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## Application of biochar-based catalysts in biomass upgrading: a review

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Biochar is a low-cost carbon-rich material derived from the thermochemical degradation of biomass. Due to its unique chemical structure, biochar with a large surface area and tailored surface functional groups can be easily prepared by activation and/or functionalization, and shows great potential to be used as a versatile catalyst and/or catalyst support in many chemical processes. However, the application of biochars as versatile catalysts and/or catalyst supports for biomass upgrading has not been systematically overviewed so far. In this work, the formation of pyrochar and hydrochar is proposed, and the activation and/or functionalization of biochar are also included. Subsequently, the application of biochar-based catalysts in biomass upgrading, including biochar-based solid acids for biomass hydrolysis and dehydration, biochar-based catalysts for biodiesel production, and biochars as catalyst supports for biomass pyrolysis, gasification, and bio-oil upgrading, are discussed in detail.

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### 1. Introduction

As the most abundant and renewable resource in the world, biomass is considered as a promising alternative to fossil resources for providing sustainable fuels and chemicals.<sup>1</sup> For decades, upgrading biomass into fuels, fine chemicals, and materials has attracted worldwide attention.<sup>2</sup> Generally, biomass can be converted into biofuels or biochemicals using different technologies, such as thermochemical, chemical, and biochemical processes. Among these, thermochemical processing, including pyrolysis, gasification, and hydrothermal conversion, has been proposed as one of the most promising technologies for biomass upgrading due to its high efficiency.<sup>3</sup>

Through the thermochemical process, various important fuels or chemicals, such as syngas, bio-oils, biochars, platform chemicals, *etc.*, can be obtained from the degradation of biomass.<sup>3,4</sup> However, many reactions take place during the biomass upgrading process, and a mixture containing various kinds of degradation products with high dispersion and low yield is always obtained.<sup>5–7</sup> This complex composition of the products from biomass upgrading restricts to some degree its further utilization. Nevertheless, several previous reports showed that both the reaction rate and reaction selectivity during the biomass upgrading process could be improved to varying degrees in the presence of suitable catalysts.<sup>2,4,8</sup> Therefore, catalytic biomass upgrading plays a crucial role in

converting renewable biomass resource into a variety of commodity chemicals or liquid fuels.

Biochar is a carbonaceous material, which is a residual byproduct from the thermochemical degradation of biomass.<sup>9</sup> Biochar can be produced from various thermochemical degradation processes, such as pyrolysis, gasification, hydrothermal carbonization, *etc.*<sup>10,11</sup> As compared to carbonaceous materials from other chemical processes, biochar is an inexpensive, environmentally friendly, and easily-produced charcoal, which can be used for many purposes.<sup>10,12–14</sup> However, the utilization of these as-prepared biochars is not ideal because of their poor physicochemical properties. In order to improve the physicochemical properties of the as-prepared biochars, various activation and functionalization approaches have been investigated to extend their applications.<sup>15,16</sup> The physicochemical properties of biochar vary significantly according to the raw biomass material type derived, the carbonization process, and activation or functionalization methods.<sup>16–19</sup> After activation or functionalization, the biochar shows several interesting properties, such as large surface area, multi-scale porous structure, and abundant surface functional groups. The activated biochars are widely used as activated carbon, soil amendments, carbon sequestration agents, environmental adsorbents for organic and heavy metal pollution removal, *etc.*<sup>16–20</sup> More importantly, due to the large surface area and abundant surface functional groups, activated or functionalized biochars show great potential to be used as versatile catalysts and/or catalyst supports in many chemical processes.<sup>10,21–25</sup>

Cha *et al.*<sup>10</sup> overviewed the production and utilization of biochars in various environmental application fields, and the application of the biochars as catalysts for syngas upgrading, biodiesel production, and air pollutant treatment were also

