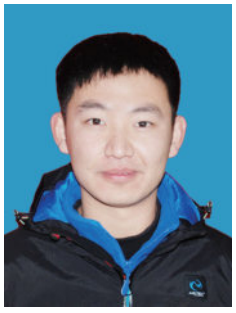
Biochar–based Solid Acids as Catalysts for Carbohydrate Hydrolysis: A Critical Review

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Abstract: Recently, increasing interest has been focused on the hydrolysis of carbohydrates to monosaccharides, among which, glucose and xylose as typical platform sugars can be used to produce chemicals and biofuels. As heterogeneous catalysts, solid acids have gained extensive attention for biomass biorefinery and could replace the conventional process owing to their excellent properties, including acceptable acidity and easy separation. In particular, biochar-based solid acids derived from biomass are promising for biomass conversion owing to the low-cost of feedstocks and the simple preparation procedure. Herein, we attempt to provide a critical overview of biochar-based solid acids for hydrolysis of carbohydrates into glucose and xylose. The preparation methods and properties of biochar-based catalysts as well as the influence of their properties on catalytic performance were discussed in detail. We also highlight the major challenges facing the use of biochar-based solid acids for carbohydrate hydrolysis.

Keywords: biochar-based solid acid catalysts; preparation; properties; carbohydrate; hydrolysis

1 Introduction

Owing to the increase in environmental pollution and decrease in fossil resources, an increasing amount of research is being devoted to exploring renewable resources as sustainable alternatives to fossil fuels to ensure a secure energy supply in the future[1]. Biomass, the most abundant renewable resource, could be applied as a substitute for petroleum to produce chemicals and biofuels[2]. Biomass is an organic material, usually produced by plant photosynthesis, which includes plants and their waste[3].

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Lignocellulosic biomass is composed of 30%～50% cellulose, 20%～35% hemicellulose, and 10%～25% lignin[4]. A schematic of the biorefinery process for utilizing lignocellulose is shown in Fig.1[5]. Platform chemicals and biofuels, such as ethanol, alkanes, methanol, hydrogen, liquid fuels, and aromatic hydrocarbons, could be derived from lignocellulose. In this biorefinery scheme, hydrolysis is an important process to produce sugars, which could be used as feed stocks and further transformed into biofuels and platform chemicals. Hydrolysis of lignocellulosic carbohydrates (cellulose and hemicellulose) into platform sugar molecules is a key step in developing the concept of integrated biorefinery.

Although approximately 220 billion tons of biomass are produced every year[6], only 3%～4% of carbohydrates are used effectively. In particular, the proportion of chemical industrial products produced directly from biomass is less than 2% of the total annual production. Thus, it is necessary to transform carbohydrates into biofuels (biodiesel and bioethanol) and important platform chemicals (furfural, 5-hydroxymethylfurfural, acetic acid, acetone, and lactic acid)[7-8]. Cellulose and hemicellulose are the major components in lignocellulosic biomass. Cellulose can be hydrolyzed to glucose (C6 sugars) and subsequently fermented into bioethanol or converted into platforms molecules[9]. Hemicellulose, the second most abundant biopolymer after cellulose in the plant kingdom, is a type of heteropolysaccharide with a complex structure. The major types of hemicellulose include xylan (pentosan) and mannan (hexosan)[4], and hemicellulose can be catalytically hydrolyzed into sugars and further converted into platform chemicals[10].

Carbohydrates in lignocellulose biomass can be hydrolyzed into sugars by aqueous acids, such as H_2SO_4 and HCl, and organic acids[11-12]. Although liquid acids can react fully with substrates, there are many problems associated with homogeneous catalysis, such as acid corrosion equipment, large amounts of liquid acid waste, difficulties in the separation of acid and products, and catalyst recycling[13]. To solve these problems, different approaches have been investigated, including the addition of trace or small amounts of mineral acids, organic acids, and sodium hydroxide for biomass conversion into sugars during hydrothermal treatment[14-15]. In addition, anenzyme can hydrolyze lignocellulose to monosaccharaides. However, the high cost of the enzyme and the harsh reaction conditions have restricted its application[16]. Therefore, considerable

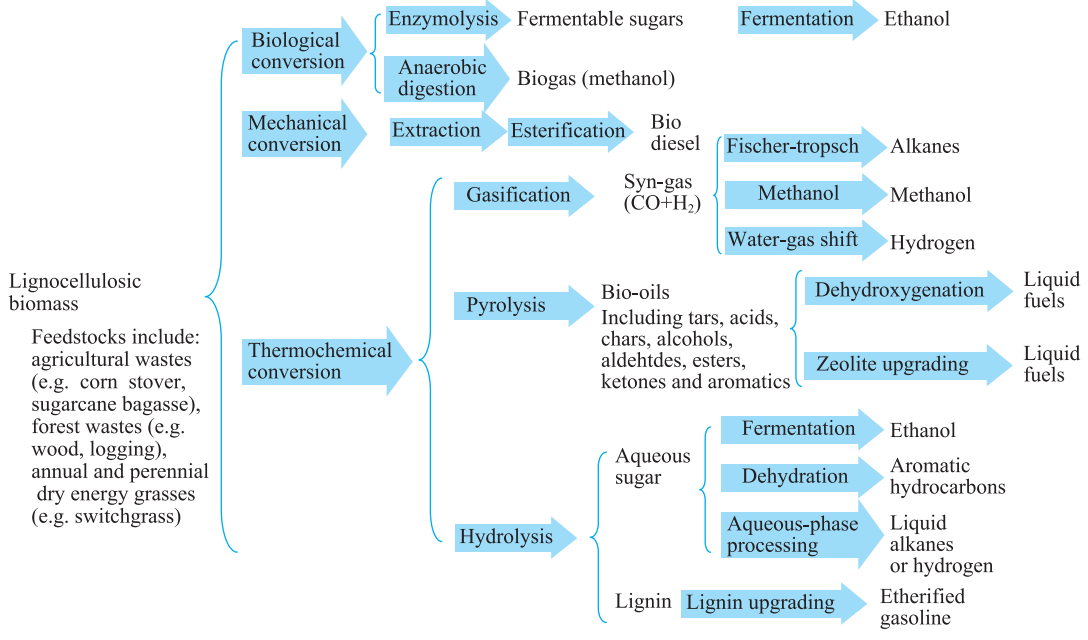


Fig.1 Schematic of the biorefinery process for utilization of lignocellulose

efforts have been devoted to using heterogeneous solid acid catalysts to replace mineral acids or enzymes in carbohydrate hydrolysis. Among heterogeneous solid acid catalysts, biochar-based solid acids have attracted much attention owing to their low cost, environmental friendliness, and thermal stability[7].

Biochar is a carbon material obtained by thermal decomposition of biomass with little or no available air at moderate temperatures. Biochar has excellent physical and chemical properties that can be easily tuned according to the required application. Biochar can be used to prepare functional materials for various applications, such as CO_2 capture, pollutant removal, soil remediation, biomass hydrolysis, and energy storage[17]. In the past few years, owing to the excellent catalytic properties of biochar-based materials, they have been applied in heterogeneous catalysis reactions of biomass to produce biodiesel, methane gas, and platform chemicals[18]. Biochar is a highly porous carbon material possessing abundant surface functional groups. The porosity and catalytic properties of biochar can be regulated by various processes, such as *in situ* reduction, gas activation, acid and alkali pretreatment, and carbonization[19-20].

Recently, many studies have reported carbohydrate hydrolysis involving the degradation of cellulose and hemicellulose into monosaccharides[21-22]. Some reviews have focused on the classification of solid catalysts and their catalytic performance for the hydrolysis of carbohydrates. However, there has been limited discussion of biochar-based solid acid catalysts. This paper reviews research advances in biochar-based solid acid catalysts for carbohydrate hydrolysis and predicts future trends. The main focus of this review is the preparation and properties of biochar-based solid acid catalysts, as well as their catalytic performance for the hydrolysis of cellulose and hemicellulose (Fig.2). The major challenges in the process of carbohydrate hydrolysis using biochar-based catalysts are also highlighted.

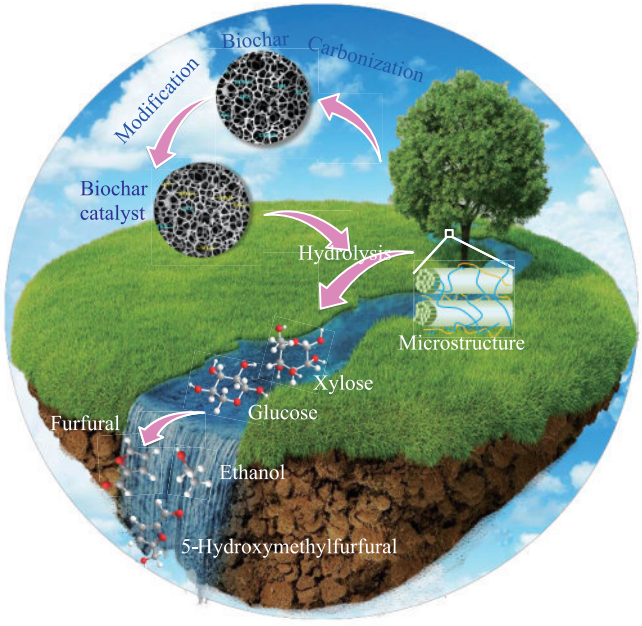


Fig.2 Biomass-based solid acid catalysts for the hydrolysis of cellulose and hemicellulose

2 Preparation and properties of biochar–based solid acid catalysts

The supporting material of biochar-based catalysts is biochar. Biochar is initially generated as a byproduct in the pyrolysis of feedstock under limited oxygen conditions. It is defined as a solid material prepared by thermochemical conversion of biomass in an inert atmosphere[23]. Generally, biochar is produced in the form of a solid by pyrolysis (slow/fast pyrolysis and gasification) and hydrothermal treatment of biomass[24].

