their work provided an effective way to use biomass for its conversion into high-value chemicals and liquid fuels.

In conclusion, the biochar of doped Fe, Pd, or Al had a high conversion to phenol-rich bio-oil and lignin, among which the interactions of Pd-Al could alter its electronic structure and activate dehydroxylation at $\text{C}_\gamma\text{-OH}$. Meanwhile, the structure of biochar prepared at 800–1000 °C is more stable and the conductivity is higher than that made at 500–700 °C. Therefore, it could contribute to the reinforced effect in chain elongation to enhance the bioproduction yield of acids (caproate and caprylate). The yield of furans and levoglucosan (LG) could be facilitated via chemical pretreatment. In particular, weak acids (H_3PO_4) are more favorable for reducing LG compared with strong acids.

5 Future perspectives

With continual innovation and further development of technology, the biochar catalyst selectivity for biofuels and high-value chemicals is very likely to realize further advancement and become possible for industrial application. In this process, the synthesis of biochar catalysts should be focused on, including the consideration of high selectivity for product, high recyclability, and low toxicity to the environment. The biocarbon-based catalysts catalysis is of paramount significance for high-efficiency energy production and chemical transformation. The biocarbon-based catalysts depend on the properties of biomass feedstock, operating temperature, and atmosphere of the reaction system, etc. Meanwhile, it is critical to modulate the catalytic mechanism of the catalysts *in situ* characterization and advanced equipment. The keys

to the implementation of biocarbon-based catalysts selectivity for biofuels and high-value chemicals are related to technology and industrial structure and environmental footprints. Technology is vital for biofuel. At the same time, according to the characteristics of different products, corresponding devices could be designed and existing processes could be adjusted to improve the yield of products and reduce energy consumption.

It can be seen that the continuous research development and the production technology of biocarbon-based catalysts selectivity for biofuels and high-value chemicals will surely make greater progress and breakthroughs.

6 Conclusions

This paper highlighted the impact of biochar-based catalyst preparation (metal-modified biochar, acid and alkali modified biochar, nitrogen-doped biochar) on selectivity for biofuel and valuable chemical. It investigated, in depth, the mechanism of improving the selectivity for biofuel and valuable chemical, as well as the factors (such as temperature, reaction time, and impregnation ratio) have been. In addition, it described, in detail, the process of synthesizing biochar from various waste biomass, and summarized the optimal experimental conditions and selectivity for synthesizing biofuels and high-value products, demonstrating the feasibility of using biomass from abundant and wide range of resources as a raw material for sustainable energy preparation. At present, it seems that biochar catalysts are widely used in the preparation of fuels and high-value products because of their wide sources, non-polluting and high-activity features compared with other catalyst systems. This concept is consistent with sustainable development, and is very likely an indispensable force for industrial applications in the future.

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