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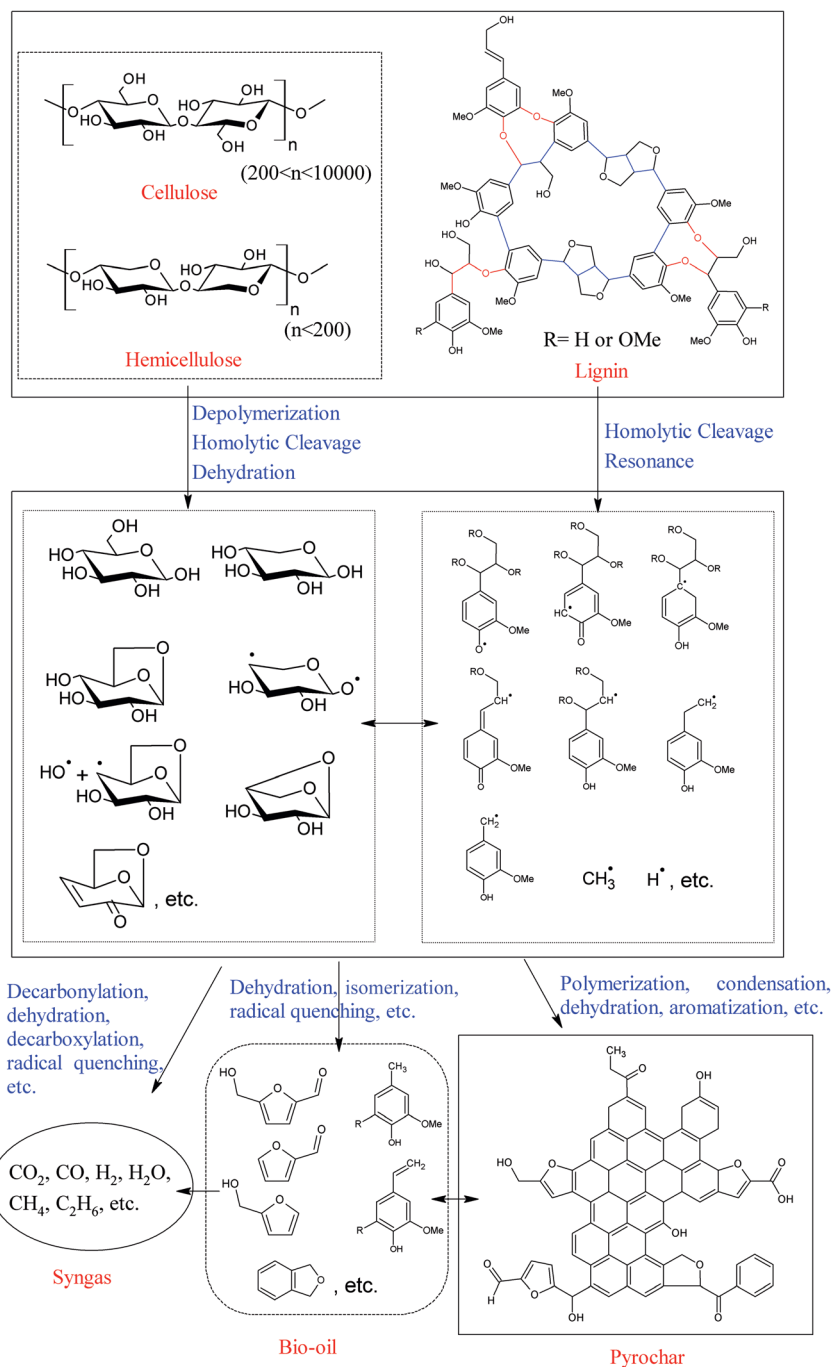


Fig. 1 A possible formation pathway of pyrochar.

subsequently react with the soluble phenolic compounds derived from lignin, forming “dispersed hydrochars” through polymerization.<sup>42</sup> The reactive oxygen-containing groups on the surface of the “dispersed hydrochars” further react with the “aggregated hydrochars” and cover the surface of the “aggregated hydrochars”, resulting in a hydrochar with relatively low specific surface area and poor porosity.<sup>41,42</sup> More detailed information on hydrothermal degradation mechanism of biomass components can be found in previous review articles.<sup>6,11</sup>

### 3. Activation and functionalization of biochars as catalysts or catalyst supports

Usually, the biochar directly obtained from the pyrolysis of biomass shows relatively low specific surface area, poor porosity, and limited surface functional groups.<sup>24</sup> These inherent disadvantages hinder to some degree the application of biochars as useful catalysts or catalyst supports.