2.1 Biochar generation

Pyrolysis is a thermochemical reaction that converts biomass into char, bio-oil, and gases by heating in an inert atmosphere[25]. Biochar yield and characteristics are mainly dependent on the feedstock and pyrolysis conditions, including heating temperature, heating rate, and retention time[26]. Pyrolysis processes include fast pyrolysis, slow pyrolysis, and gasification, as shown in Table 1. Biochar is the main product at low temperatures under slow pyrolysis. High temperatures and high heating rates produce mostly gas. In the intermediate temperature range of 450～550℃ at high heating rates, the main products are condensable vapors and aerosols[27].

Slow pyrolysis, also called conventional carbonization, is characterized by a wide temperature range (300～800℃),

Table 1 Typical biochar yields from thermochemical processes

	Biomass	Temperature /℃	Time	Heating rate	Biochar yield /wt%	Ref.
Slow pyrolysis	Wood bark, cocopeat, palm kernel shell	500	1 h	10℃/ min	20~40	[28]
	Citrus waste	200～650	0.5 h	50℃/ min		[29]
	Soursop seed cake	400	1.5 h	15℃/min		[30]
	Cow manure	300～700	0.5~2 h	10℃/ min		[26]
	Eucalyptus bark	600	1 h	3℃/ min		[31]
Fast pyrolysis	Switch grass	425	1 min	—	10~20	[32]
	Cotton stalk	600	1 min	13℃/s		[33]
	Cellulose	500	1 min	500℃/s		[34]
	Wood	550	<1 s	—		[35]
	Hybrid poplar	550～600	<1 s	1000℃/s		[36]
Gasification	Douglas fir	900～1000	1 s	—	<10	[37]
	Pine wood	1200	—	—		[38]
	Winter wheat	750	—	—		
Hydrothermal carbonization	Banana peels	230	2 h	—	40~60	[39]
	Sewage sludge	180～200	4~8 h	—		[40]

slow heating rate (3～50℃/min), and long retention time (usually more than 0.5 h). The influence of slow pyrolysis on the evolution of solid products was investigated in the temperature range of 200～650℃[29]. Below 300℃, changes in the solid matrix were attributable to decomposition of aliphatic compounds. Between 300℃ and 500℃, the structure of char changed obviously because of secondary char–tar reactions. Above 500℃, the structural changes of char were mainly due to the interaction for solid matrix, which became gradually less reactive.

The biochar yield decreased and the carbon content increased when either the temperature or the retention time was increased[26]. The decrease in the biochar yield was ascribed to the conversion of cellulose, hemicellulose, and lignin to bio-oil and syngas during the pyrolysis process[41]. The increase in carbon content was indicative of polymerization, aromatization, and carbonization of biochar[42].

Chemical and physical analyses of the fractions from soursop seed cake were conducted under slow pyrolysis conditions, and bio-oil (18.64%), aqueous fraction (31.48%), biochar (maximum value of 32.16%), and gas (17.72%) were obtained as pyrolysis products[30]. Slow pyrolysis is the traditional biochar-producing technology and is still widely used for biochar production, but it has the drawbacks of being time-consuming and energy inefficient.

Fast pyrolysis is usually described as the thermal degradation of low energy-density biomass (heating value about 11 MJ/kg) in the absence of air. It was initially used to produce gas and oil from biomass as a substitute for the traditional slow pyrolysis process. Compared with slow pyrolysis, the features of fast pyrolysis are a higher heating rate (>300℃/min), a short retention time (<60 s), and a higher reaction temperature (~500℃). A short retention time is beneficial for the generation of bio-oil, whereas longer retention times can lead to secondary reaction of the primary products, which may result in gas production. The physical processes and chemical reactions occurring during pyrolysis are very complex and depend on the reaction conditions and biomass properties. The influence of lignin content and reaction temperature on the properties of hybrid poplar char and the gases produced by fast pyrolysis has been discussed[36]. At the typical fast pyrolysis temperature of around 500℃, increasing the lignin content in the raw biomass produced more solid char than bio-oil.

Gasification biochar is prepared at high temperatures (700～2000℃), resulting in byproducts with lower carbon contents (20%～60%) than the biochar produced by slow/fast pyrolysis (50%～80% carbon content)[43]. The typical yield of gasification biocharis about 10 wt% biomass[44]. Compared with conventional gasification, microwave-assisted gasification methods can produce the same products at lower temperatures. The gas composition obtained using a traditional heating method at 800℃ was consistent with that obtained using the microwave-assisted method at 550℃[38], which means that low-temperature gasification can be achieved.

Hydrothermal carbonization (HTC), also called wet

pyrolysis, direct liquefaction, or hydrothermal pyrolysis, as an important method for biomass carbonization. This process is generally described as the HTC of biomass at high temperature and pressure in water. A mixture of char–water–slurry is formed at elevated reaction temperatures (160～350℃)[45]. The dominant products of high-temperature HTC (300～800℃) are gases such as methane and hydrogen because the reaction temperature is higher than the temperatures at which most organic compounds are stable[46-47]. The main product of low-temperature HTC (<300℃) is char, and the yield of char is in the range of 30%～60%, depending on the substrate properties and reaction conditions[48]. HTC not only produces biochar, but also helps to the conversion of biomass. Biochar produced by HTC is different from that prepared by gasification or pyrolysis. HTC biochar is rich in alkyl groups and has a lower proportion of aromatic compounds. An in-depth exploration of the differences between biochars prepared by pyrolysis and HTC revealed that HTC biochars tend to be less recalcitrant than pyrolysis biochars[40]. Therefore, HTC biochars are less stable than pyrolysis biochars.

Lignocellulosic biomass contains cellulose, hemicellulose, lignin, and a small amount of other organics, each of which is pyrolyzed or degraded to biochar by a different pathway (Fig.3). In the pyrolysis process, cellulose is first degraded to form oligosaccharides, followed by the formation of *D*-glucopyranose via cleavage of the glucosidic bond. Subsequently, levoglucosan is produced by intramolecular rearrangement. Further, biochar can be

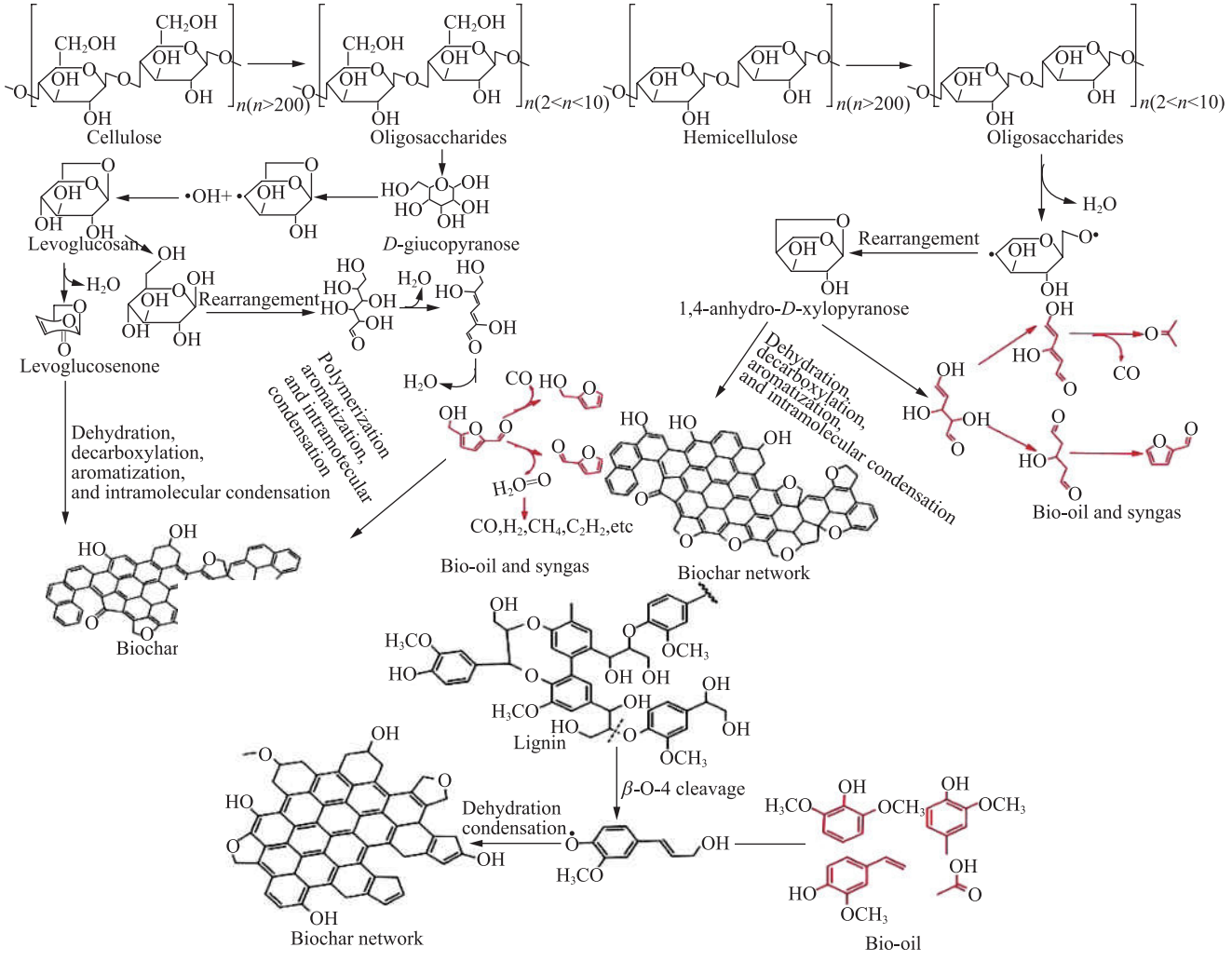


Fig.3 Cellulose, hemicellulose, and lignin pyrolysis: biochar formation mechanisms

formed from levoglucosan by a series of pathways, including dehydration, decarboxylation, aromatization, and intramolecular condensation. The mechanism of hemicellulose pyrolysis is similar to that of cellulose. The degradation of lignin mainly involves free-radical reactions, including chain initiation, chain propagation, and chain termination[49-50].