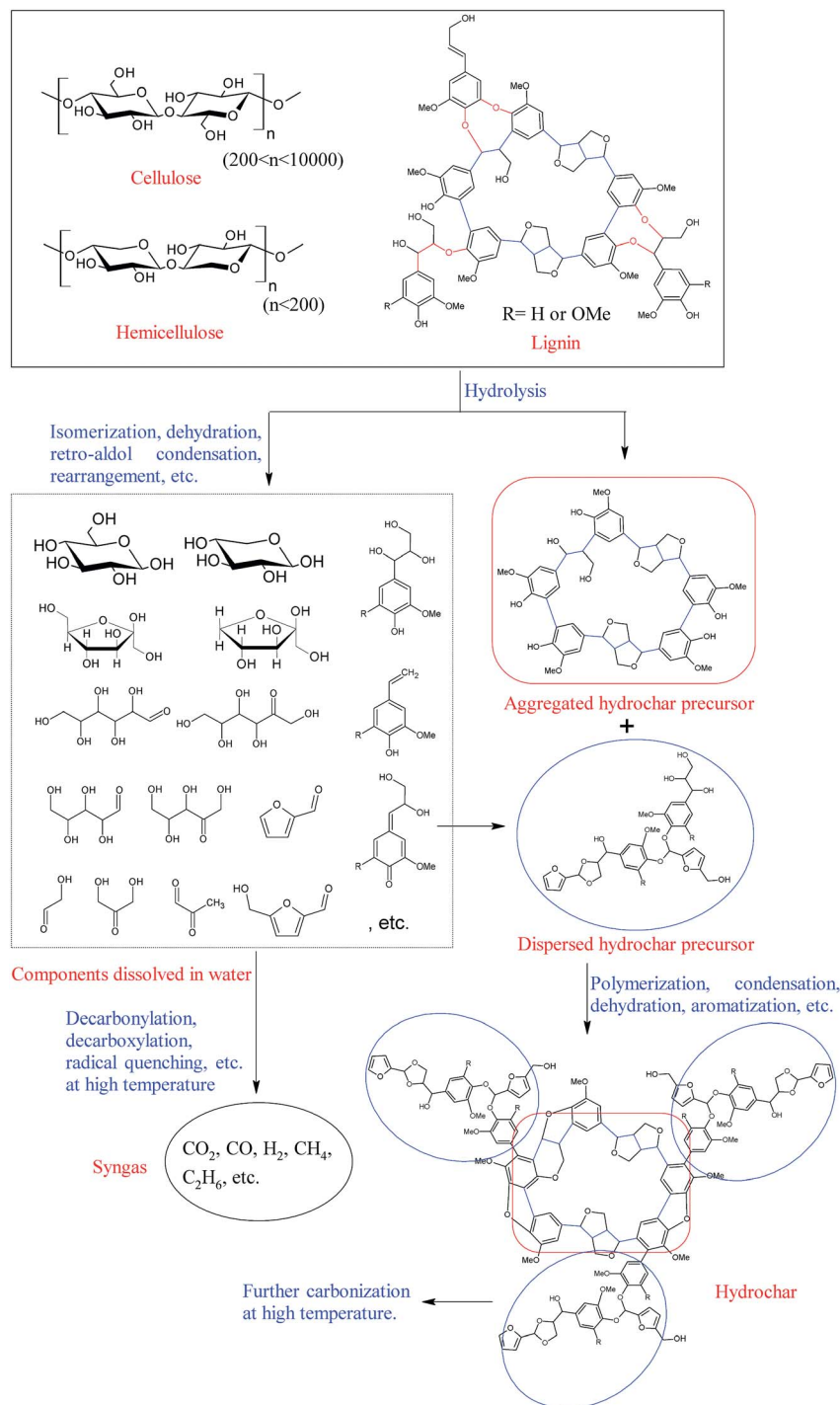


Fig. 2 A possible formation pathway of hydrochar.

Although, fortunately, these properties of the biochars can be easily tuned by the appropriate activation or functionalization processes.<sup>10,11,43</sup> In this section, the activation and functionalization of the biochars as catalysts or catalyst supports for biomass upgrading are discussed in detail. The activation and functionalization methods of the biochars for other applications are beyond the scope of this review.