2.2 Properties of biochar-based solid acid catalysts

For biochar, catalytic activity is determined by the surface functional groups and the active sites dispersed in pores[51]. Although biochar is a porous material, the surface functionalities and the porosity of biochar obtained directly by biomass pyrolysis exhibit poor catalytic properties[52]. The effect of structural properties, including average pore diameter, specific surface area, and pore volume, on the catalytic activity is related to the diffusion capability of the reactants through the catalyst framework and interactions with active sites during reaction[17]. To improve the catalytic performance of biochar-based catalysts, considerable efforts have been made to modify biochar pore structures via various treatments and tuning of surface acidity.

2.2.1 Pore structure tailoring

In situ reduction is a common method for tuning the pore structure of biochars during pyrolysis of biomass. This process usually requires the addition of certain chemicals, such as acids, alkalis, and salts, for example, $ZnCl_2$ and H_3PO_4[53]. As a kind of activating agent, H_3PO_4 plays a key role in the pyrolysis of biomass, promoting in the formation of a microporous structure and the introduction of phosphorous groups into biochar, which can improve the catalytic activity of biochar catalysts[53].

Among well-known activation chemicals, $ZnCl_2$ has been shown to act as an efficient reagent. For example, $ZnCl_2$ was applied as an activating agent to produce activated carbon (AC) from palm shell and a surface area of 743 m^2/g was achieved[54-55]. AC from sugarcane bagasse, prepared by chemical activation with $ZnCl_2$ at a low temperature, had a high surface area of 1500 m^2/g with a large pore volume and a narrow micropore size[56]. Post-activation processes can also be used to tailor the pore structure of biochar. Post-activation processes are divided into physical activation methods, using different gases including CO_2, steam, or their mixtures, and chemical activation methods, using KOH, NaOH, H_3PO_4, or $ZnCl_2$[44].

For physical activation, the original biochar with a basic pore structure is exposed to a gas to eliminate most volatile substances. Subsequently, a gasification reaction occurs at 350～1000℃. A pore structure and a high surface area are obtained by the gasification process owing to the removal of most reactive carbon atoms from the original biochar[17]. Activation with various gases or their mixtures can improve the carbon porosity, and the activated biochar usually displays a well-developed surface area and structure. In a typical case, biochar obtained from poplar wood was activated using different gas environments and a combination of N_2–CO_2 at 750～920℃[57]. The surface area of the activated biochar was found to increase from 435 m^2/g to 687 m^2/g in 10% CO_2/90% N_2 under atmospheric conditions and from 429 m^2/g to 621 m^2/g on extending the reaction time from 0.5 h to 1 h. In addition, the pore volume of the biochar increased from 0.18 cm^3/g to 0.3 cm^3/g with increasing the temperature from 750℃ to 920℃. Steam, CO_2, and a mixture of steam and CO_2 under microwave-assisted conditions were applied to activate biochar obtained from coconut shell[58]. With all these activating agents, the BET surface areas of the activated biochars were over 2000 m^2/g, and the micropores of the activated biochars contributed about 80% of the total pore volume.

In the chemical activation process, the original biochar is first mixed with an activating agent, such as KOH, NaOH, H_3PO_4, or $ZnCl_2$, and then heated at a temperature in the range of 450～900℃[59]. The properties of the biochar pore structure are determined by the amount of activating agent and the mixture time[60]. KOH, which is one of the most commonly used activating agents, can considerably improve the surface area and pore size of biochar. The surface area of hardwood-derived biochar increased from 0.13 m^2/g

to 207 m^2/g by KOH activation at 25℃[25]. With KOH activation, the surface area of hair-derived biochar increased significantly from 669 m^2/g to 1306 m^2/g with a corresponding change in the pore volume from 0.38 cm^3/g to 0.90 cm^3/g[61]. Compared with activation by KOH alone, co-activation, which combines KOH activation and hydrothermal treatment, improved the physical properties of biochar. In some representative cases, such as rice straw biochar, KOH treatment at 60℃ accompanied by heating under H_2O at 700℃ resulted in micro porous biochars with surface areas of 140～772 m^2/g and pore volumes of 0.09～0.42 cm^3/g. Under the same co-activation conditions, the surface area of a sewage sludge biochar increased from 18 m^2/g to 783 m^2/g and the pore volume increased from 0.02 cm^3/g to 0.61 cm^3/g [40].

As discussed above, the surface area and pore size of biochar can be improved by physical or chemical activation methods. In addition to the above methods, it is possible to improve the surface area and pore size with simple hydrothermal treatment by selecting a suitable raw material. The surface area, total volume, and micropore volume of coconut-shell-derived biochar improved from 130 m^2/g to 702 m^2/g, from 0.19 cm^3/g to 0.53 cm^3/g, and from 0.03 cm^3/g to 0.35 cm^3/g, respectively, with increasing the temperature from 400℃ to 1000℃[62]. The properties of biochar also depend on the source of biomass. Under the same pyrolysis conditions, rice straw biochar (139.5 m^2/g and 0.092 cm^3/g) had a 7.5-fold larger surface area and a 4.5-fold larger pore volume than sewage sludge biochar (17.9 m^2/g and 0.018 cm^3/g). The surface area of pine biochar (772.3 m^2/g) was twice that of peanut hull biochar (363 m^2/g) under the same pyrolysis conditions[13].

2.2.2 Surface acidity modification

Biochars obtained by direct hydrothermal treatment of biomass have small surface areas and pore sizes, as well as few active sites, which limits the applications of biochar-based catalysts. To solve this problem, biochar modification has been carried out by surface oxidation and surface sulfonation.

(1) Surface oxidation

Oxidation can introduce a large number of oxygen functional groups onto biochar, and some of these functional groups are acidic groups, such as carboxylic acids, phenolic groups, and lactonic groups[63]. The introduced oxygen functional groups can greatly improve the hydrophilicity of biochar, and consequently enhance its performance in aqueous systems. In the cellulose hydrolysis process, after carbonization and sulfonation, starch and polyvinyl chloride (PVC) were converted into a biochar solid acid with many functional groups, including —COOH, —SO_3H, —OH, and —Cl. Among these functional groups, phenolic hydroxyl groups have the ability to adsorb cellulose[64], increasing the contact between the catalyst and the reactant, although the adsorption effect is not efficient for breaking hydrogen bonds in cellulose.

Chemical oxidation using oxidation reagents such as H_2O_2, O_3, $KMnO_4$, and HNO_3 can create oxygenated acidic functional groups. The concentration and type of oxidation reagent affect the amount of oxygen functional groups in the catalyst and the catalyst structure, as shown in Table 2. The BET surface area decreased after chemical treatment, whereas the total pore volume increased because oxidation could lead to the collapse of pore walls and the formation of mesopores or macropores[65]. Various oxidation reagents, such as H_2O_2, $(NH_4)_2S_2O_8$, and HNO_3, were used to oxidize olive-stone-derived biochar, and the highest total surface acidity of 0.69 mmol/g was obtained after HNO_3 treatment, followed by H_2O_2 and $(NH_4)_2S_2O_8$ treatment[66]. Oxygen functional groups produced by chemical modification played key roles in catalysis, with the effect decreasing in the order of carboxylic groups>lactonic groups>phenolic groups, mainly owing to the condensation of adjacent carboxylic and phenolic groups during the oxidation process[67]. Biochar treated with O_3 formed a weak acid catalyst, which was not active. The catalytic activities of sulfonated chars were similar to those of sulfonated chars after ozonation[63], indicating that oxidation treatment had no further influence on the biochar sulfonation.

Thermal treatment under a weak oxidizing

Table 2 Properties of various biochar–based solid catalysts

Biomass	Biochar preparation	Surface acidity modification	Surface area /($m^2 \cdot g^{-1}$)	Total pore volume /($cm^3 \cdot g^{-1}$)	SO_3H density /(mmol · g^{-1})	Total acidity /(mmol · g^{-1})	Ref.
Olive stone	N_2, 1000℃, 1 h; then steam activation, 850℃	None	928	—	—	0	[66]
		$(NH_4)_2S_2O_8$	780	—	—	0.405	
		HNO_3	738	—	—	1.095	
		H_2O_2	769	—	—	0.480	
Waste tea	H_3PO_4 activation; then carbonization, 450℃, 1 h	None	1417	1.1866	—	0.373	[67]
		20% HNO_3	644	0.4380	—	0.850	
		40% HNO_3	524	0.2855	—	2.060	
		80% HNO_3	49	0.0205	—	0.832	
Bamboo	N_2, 550℃, 1 h	None	42.8	0.022	—	0.310	[68]
		$KMnO_4$	27.2	0.027	—	0.390	
		HNO_3	0.5	—	—	0.545	
		Atmospheric nitrogen	494.2	0.240	—	0.190	
Powdered peanuts hulls	Slow pyrolysis, 400℃, 1 h, N_2	None	1.13	0.0007	0.0	0.6	[63]
		Concentrated H_2SO_4, 100℃, 12～18 h	338	0.18	0.45	5.9	
		SO_3, room temperature, 6 days	1.23	0.0005	0.86	—	
Microcrystalline cellulose powder	400℃, 5 h, N_2	Fuming H_2SO_4 solution (15 wt%), 80℃, 10 h	<5	—	1.8	—	[69]
	500℃, 5 h, N_2		<5	—	1.6	—	
	600℃, 5 h, N_2		<5	—	0.89	—	
	650℃, 5 h, N_2		<5	—	0.75	—	
	700℃, 5 h, N_2		<5	—	0.92	—	
Pyrolyzed hardwood char samples (fast pyrolysis)		Concentrated H_2SO_4, 150℃, 24 h	2.74～14.38	—	0.585～0.650	0.0363～0.0834	
Biochar samples from Dyna Motiv Inc. (without KOH treatment)		None	0.129	—	—	—	[25]
		Fuming H_2SO_4 (20% free SO_3), 150℃, 5 and 15 h	0.79～2.61	—	1.04～1.09	2.8～3.2	
Biochar samples from Dyna Motiv Inc. (with KOH treatment)		None	207	—	—	—	
		Fuming H_2SO_4 (20% free SO_3), 150℃, 5 and 15 h	1.37～1.88	—	0.935～1.00	2.5～2.6	

atmosphere, such as 5% O_2 (in N_2) and 50% N_2O (in N_2) also formed oxygen functional groups on the biochar surface. It was confirmed that chemical treatment improved the concentration of carboxylic acid groups, whereas thermal treatment mainly increased the concentrations of hydroxyl and carbonyl groups[68]. Chemical treatment led to an increase in the total surface acidity, but thermal treatment increased the acidity or basicity of biochar, depending on the gas composition. Thermal treatment was beneficial to the formation of micropores in the oxidized biochar owing to the decomposition of oxygen functional groups, which may either be retained in the micropores or block the micropore entrances[65].

Although surface oxidation can introduce acidic groups onto biochar, the strength of the acidic groups is not sufficient for catalytic processes. Thus, oxidized biochar is widely used for pollutant and metal adsorption.

(2) Surface sulfonation

Sulfonation involves the introduction of sulfonate groups (—SO_3H) into biochar. Sulfonic groups can replace acids (H_2SO_4 and HCl) for many catalytic reactions[70]. To prepare sulfonated biochar-based solid acids, liquid sulfonation was conducted using concentrated H_2SO_4 or its derivatives (e.g., benzene

sulfonic acid and naphthalene sulfonic acid) in the temperature range of 90～150℃. Alternatively, gaseous sulfonation was conducted using SO_3 (>20%) at temperatures between 25℃ and 150℃[71]. Generally, the temperature used for gaseous SO_3 treatment is much lower than that for H_2SO_4 treatment, but the required time is much longer than that for the latter process. In some studies, H_2SO_4 treatment of biochar produced a lower density of SO_3H acid sites than gaseous SO_3 treatment[63]. Nonetheless, H_2SO_4 treatment generally provides a higher density of SO_3H groups, reaching up to 2.5 mmol H^+/g[63]. The BET surface area and the pore structure of biochar can increase significantly following sulfonation using H_2SO_4, indicating that activation or oxidation of the biochar also occurs by sulfonation[15]. However, the surface area may increase or decrease after sulfonation, depending on the properties of the biochar and the sulfonation method. Additionally, biochar samples treated with KOH showed drastic structural collapse and a reduction in specific surface area after sulfonation[25]. The decrease in the specific surface area was attributable to strong sulfonation of the biochar[72].

In addition to strong acidity, biochar-based solid acids can also be endowed with other functional groups and properties, such as magnetism. A magnetic porous biochar catalyst was successfully produced from sawdust by an integrated fast pyrolysis–sulfonation process[73]. First, Fe-loaded sawdust was prepared by an adsorption process in $FeCl_3$ solution, and then this precursor was subjected to fast pyrolysis and sulfonation with concentrated H_2SO_4 (Fig.4). The resultant biochar-based catalyst had a high surface area of 296.4 m^2/g and also exhibited strong magnetism[73]. A bamboo biochar-based catalyst, which had an excellent mimetic cellulose binding domain and a catalysis domain, was synthesized by grafting 1-(trimethoxypropylsilyl)-3-methylimidazolium chloride onto the —OH groups of the biochar-based sulfonic acid[74]. Using co-carbonized starch and PVC[64], the chlorine from PVC was covalently bonded to the edges of aromatic carbon sheets as new



Fig.4 Schematic illustration of the synthesis of a magnetic biochar-based solid acid catalyst

active groups. In this catalyst, the chlorine groups can strongly interact with the —OH groups of cellulose and the bridge bonds cause the carbon framework to stretch fully, reducing hindrance between —SO_3H groups and glycosidic bonds to promote the catalytic performance for cellulose hydrolysis. In addition, biochar-based solid acid catalysts obtained by pyrolysis and sulfonation contained functional groups such as —COOH and —OH owing to the strong oxidation ability of concentrated H_2SO_4[75]. Biochar-based solid acids can be endowed with many excellent properties, such as magnetism, hydrophilicity, and redox activity, which facilitate their further functionalization. Biochar-based solid acids exhibit potential for catalysis applications, but the catalyst acidity needs to be further improved. Thus, further research should focus on the modification of biochar-based solid acids to meet the requirements of catalysis, especially for the catalytic conversion of biomass.

3 Lignocellulosic biomass hydrolysis using biochar–based catalysts

Biochar containing —SO_3H groups, also known as biochar-based solid acid, represents a class of metal-free catalysts that are widely used in various chemical reactions, including oxidation and reduction reactions, acylation reactions, esterification reactions, and biomass hydrolysis[76]. In addition, depending on its pore size and functionalities, biochar is used as a support for metal nanoparticles for various catalytic reactions, including Fischer-Tropsch reactions, biomass hydrolysis, and methane reforming[77]. Carbohydrate hydrolysis is an important process in biorefinery, and

our focus is on biochar-based catalysts for carbohydrate hydrolysis.

3.1 Cellulose hydrolysis

Sulfonated biochar-based catalysts show good catalytic performance for cellulose hydrolysis owing to the presence of Brønsted acid sites of —SO_3H groups. For example, a sulfonated biochar catalyst used to hydrolyze cellobiose into glucose realized a glucose yield of nearly 100% at 110℃ for 24 h[78]. The catalyst was prepared using palm kernel shell as a carbon source and the acid density (sulfonic acid groups) was shown to depend on the carbonization temperature. The sulfonation efficiency was maximized at carbonization temperatures between 300℃ and 350℃, and the sulfonated biochar-based catalysts possessed suitable acid densities (0.4～0.5 mmol/g) and high hydrolysis capacities. In addition to carbonization conditions, the biochar source and the sulfonation process also had a significant effect on the catalytic performance of the catalyst. Changing the sulfonation temperature of the active carbon gave catalysts with varying catalytic performance for biomass hydrolysis[16]. When the sulfonation temperature was increased from 150℃ to 250℃, the glucose yield increased from 7.1% to 61.0% for 24 h. However, the yield of glucose decreased when the sulfonation temperature was further increased because the high temperature (>250℃) caused degradation of the sulfonic acid group. In addition to hydrolysis performance, the surface properties of the catalyst were investigated. The total acid density of the biochar increased from 0.8 mmol/g to 2.19 mmol/g on increasing the sulfonation temperature from 150℃ to 300℃. The density of —SO_3H groups and the specific surface area were enhanced from 0.19 mmol/g to 0.24 mmol/g and from 709 m^2/g to 945 m^2/g, respectively, with increasing the temperature from 150℃ to 250℃. Three kinds of solid acids were prepared from different biochar sources, namely, sucrose, glucose, and nut shell, and their catalytic performances were investigated for the hydrolysis of microcrystalline cellulose[79]. For nut-shell-biochar-based solid acid catalysts, the yield of glucose obtained at 120℃ for 4 h was less than 7%, which was only higher than that of the blank without a catalyst. The nut-shell-biochar-based solid acid possessed lower catalytic activity than the sucrose-carbon (36%) and glucose-carbon (31%) solid acids for crystalline cellulose hydrolysis. Fewer —SO_3H groups in the nut-shell-biochar led to lower acidity and fewer —OH groups decreased the affinity with the reaction substrate. Additionally, many biochar-based solid acid catalysts have been prepared from different carbon sources for cellulose hydrolysis, as shown in Table 3. The biochar-based catalysts prepared from different carbon sources showed varying catalytic performances for hydrolysis of cellulose, with glucose yields ranging from 4.6% to 74.5%. It was also found that the glucose yield corresponded to the —SO_3H densities of the biomass-derived solid acid catalysts, except for the microcrystalline-derived catalyst. Although the acid density of the microcrystalline-derived catalyst was high, the BET surface area was low, which decreased the available catalytic sites for cellulose hydrolysis. Thus, appropriate specific surface areas and —SO_3H densities play key roles in the hydrolysis of cellulose.

Table 3 Literature survey of biomass–derived solid acid catalysts for cellulose hydrolysis

Biomass	Substrate	BET /($m^2 \cdot g^{-1}$)	—SO_3H /(mmol · g^{-1})	Glucose yield/%	Ref.
Bamboo	Cellulose	—	1.8750	16.7	[80]
Cotton	Cellulose	—	1.9866	19.8	
Starch	Cellulose	—	1.1357	4.6	
Sucrose	Cellulose	412	0.63	74.5	[16]
Coconut shell	Cellulose	981	0.33	47.2	
Microcrystalline	Cellulose	6	2.01	39.3	

Notably, the hydrolysis of cellulose is related to the properties of the catalyst originating from the biochar source and carbonization and sulfonation conditions. Moreover, the acidity of the catalyst and interactions between the active sites and cellulose units significantly influence cellulose hydrolysis. The surfaces of biochar-based catalysts have —COOH groups, phenolic hydroxyl groups, and —SO_3H groups, and such catalysts exhibit strong acidity, attributed to the synergic effect of these

three types of groups[81]. For the hydrolysis of cellulose, —COOH groups and phenolic hydroxyl group can adsorb β-1,4-glucan, whereas the —SO_3H groups can attack the glycosidic bonds in cellulose (Fig.5)[82].

The adsorption capacities of different catalysts for β-1,4-glucan were compared. The results showed that traditional solid acids, such as niobic acid, H-mordenite, Nafion, and Amberlyst-15, did not have the ability to adsorb β-1,4-glucan, whereas the carbon material adsorbed 64% of the β-1,4-glucan within 3 h, implying that the carbon material had a stronger affinity for β-1,4-glucan[83]. After reacting for 3 h, glucose yields of 10% and 4% were obtained by using H_2SO_4 and a carbon-based catalyst, respectively, for cellulose hydrolysis. This result indicated that the catalytic capacity of the carbon material was weaker than that of H_2SO_4 for the hydrolysis of crystalline cellulose because the acidity of the biochar-based catalyst is lower than that of H_2SO_4. These findings emphasize that future research should focus on improving the acidity of catalysts to promote the catalytic performance for cellulose hydrolysis.