### 3.1. Biochar activation

The main purpose of biochar activation is to increase its specific surface area and porosity prior to use. After activation, the specific surface area and porosity of the biochar can be significantly improved due to the development and opening of internal porous structure of the as-prepared biochar.<sup>11,44</sup> As a result, the activated biochars can be further used in various applications, such as activated carbon, soil amendments,





sesame straw biochar and examined the phosphorus adsorption capacities of these activated biochars. According to their studies,  $\text{ZnCl}_2$  and  $\text{MgO}$  were more effective in improving the phosphorus adsorption characteristics of the biochar than the other activation agents. A maximum phosphorus adsorption capacity of  $15 \text{ g kg}^{-1}$  was achieved by the  $\text{ZnCl}_2$  activated biochar.<sup>51</sup>

Generally, short activation time and low activation temperature are required for the chemical activation, but chemical consumption, equipment corrosion, and wastewater treatment should be considered in the chemical activation process. The physical activation process is more simple and clean than the chemical activation process, but relatively high activation temperature, extended activation time, high energy consumption, and relatively low specific surface area are usually found in the physical activation process. Besides physical activation and chemical activation, the morphology, specific surface area and porosity of the formed biochar are closely related to the microstructure of the biomass. Previous studies from Zhang *et al.*<sup>35</sup> showed that a pyrochar with specific surface area as high as  $1610 \text{ m}^2 \text{ g}^{-1}$  was obtained from lotus stem without any extra activation process, which was about 55% higher than that from lotus leaves.

### 3.2. Biochar functionalization

Biochar functionalization is mainly used to confer specific performance properties to the biochar. Due to the limited surface functional groups of the as-prepared biochars, a suitable functionalization process is indispensable for the biochars intended to be used as catalysts. Generally, biochar can gain a desirable catalytic capacity *via* surface modification or active substances deposition.<sup>10,43,53–56</sup>

Biochar modification can be easily accomplished by introducing specific functional groups, especially acid groups, onto the surface of the organic biochar. The most commonly used biochar modification method is sulfonation with concentrated  $\text{H}_2\text{SO}_4$  or its derivatives.<sup>23,24</sup> Following sulfonation, the modified biochars can be widely used as solid acid catalysts for polysaccharide hydrolysis, sugar dehydration, biodiesel production, *etc.*<sup>23,56,57</sup> Besides the  $-\text{SO}_3\text{H}$  group, other weak acid groups, like the  $-\text{COOH}$  group, can also be introduced into the biochar matrix.<sup>58</sup> These biochar-based solid acids show relatively high reaction activity and good recyclability, which are promising alternatives to mineral acid catalysts.<sup>23,25,56–61</sup> The application of these biochar-based solid acids as effective catalysts for biomass upgrading will be discussed in detail in Sections 4.1 and 4.2.

Besides their use as catalysts, the activated biochars are also promising materials to be used as catalyst supports.<sup>24,54,55,62,63</sup> Metals and/or metal oxides with catalytic activity can be loaded onto the biochar supports by preloading the metal precursors into the biomass matrix before pyrolysis<sup>55,64–66</sup> or by impregnating the activated biochars with the metal precursors.<sup>62,66–68</sup> Previous studies reported that various biochar-supported metal catalysts with high dispersion could be prepared according to the above mentioned methods.<sup>24,64,65</sup> In this review, the

application of these biochar-supported catalysts for biomass pyrolysis, gasification, and bio-oil upgrading will be discussed in detail in Section 4.3.

## 4. Biochar based catalysts for biomass upgrading

Carbonaceous materials have been used in heterogeneous catalysis for a long time, because of their specific physico-chemical properties, such as large surface area, multi-scale porous structure, and tailoring surface functional groups.<sup>10,24,25,29,69</sup> As compared to carbonaceous materials from other chemical processes, biochar is inexpensive, environmentally friendly, and easily-produced, which are characteristics that make biochar a promising alternative to conventional carbonaceous materials. Functionalized biochars show great potential to be used as direct catalysts or catalyst supports in many industrial applications.<sup>10,24,25,29</sup> In this section, the utilization of biochars as versatile catalysts and/or catalyst supports for biomass upgrading is evaluated.

### 4.1. Biochar-based solid acids for biomass hydrolysis and dehydration

Biomass has great potential to be used as a sustainable resource to provide biofuels, biochemical, and biomaterials. As the most abundant biopolymers in biomass, cellulose and hemicelluloses are the largest components of the earth's biomass. Thus, effectively converting these components into useful platform compounds, such as sugars, furfural (FF), 5-hydroxymethylfurfural (HMF), *etc.*, is a highly desirable endeavor.<sup>4</sup> The sugars from the hydrolysis of cellulose and hemicelluloses can be further utilized to produce alcohols. The FF and HMF from the dehydration of sugars can be converted into various corresponding furan derivatives for various applications.<sup>70,71</sup> Therefore, the hydrolysis of biomass and its further conversion is one of the most important research topics in biomass upgrading.