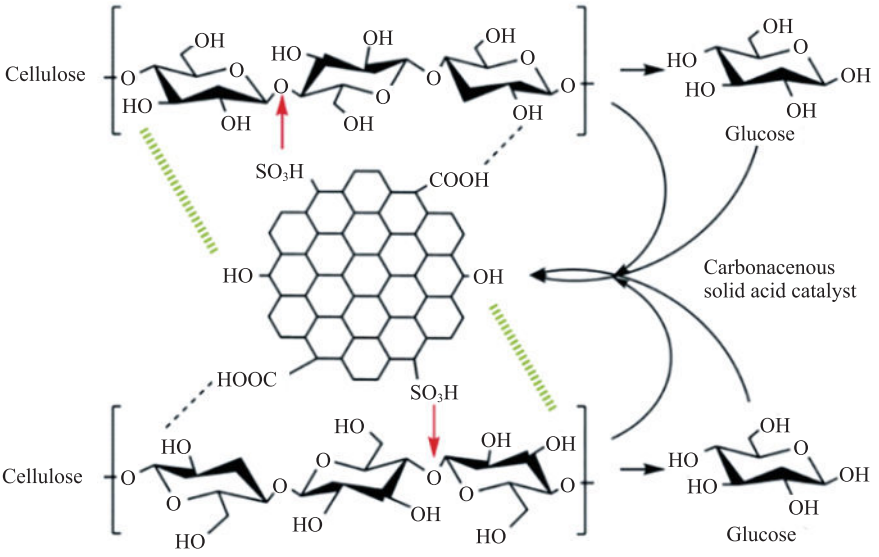


Fig.5 Hydrolysis of cellulose into glucose with biochar-based solid acid catalysts

Table 4 Catalytic recyclability of different biomass–based catalysts

Entry	Biomass	Catalyst	Cycle times	Substrate	Range/% (TRS)	Loss rate/%	Ref.
1	SUCRA	SUCRA-SO_3H	10	Cellobiose	100～56	44	[85]
2	Enzymatic corn stover	Cl-CMC-SO_3H	5	Microcrystalline cellulose	78.5～72.6	5.9	[86]
3	Cellulose	PCM-SO_3H	3	Cellulose	68～43	25	[87]
4	Willow	Willow-SO_3H	3	Cellulose	65～50.9	14.9	[84]
5	Glucose	Glucose-SO_3H	5	Cellulose	61～55	6	[81]
6	Glucose	Fe_3O_4@C-SO_3H	6	Cellulose	＜1	＜1	[88]
7	Corncob residue	CSA	2	Corncob	55.6～26.7	28.9	[89]
8	Bamboo	BC-SO_3H-IL-Zn	3	Cellulose	＜1	＜1	[90]
9	Bamboo	BC-SO_3H-IL-Zn	3	Bamboo	＜5	＜5	
10	Black liquor	Black liquor-SO_3H	5	Rice straw	63.4～44.4	19	[91]

Besides catalytic properties, the stability of biochar catalysts is also of vital importance. Table 4 summarizes the cycling stabilities of different biochars. The stabilities of the biochar catalysts were affected by many factors, including biochar source, surface functional groups, cycle times, and hydrolysis substrates. After being used and recycled several times, the activities of almost all the biochar catalysts decreased to some extent, mainly because of the loss of sulfonate groups[84]. In the presence of nano-metal ions, such as iron and zinc, which increased interactions between the sulfonate groups and biochar, the stabilities of the biochar catalysts were improved obviously (Table 4, entries 6 and 8). Similarly, the presence of chloride also increased the stabilities of biochar catalysts. When the biochar catalyst was reused three times, the reducing sugar yield was decreased by less than 5%. (Table 4, entry 9). Therefore, the stability of biochar catalysts can be enhanced by loading with nano-metal ions and other ions.

As mentioned above, the stability and the acid are important factors that have an impact on catalytic

performance. Another important factor is the effective interaction between cellulose units and the catalyst surface, which can be induced by auxiliary means. Cellulose has a very high solubility in ionic liquids, which facilitates complete contact with catalytic sites. It was reported that cellulose could be effectively hydrolyzed to reducing sugars in 1-butyl-3-methyl chloride ([BMIM]Cl) ionic liquids using aglucose-derived biochar-based solid acid catalyst[81]. The highest total reducing sugar yield of 72.7% was achieved at 110℃. The catalytic activity of the biochar-based catalyst was attributed to its surface phenolic hydroxyl groups or —COOH groups, which effectively adsorbed cellulose and water molecules, and —SO_3H groups, which broke the hydrogen bonds and hydrolyzed the β-1,4-glycosidic bonds in the adsorbed cellulose molecules. In addition, the influence of water molecules in ionic liquids was studied, and the results showed that a water content of more than 2% decreased the yield of reducing sugar owing to a decrease in the solubility of cellulose in the medium. Similar studies on the hydrolysis of cellulose in [BMIM]Cl ionic liquids were carried out with sulfonated carbon catalysts derived from sucrose, glucose, and nut shells[79]. The sucrose-derived catalyst exhibited the highest catalytic performance, with a 59% yield of glucose at 120℃ for 4 h. The yield of glucose decreased with prolonged reaction time, which was ascribed to the occurrence of side reactions resulting from 5-hydroxymethylfurfural. The catalytic activity of the nut-shell-derived catalyst was inferior to that of the sucrose- or glucose-derived catalyst for cellulose hydrolysis, which was attributed to the low amount of —SO_3H groups on the nut-shell-derived catalyst. Fewer —SO_3H groups on a catalyst led to lower acidity[90].

In a subsequent study, a cellulose-derived super paramagnetic biochar-based catalyst was produced by HTC of cellulose. This catalyst exhibited good catalytic performance in the cellulose hydrolysis in [BMIM]Cl, with a 68.9% yield of total reducing sugars at 130℃ for 3 h[87]. In contrast, in water, the yield of reducing sugars was 51% at 180℃ for 9 h. Thus, ionic liquids are more conducive to hydrolysis of cellulose than water.

Another common pretreatment methods used in the hydrolysis of cellulose is ball milling, which obviously reduces the crystallinity of cellulose, consequently improving accessibility and increasing the yield of glucose[92]. Ball milling techniques can be divided into mixed ball milling and single ball milling. For the hydrolysis of cellulose, the effect of mixed ball milling is better than that of single ball milling. Mixed-ball-milled samples (cellulose and solid acid catalyst) and single-ball-milling cellulose were hydrolyzed in dilute HCl solution, giving glucose yields of 88.0% and 30.0%, respectively, at 180℃ for 20 min, indicating that mixing ball milling was a more efficient method[93]. For a better understanding of this pretreatment method, mixed ball milling of cellulose and different catalysts were investigated[93]. In this study, three model reactions were investigated: ① cellulose and alkali-activated carbon solid acid, ② cellobiose and alkali-activated carbon solid acid, and ③ cellulose and benzoic acid. The results showed that only mixed ball milling of cellulose and the alkali-activated carbon solid acid catalyst (solid–solid reaction) obviously increased the hydrolysis efficiency. The yield of reducing sugars increased from 12.9% to 90.0% for cellobiose hydrolysis at 180℃ for 20 min when mixed ball milling (solid acid catalyst and cellobiose) was used instead of single ball milling, indicating that mixed ball milling could improve the interaction of cellulose with the catalyst during cellulose hydrolysis. The hydrolysis efficiency of cellulose was enhanced by mixed ball milling because this process improved the physical contact between cellulose and the biochar-based catalyst, which increased the contact area between the active sites of the catalyst and the β-1,4-glycosidic bonds on the surface of cellulose[93]. Ball milling is a highly efficient pretreatment technology for cellulose hydrolysis, but it requires long pretreatment time (24～96 h) and considerable energy to achieve the desired results.

The effects of conventional heating and microwave irradiation were compared for the hydrolysis of cellulose

using biochar-based solid acid catalysts derived from bamboo, as shown in Fig.6[80]. The results showed that high temperatures promoted the hydrolysis of cellulose with either microwave irradiation or conventional heating. The yield of glucose first increased as the temperature was increased from 70℃ to 90℃, and then began to decrease when the temperature was increased further to 100℃, which was ascribed to the consumption of glucose in side reactions. Microwave irradiation was more beneficial than conventional heating for the hydrolysis of cellulose. The yield of glucose with the microwave irradiation was 5.3-fold higher than that with conventional heating at 90℃ for 60 min. Microwave irradiation can promote the hydrolysis of cellulose by destroying the crystal structure and enhancing collision opportunities between cellulose and the catalyst active sites. Biochar-based catalysts could also be applied for lignocelluloses biomass hydrolysis with microwave irradiation.

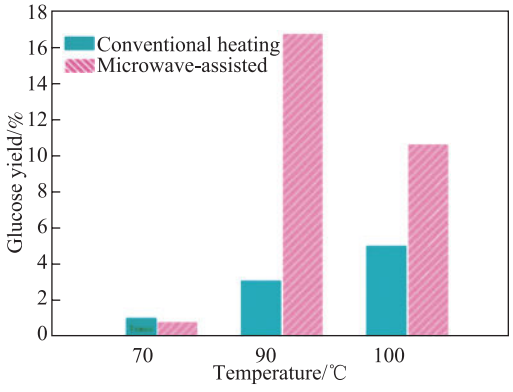


Fig.6 Comparison glucose yields obtained by conventional heating and microwave-assisted hydrolysis of crystalline cellulose catalyzed by BC-SO_3H

The hydrolysis of corncob using a self-derived biochar-based solid acid catalyst was investigated with microwave irradiation. The maximum yields of glucose, xylose, and arabinose were 34.6%, 77.3%, and 100%, respectively, at 140, 130, and 130℃ for 1 h microwave irradiation. In addition, the glucose yield of 34.6% obtained with microwave irradiation was about 3.9-fold higher than that obtained with conventional heating under the same conditions. This phenomenon was consistent with previous reports, confirming that microwave irradiation contributes to the hydrolysis of cellulose[89]. More importantly, the whole biomass was used in this process. Sugars were obtained by hydrolysis of cellulose and hemicelluloses in the corncob and the unconverted solid residue were used to prepare the biochar-based solid acid catalyst.

Some studies have focused on magnetic biochar-based catalysts for the hydrolysis of cellulose. A magnetic sulfonated carbon-based nanoparticle catalyst with a core–shell structure (Fe_3O_4@C-SO_3H) was prepared for the hydrolysis of cellulose in water. The catalyst displayed highly stable activity and magnetization during recycling tests because the carbon shell prevented the elution of the Fe_3O_4 core during the reaction[94]. Thus, the core–shell structure of the biochar-based catalyst was beneficial for the hydrolysis of cellulose. However, a 25.3% yield of glucose was obtained, indicating that the catalytic performance of this catalyst is lower than those of other reported sulfonated carbon catalysts[16]. Another magnetic biochar-based solid acid catalyst, synthesized by HTC of cellulose under mild conditions, was used to hydrolyze microcrystalline cellulose in [BMIM]Cl and in water. For the hydrolysis of microcrystalline cellulose, the yield of reducing sugars in [BMIM]Cl (68.9% at 130℃ for 3 h) was considerably higher than that in water (51% at 180℃ for 9 h). These results were ascribed to the good solubility of cellulose in the ionic liquid, as the β-1,4-glycosidic bonds of the cellulose chain could be quickly attacked and decomposed by the solid acid catalyst[87]. Thus, this magnetic solid acid catalyst exhibited high catalytic performance for cellulose hydrolysis in an ionic liquid.

To improve the catalytic performance of biochar-based solid acid catalysts, various catalysts have been loaded with metal or nonmetal atoms, such as Zn and Cl. A novel biochar-based solid acid catalyst was synthesized by co-carbonization of starch and PVC, which significantly increased the yield of reducing sugars, reaching a maximum yield of 94.2%[64]. The increased yield was attributed to the participation of Cl atoms on the biochar-based catalyst, which could attack

the hydroxyl protons of cellulose to form hydrogen bonds. Thus, the intra-and intermolecular hydrogen bonds of cellulose were broken, exposing the glycosidic bonds, which facilitated contact between the sulfonic acid groups on the catalyst and the glycosidic bonds, consequently accelerating cellulose hydrolysis. For the hydrolysis of cellulose under microwave irradiation, an ionic liquid (chlorozincate) and H_2SO_4-functionalized bamboo-derived biochar catalyst (BC-SO_3H-IL-Zn) in water gave a reducing sugar yield of 58.7%, whereas bamboo powder gave a reducing sugar yield of only 30.3%. The BC-SO_3H-IL-Zn catalyst exhibited excellent performance for cellulose hydrolysis owing to the introduction of an ionic liquid and nano-zinc[90].

3.2 Hemicellulose hydrolysis

Biochar-based catalysts can also be applied for the hydrolysis of hemicellulose. Hemicellulose is an important component of carbohydrates and its hydrolysis products include xylose, arabinose, mannose, and xylooligosaccharides[95-96]. However, only a few studies have reported on the hydrolysis of hemicellulose by biochar-based solid acid catalysts, as summarized in Table 5.

Recently, biochar-based solid acid catalysts were prepared from pine wood chips and peanut hulls by carbonization and sulfonation[13]. The pine chip biochar catalyst was applied to hydrolyze xylan and the conversion rate reached 85% (initial xylan concentration: 7.5 g/L) in 2 h at 120℃, which was better than the performance of an AC catalyst (57% conversion in 24 h). The increased catalytic activity was ascribed to a higher acid site density for xylan, indicating that the catalytic performance of that biochar catalyst was better than that of AC for xylan hydrolysis. Moreover, the initial reaction rate of xylan hydrolysis was higher with the pine chip biochar catalyst than AC and Amberlyst-15 catalysts[13]. Loss of catalytic activity occurred with increasing reaction time owing to leaching of the acid sites. Therefore, future research should focus on catalyst stability and the mechanism of active site leaching.

A corn-stover-biochar-based solid acid was prepared and used for the hydrolysis of corn stover, switch grass, and prairie cord grass, exhibiting xylose selectivities of 41.6%, 33.14%, and 50.39%, respectively. Further, the xylose selectivities were 29.82%, 22.56%, and 35.22% when using H_2SO_4 as the catalyst[71]. The results showed that the selectivity for xylose with the biochar catalyst was higher than that with the homogeneous H_2SO_4 catalyst because the high stability of the biochar catalyst minimized the amount of free H_2SO_4 in solution[99]. Hydrolysis of the biomasses of three different raw materials (corn stover, switch grass, and prairie cord grass) using a corn-stover-biochar-based catalyst gave total reducing sugar yields of 240, 300, and 310 mg/g, respectively, and xylose yields of 48, 58, and 47 mg/g, respectively. With the homogeneous catalysts (H_2SO_4) under the same conditions, the yields of reducing sugars for hydrolysis of corn stover,

Table 5 Hydrolysis of hemicellulose by biochar–based catalysts

Catalyst	Substrate	—SO_3H density /(mmol·g^{-1})	Solvent	Conditions	Xylose yield/%	Ref.
Sulfonated bamboo-based carbon material (BCS)	Bamboo hemicelluloses	—	H_2O	150°C, 60 min, microwave irradiation	76.5	[96]
CSA (corncob residue)	Corncob powder	—	H_2O	140℃, 20 min, microwave irradiation	77.3	[89]
Fe_3O_4—C—SO_3H	Corncobs	—	H_2O	160℃, 16 h	44.3	[97]
MCN-based materials	Xylan	0.4	Sodium acetate buffer	150℃, 4 h	74	[98]
Eucalyptus-based catalyst	Eucalyptus	—	H_2O + trace HCl	215℃, 17 min	89	[96]
Pine chip biochar catalyst	Pine chip	0.7	H_2O	120℃, 2 h	—	[13]
Wood-derived catalyst	Wood	0.2	H_2O	120℃, 24 h	—	
Corn stover biochar	Corn stover	0.7	H_2O	100℃, 60 min	>90	[71]

switch grass, and prairie cord grass were 140, 160, and 170 mg/g, respectively, and those of xylose were 50, 58, and 46 mg/g, respectively. Thus, the biochar-based catalyst showed better catalytic performance for cellulose hydrolysis than H_2SO_4. However, the biochar-based catalyst exhibited poorer hydrolysis performance for hemicellulose than H_2SO_4 in the same hydrolysis process. This difference occurred because adsorption of hemicellulose on the surface of the biochar-based catalyst was more difficult than the adsorption of cellulose, which was ascribed to the higher hydrophilicity of hemicellulose than cellulose.

In addition, a magnetic glucose-derived biochar catalyst with a core-shell structure was prepared for the hydrolysis of hemicellulose from corncobs[97]. The yield of xylose was 44.3% at 160℃ for 16 h, and after cycling three times, the recovery of the catalyst was over 89%, indicating the good performance and recyclability of the magnetic glucose-derived biochar catalyst. In addition, a new solid acid catalyst was synthesized from sulfonated bamboo-based biochar, and this catalyst was used to hydrolyze bamboo hemicellulose into xylooligosaccharides[95]. The maximum yield of xylooligosaccharides was 57.3% (based on xylan content) at 150℃ for 45 min using the biochar-based catalyst. The xylose yield was 76.5% (based on xylan content) at 160℃ for 45 min using the same biochar-based catalyst. The efficiency and selectivity of biochar-based solid acid catalyst in the hydrolysis of hemicellulose are beneficial for the development and application of biochar. However, for hemicellulose hydrolysis by biochar solid acids, considerable challenges need to be addressed, including improvements to the acidity, the selectivity, and the thermal stability of catalysts.

4 Perspectives on biochar–based catalysts for carbohydrate hydrolysis

Great achievements have been obtained in the hydrolysis of carbohydrates, but focus still needs to be placed on further improvements in catalysts and hydrolysis processes. Using biochar-based catalysts for the hydrolysis of carbohydrates provides relatively high yields of monosaccharides in water. Water is a green, low-cost, nontoxic, safe, and reliable medium, which is the perfect reaction medium. However, biochar-based catalysts are not stable in water and acid sites are easily leached. Thus, the development of biochar-based catalysts that are highly active and stable in the aqueous phase is essential. Moreover, further in-depth research on carbohydrate hydrolysis is required, especially on the hydrolysis of hemicellulose into xylose and the catalytic mechanism of hemicellulose hydrolysis. In addition, follow-up research should be focused on the preparation process, especially on biomass resources, biochar generation conditions, and pretreatment processes. Furthermore, additional attention should be paid to structure–function relationships to facilitate catalyst optimization.

5 Conclusions

This review highlighted recent advances in the preparation methods of biochar-based catalysts, their properties, and the catalytic performance of these catalysts for the hydrolysis of cellulose and hemicellulose. Biochar can be obtained by carbonization of biomass, and its characteristics and yield depend on the pyrolysis temperature, pyrolysis time, and biomass source. The catalytic performance of biochar-based catalysts for the hydrolysis of cellulose and hemicellulose can be improved by enlarging pore sizes and through surface modification (sulfonation). Overall, biochar-based catalysts, which are low cost, have a wide variety of source materials, and have simple preparation procedures, exhibit considerable potential for application to carbohydrate hydrolysis. Future research in this area needs to focus on improvements of catalysts and hydrolysis processes.

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References

[1] FalcãoAntónio F O, HenriquesJoão C C. Oscillating-water-column wave energy converters and air turbines: A review[J]. Renewable Energy, 2016, 85: 1391-1424.

[2] Shen Y, Jarboe L, Brown R, et al. A thermochemical-biochemical hybrid processing of lignocellulosic biomass for producing fuels and chemicals[J]. Biotechnology Advances, 2015, 33(8): 1799-1813.

[3] Serrano-Ruiz J C, Luque R, Sepúlveda-Escribano A. Transformations of biomass-derived platform molecules: from high added-value chemicals to fuels via aqueous-phase processing[J]. Chemical Society Reviews, 2011, 40(11): 5266-5281.

[4] Xiao L P, Sun Z J, Shi Z J, et al. Impact of hot compressed water pretreatment on the structural changes of woody biomass for bioethanol production[J]. Bioresources, 2011, 6(2): 1576-1598.

[5] Huber G W, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering[J]. Chemical Reviews, 2006, 106(9): 4044-4098.

[6] De L H, Salaices E, Mazumder J, et al. Catalytic steam gasification of biomass: catalysts, thermodynamics and kinetics[J]. Chemical Reviews, 2011, 111(9): 5404-5433.

[7] Deng A J, Lin Q X, Yan Y H, et al. A feasible process for furfural production from the pre-hydrolysis liquor of corncob via biochar catalysts in a new biphasic system[J]. Bioresource Technology, 2016, 216: 754-760.

[8] Regalbuto J R. Cellulosic biofuels-got gasoline[J]. Science, 2009, 325(5942): 822-824.

[9] Geboers J A, Vyver S V D, Ooms R, et al. Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls[J]. Catalysis Science & Technology, 2011, 1(5): 714-726.

[10] Li H L, Chen X F, Ren J L, et al. Functional relationship of furfural yields and the hemicellulose-derived sugars in the hydrolysates from corncob by microwave-assisted hydrothermal pretreatment[J]. Biotechnology for Biofuels, 2015, 8(1): 127-139.

[11] Kumar P, Barrett D M, Delwiche Michael J, et al. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production[J]. Industrial & Engineering Chemistry Research, 2009, 48(8): 3713-3729.

[12] Lin Q X, Li H L, Ren J L, et al. Production of xylooligosaccharides by microwave-induced, organic acid-catalyzed hydrolysis of different xylan-type hemicelluloses: Optimization by response surface methodology[J]. Carbohydrate Polymer, 2017, 157: 214-225.

[13] Ormsby R, Kastner J R, Miller J. Hemicellulose hydrolysis using solid acid catalysts generated from biochar[J]. Catalysis Today, 2012, 190(1): 89-97.

[14] Yan Y H, Li H L, Ren J L, et al. Xylo-sugars production by microwave-induced hydrothermal treatment of corncob: Trace sodium hydroxide addition for suppression of side effects[J]. Industrial Crops & Products, 2017, 101: 36-45.

[15] Deng A J, Ren J L, Wang W J, et al. Production of xylo-sugars from corncob by oxalic acid-assisted ball milling and microwave-induced hydrothermal treatments[J]. Industrial Crops & Products, 2016, 79: 137-145.

[16] Pang J, Wang A, Zheng M, et al. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures[J]. Chemical Communications, 2010, 46(37): 6935-6937.

[17] Liu W J, Jiang H, Yu H Q. Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material[J]. Chemical Reviews, 2015, 115(22): 12251-12285.

[18] Zhu L, Yin S, Yin Q, et al. Biochar: a new promising catalyst support using methanation as a probe reaction[J]. Energy Science & Engineering, 2015, 3(2): 126-134.

[19] Rajapaksha A U, Chen S S, Tsang D C, et al. Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and implication of biochar modification[J]. Chemosphere, 2016, 148(4): 276-291.

[20] Kambo H S, Dutta A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications[J]. Renewable & Sustainable Energy Reviews, 2015, 45(5): 359-378.

[21] Konwar L J, Boro J, Deka D. Review on latest developments in biodiesel production using carbon-based catalysts[J]. Renewable & Sustainable Energy Reviews, 2014, 29(7): 546-564.

[22] Huang Y B, Fu Y. Hydrolysis of cellulose to glucose by solid acid catalysts[J]. Green Chemistry, 2013, 15(5): 1095-111.

[23] International Biochar Initiative. IBI biochar standards: 2012 Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil[S]. 2012.

[24] Qian K, Kumar A, Zhang H, et al. Recent advances in utilization of biochar[J]. Renewable & Sustainable Energy Reviews, 2015, 42(1): 1055-1064.

[25] Dehkhoda A M, West A H, Ellis N. Biochar based solid acid catalyst for biodiesel production[J]. Applied Catalysis A General, 2010, 382(2): 197-204.

[26] Yue Y, Lin Q, Xu Y, et al. Slow pyrolysis as a measure for rapidly treating cow manure and the biochar characteristics[J]. Journal of Analytical & Applied

Pyrolysis, 2017, 355-361.

[27] Bridgwater A V, Meier D, Radlein D. An overview of fast pyrolysis of biomass[J]. Organic Geochemistry, 1999, 30(12): 1479-1493.

[28] Igalavithana A D, Park J, Ryu C, et al. Slow pyrolyzedbiochars from crop residues for soil metal (loid) immobilization and microbial community abundance in contaminated agricultural soils[J]. Chemosphere, 2017, 177: 157-166.

[29] Volpe R, Messineo A, Menendez J M B, et al. Evolution of chars during slow pyrolysis of citrus waste[J]. Fuel Processing Technology, 2017, 158 (4): 255-263.

[30] Schroeder P, Nascimento B P D, Romeiro Go A, et al. Chemical and physical analysis of the liquid fractions from soursop seed cake obtained using slow pyrolysis conditions[J]. Journal of Analytical & Applied Pyrolysis, 2017, 124 (3): 161-174.

[31] Mandal A, Singh N, Purakayastha T J. Characterization of pesticide sorption behaviour of slow pyrolysis biochars as low cost adsorbent for atrazine and imidacloprid removal[J]. Science of the Total Environment, 2017, 577(1): 376-385.

[32] Essandoh M, Wolgemuth D, Jr Charles U P, et al. Phenoxy herbicide removal from aqueous solutions using fast pyrolysis switchgrass biochar[J]. Chemosphere, 2017, 174(5): 49-57.

[33] Xu C, Chen Y, Yang H, et al. Fast pyrolysis of cotton stalk biomass using calcium oxide[J]. Bioresource Technology, 2017, 233(6): 15-20.

[34] Pecha M B, Montoya J I, Chejne F, et al. Effect of Vacuum on the Fast Pyrolysis of Cellulose: Nature of Secondary Reactions in Liquid Intermediate[J]. Industrial & Engineering Chemistry Research, 2017, 56(15): 4288-4301.

[35] Staš M, Chudoba J, Auersvald M, et al. Application of orbitrap mass spectrometry for analysis of model bio-oil compounds and fast pyrolysis bio-oils from different biomass sources[J]. Journal of Analytical & Applied Pyrolysis, 2017, 124(3): 230-238.

[36] Klemetsrud B, Eatherton D, Shonnard D. Effects of Lignin Content and Temperature on the Properties of Hybrid Poplar Bio-Oil, Char, and Gas Obtained by Fast Pyrolysis[J]. Energy & Fuels, 2017, 31(3): 2879-2886.

[37] Karunanayake A G, Todd O A, Crowley M L, et al. Rapid removal of salicylic acid, 4-nitroaniline, benzoic acid and phthalic acid from wastewater using magnetized fast pyrolysis biochar from waste Douglas fir[J]. Chemical Engineering Journal, 2017, 319(7): 75-88.

[38] Na X, Hu L, Wei W Q, et al. Microwave-assisted gasification of rice straw pyrolytic biochar promoted by alkali and alkaline earth metals[J]. Journal of Analytical & Applied Pyrolysis, 2015, 112(3): 173-179.

[39] Zhou N, Chen H, Xi J, et al. Biochars with excellent Pb (II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization[J]. Bioresource Technology, 2017, 232(5): 204-210.

[40] Breulmann M, Afferden M Van, Müller Roland A, et al. Process conditions of pyrolysis and hydrothermal carbonization affect the potential of sewage sludge for soil carbon sequestration and amelioration[J]. Journal of Analytical & Applied Pyrolysis, 2017,124(3): 256-265.

[41] Imam T, Capareda S. Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures[J]. Journal of Analytical & Applied Pyrolysis, 2012, 93(1): 170-177.

[42] Demirbaş A. Mechanisms of liquefaction and pyrolysis reactions of biomass[J]. Energy Conversion & Management, 2000, 41(6): 633-646.

[43] Hansen V, Hauggaard-Nielsen H, Petersen C T, et al. Effects of gasification biochar on plant-available water capacity and plant growth in two contrasting soil types[J]. Soil & Tillage Research, 2016, 161(8): 1-9.

[44] Qian K Z, Kumar A, Patil K, et al. Effects of biomass feedstocks and gasification conditions on the physiochemical properties of char[J]. Energies, 2013, 6(8): 3972-3986.

[45] Libra J A, Ro K S, Kammann C, et al. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis[J]. Biofuels, 2011, 2(1): 71-106.

[46] Hu B, Wang K, Wu L, et al. Engineering carbon materials from the hydrothermal carbonization process of biomass[J]. Advanced Materials, 2010, 22(7): 813-828.

[47] Kruse A, Funke A, Titirici M M. Hydrothermal conversion of biomass to fuels and energetic materials[J]. Current Opinion in Chemical Biology, 2013, 17(3): 515-521.

[48] Titirici M M, White R J, Falco C, et al. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage[J]. Energy & Environmental Science, 2012, 5(5): 6796-6822.

[49] Shen D K, Gu S, Bridgwater A V. Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR[J]. Journal of Analytical & Applied Pyrolysis, 2010, 87(2): 199-206.

[50] Kosa M, Ben H X, Theliander H, et al. Pyrolysis oils from CO_2 precipitated Kraft lignin[J]. Green Chemistry, 2011, 13(11): 3196-3202.

[51] Lin Y C, Huber G W. The critical role of heterogeneous catalysis in lignocellulosic biomass conversion[J]. Energy & Environmental Science, 2008, 2(1): 68-80.

[52] Mullen C A, Boateng A A, Goldberg N M, et al. Bio-oil and bio-char production from corn cobs and stover by fast

pyrolysis [J]. Biomass & Bioenergy, 2010, 34(1): 67-74.

[53] Hulicovajurcakova D, Puziy A M, Poddubnaya O I, et al. Highly Stable Performance of Supercapacitors from Phosphorus-Enriched Carbons[J]. Journal of the American Chemical Society, 2009, 131(14): 5026-5027.

[54] Hadi P, Xu Mg, Ning C, et al. A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment[J]. Chemical Engineering Journal, 2015, 260(1): 895-906.

[55] Yuliusman N, Afdhol M K, et al. Preparation of Activated Carbon from Palm Shells Using KOH and $ZnCl_2$ as the Activating Agent[C]// Earth and Environmental Science Conference. 2017: 1315-1327.

[56] Van T T, Qtp B, Nguyen T D, et al. Application of response surface methodology to optimize the fabrication of $ZnCl_2$-activated carbon from sugarcane bagasse for the removal of Cu2[J]. Water Science & Technology, 2017, 75(9): 2047-2055.

[57] Klinghoffer N B, Castaldi M J, Nzihou A. Catalyst Properties and Catalytic Performance of Char from Biomass Gasification[J]. Indengchemres, 2012, 51(40): 13113-13122.

[58] Yang K, Peng J, Srinivasakannan C, et al. Preparation of high surface area activated carbon from coconut shells using microwave heating[J]. Bioresource Technology, 2010, 101(15): 6163-6169.

[59] Sevilla M, Mokaya R. Energy storage applications of activated carbons: super capacitors and hydrogen storage[J]. Energy & Environmental Science, 2014, 7(4): 1250-1280.

[60] Toda M, Takagaki A, Okamura M, et al. Green chemistry: biodiesel made with sugar catalyst[J]. Nature, 2005, 438(11): 178-182.

[61] Qian W, Sun F, Xu Y, et al. Human hair-derived carbon flakes for electrochemical supercapacitors[J]. Energy & Environmental Science, 2013, 7(1): 379-386.

[62] Wei L, Yang K, Peng J, et al. Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars[J]. Industrial Crops & Products, 2008, 28(2): 190-198.

[63] Kastner J R, Miller J, Geller D P, et al. Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon[J]. Catalysis Today, 2012, 190(1): 122-132.

[64] Shen S, Cai B, Wang C, et al. Preparation of a novel carbon-based solid acid from cocarbonized starch and polyvinyl chloride for cellulose hydrolysis[J]. Applied Catalysis A General, 2014, 473(5): 70-74.

[65] Li Y, Shao J, Wang X, et al. Characterization of Modified Biochars Derived from Bamboo Pyrolysis and Their Utilization for Target Component (Furfural) Adsorption[J]. Energy & Fuels, 2014, 28(8): 5119-5127.

[66] Moreno-Castilla C, López-Ramón M V, Carrasco-MarıN F. Changes in surface chemistry of activated carbons by wet oxidation[J]. Carbon, 2000, 38(14): 1995-2001.

[67] Gokce Y, Aktas Z. Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol[J]. Applied Surface Science, 2014, 313(10): 352-359.

[68] Figueiredo J L, Pereira M F R, Freitas M M A, et al. Modification of the surface chemistry of activated carbons[J]. Carbon, 1999, 37(9): 1379-1389.

[69] Nakajima K, Hara M. Amorphous Carbon with SO_3H Groups as a Solid Brønsted Acid Catalyst[J]. ACS Catalysis, 2012, 2(7): 1296-1304.

[70] Takagaki A, Tagusagawa C, Hayashi S, et al. Nanosheets as Highly Active Solid Acid Catalysts for Green Chemical Syntheses[J]. ChemInform, 2010, 41(50): 82-93.

[71] Li S, Gu Z, Bjornson B E, et al. Biochar based solid acid catalyst hydrolyze biomass[J]. Journal of Environmental Chemical Engineering, 2013, 1(4): 1174-1181.

[72] Peng L, An P, Ke X, et al. Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids[J]. Catalysis Today, 2010, 150(1): 140-146.

[73] Liu W J, Tian K, Jiang H, et al. Facile synthesis of highly efficient and recyclable magnetic solid acid from biomass waste[J]. Scientific Reports, 2013, 3(8): 2419-2426.

[74] Zhang C, Fu Z, Liu Y C, et al. Ionic liquid-functionalized biochar sulfonic acid as a biomimetic catalyst for hydrolysis of cellulose and bamboo under microwave irradiation[J]. Green Chemistry, 2012, 14(7): 1928-1934.

[75] Hara M. Biomass conversion by a solid acid catalyst[J]. Energy & Environmental Science, 2010, 3(5): 601-607.

[76] Zhou C H, Xia X, Lin C X, et al. Catalytic Conversion of Lignocellulosic Biomass to Fine Chemicals and Fuels[J]. ChemInform, 2011, 40(11): 5588-5617.

[77] Xiu S, Shahbazi A, Li R. Characterization, Modification and Application of Biochar for Energy Storage and Catalysis: A Review[J]. 2017, 3(1): 86-101.

[78] Fraga A D C, Ximenes V L, Sousa-Aguiar E F, et al. Biomass derived solid acids as effective hydrolysis catalysts[J]. Journal of Molecular Catalysis A Chemical, 2015, 422(10): 248-257.

[79] Liu M, Jia S, Gong Y, et al. Effective Hydrolysis of Cellulose into Glucose over Sulfonated Sugar-Derived Carbon in an Ionic Liquid[J]. Industrial & Engineering Chemistry Research, 2013, 52(24): 8167-8173.

[80] Wu Y, Fu Z, Yin D, et al. Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids[J]. Green Chemistry, 2010, 12(4): 696-700.

[81] Guo H, Qi X, Li L, et al. Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid[J]. Bioresource Technology, 2012, 116(7): 355-359.

[82] Hu L, Lin L, Wu Z, et al. Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts[J]. Applied Catalysis B Environmental, 2015, s174-175(22): 225-243.

[83] Suganuma S, Nakajima K, Kitano M, et al. Hydrolysis of cellulose by amorphous carbon bearing SO_3H, COOH, and OH groups[J]. Journal of the American Chemical Society, 2008, 130(38): 12787-12793.

[84] Sun Z, Tao M, Zhao Q, et al. A highly active willow-derived sulfonated carbon material with macroporous structure for production of glucose[J]. Cellulose, 2015, 22(1): 675-682.

[85] Hu S, Smith T J, Lou W, et al. Correction to Efficient Hydrolysis of Cellulose over a Novel Sucralose-Derived Solid Acid with Cellulose-Binding and Catalytic Sites[J]. Journal of Agricultural & Food Chemistry, 2014, 62(8): 1905-1911.

[86] Hu L, Li Z, Wu Z, et al. Catalytic hydrolysis of microcrystalline and rice straw-derived cellulose over a chlorine-doped magnetic carbonaceous solid acid[J]. Industrial Crops & Products, 2016, 84(6): 408-417.

[87] Guo H, Lian Y, Yan L, et al. Cellulose-derived super paramagnetic carbonaceous solid acid catalyst for cellulose hydrolysis in an ionic liquid or aqueous reaction system[J]. Green Chemistry, 2013, 15(8): 2167-2174.

[88] Liu X, Xu Q, Liu J, et al. Hydrolysis of cellulose into reducing sugars in ionic liquids[J]. Fuel, 2016, 164(15): 46-50.

[89] Jiang Y J, Li X T, Wang XC, et al. Effective saccharification of lignocellulosic biomass over hydrolysis residue derived solid acid under microwave irradiation[J]. Green Chemistry, 2012, 14(8): 2162-2167.

[90] Zhang C, Fu Z, Dai B, et al. Biochar sulfonic acid immobilized chlorozincate ionic liquid: an efficiently biomimetic and reusable catalyst for hydrolysis of cellulose and bamboo under microwave irradiation[J]. Cellulose, 2014, 21(3): 1227-1237.

[91] Bai C, Zhu L, Feng S, et al. Black liquor-derived carbonaceous solid acid catalyst for the hydrolysis of pretreated rice straw in ionic liquid[J]. Bioresource Technology, 2016, 220(11): 656-660.

[92] Gliozzi G, Innorta A, Mancini A, et al. Zr/P/O catalyst for the direct acid chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust[J]. Applied Catalysis B Environmental, 2014, 145(1): 24-33.

[93] Yabushita M, Kobayashi H, Hara K, et al. Quantitative evaluation of ball-milling effects on the hydrolysis of cellulose catalysed by activated carbon[J]. Catalysis Science & Technology, 2014, 4(8): 2312-2317.

[94] Zhang C, Wang H, Liu F, et al. Magnetic core-shell Fe_3O_4@C-SO_3H nanoparticle catalyst for hydrolysis of cellulose[J]. Cellulose, 2013, 20(1): 127-134.

[95] Bai Y Y, Xiao L P, Sun R C. Microwave-assisted conversion of biomass derived hemicelluloses into xylo-oligosaccharides by novel sulfonated bamboo-based catalysts[J]. Biomass & Bioenergy, 2015, 75(4): 245-253.

[96] Kobayashi H, Kaiki H, Shrotri A, et al. Hydrolysis of woody biomass by a biomass-derived reusable heterogeneous catalyst[J]. Chemical Science, 2016, 7(1): 692-696.

[97] Zhang X, Tan X, Xu Y, et al. Preparation of Core-Shell Structure Magnetic Carbon-Based Solid Acid and its Catalytic Performance on Hemicellulose in Corncobs[J]. Bioresources, 2016, 11(4): 10014-10029.

[98] Chung P W, Charmot A, Olatunjiojo O A, et al. Hydrolysis Catalysis of Miscanthus Xylan to Xylose Using Weak-Acid Surface Sites[J]. ACS Catalysis, 2015, 4(1): 302-310.

[99] Onda A, Ochi T, Yanagisawa K. Selective hydrolysis of cellulose into glucose over solid acid catalysts[J]. Green Chemistry, 2008, 10(10): 1033-1037. PBM