Many hydrolysis agents, such as enzymes, mineral acids, and solid acids, have been employed in biomass hydrolysis. However, the enzymatic hydrolysis of biomass is slow and costly, and the hydrolysis of biomass by mineral acids usually produces various environmental hazards. Recently, several studies reported that biochar-based solid acid is a promising alternative to mineral acid in biomass hydrolysis and dehydration due to its high reaction activity, recyclability, and low cost.<sup>25,56,57,59–61</sup> The catalytic performances of various biochar-based acid catalysts in biomass hydrolysis and dehydration are summarized in Table 1.

Generally, the acidic active sites can be introduced into the biochar by three possible means: (i) using the weak acid groups formed during the preparation of the biochar as acid sites; (ii) introducing the acidic sites by sulfonation or copolymerization with monomers with acid groups; (iii) loading solid acid onto the surface of the biochar. Among these methods, sulfonation is the most commonly used method to prepare biochar-based solid acids, and the  $-\text{SO}_3\text{H}$  groups can be easily introduced onto the surface of the biochar using concentrated  $\text{H}_2\text{SO}_4$  or its





Table 1 The catalytic performances of various biochar-based acid catalysts in biomass hydrolysis and dehydration

Biochar	Functionalization condition	Feedstock	T (°C)	t (h)	Solvent	Conv. (%)	Yield (%)	Ref.
Corn stover biochar	Sulfonated with 30% (w/v) sulfuric acid solution at 150 °C for 24 h	Corn stover, prairie cordgrass, and switch grass	100	6	Water	18.8–21.8 (glucan) 67.9–80.5 (xylan)	—	59
Pine chip biochar	Sulfonated with sulfuric acid at 100 °C for 12–18 h	Birchwood xylan	120	2	Water	85	—	60
Bamboo biochar	4 g of biochar sulfonated with 60 mL of concentrated H <sub>2</sub> SO <sub>4</sub> at 180 °C for 12 h	Bamboo hemicellulose	150 <sup>a</sup>	0.5	Water	—	55.7 (XOS)	57
Bamboo biochar	10 g of biochar sulfonated with 50 mL of 80% sulfuric acid at 80 °C for 3 h and 50 wt% SO <sub>3</sub> at 80 °C for 2 h	Cellulose	90 <sup>a</sup>	1	Water	—	27.5 (TRS)	72
Bamboo biochar	1.1 biochar sulfonic acid (BCSA)	Cellulose	90 <sup>a</sup>	3	Water	—	34.9 (TRS)	72
Bamboo biochar	1.2 IL functionalized BCSA	Cellulose	110	2	Water	—	35.6 (TRS)	73
Bamboo biochar	1.1 biochar sulfonic acid (BCSA)	Cellulose	110	2	Water	—	58.7 (TRS)	61
Bamboo biochar	1.2 IL-Cu functionalized BCSA	Cellulose	110	2	Water	—	—	—
Bamboo biochar	1.1 biochar sulfonic acid (BCSA)	Cellulose	130	4	[BMIM][Cl]	4.5	—	58
Biochar from glucose	Containing weak acid sites	Cellulose	130	3	[BMIM][Cl]	47	—	58
Biochar from glucose	20 g of glucose and 10 g of sulfosalicylic acid copolymerization at 180 °C for 4 h	Cellulose	130	3	[BMIM][Cl]	59.4	—	58
Biochar from glucose	20 g of glucose and 10 g of acrylic acid copolymerization at 180 °C for 4 h	Cellulose	130	3	[BMIM][Cl]	~50	—	58
Corn cob biochar	Sulfonated with 0.5 M H <sub>2</sub> SO <sub>4</sub> at room temperature for 24 h under the assistance of ultrasonic vibration	Corn cob	180	2.83	Water	62.0 (xylan)	37.8 (FF)	74
Corn cob biochar	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 150 °C for 15 h	Perhydrolysate of corn cob	170	1	Dichloromethane/ water	—	81.1 (FF)	56
SnO <sub>2</sub> -Co <sub>3</sub> O <sub>4</sub> /biochar	Loaded with SnO <sub>2</sub> -Co <sub>3</sub> O <sub>4</sub> (Sn/Co molar ratio was 0.5–4.0)	Corn cob	180	3.33	Water	—	30.0 (FF)	54
Commercial activated carbon	Containing weak acid sites	Xylose	200	3	Water	~90	50 (FF)	75
Bamboo biochar	1.1 biochar sulfonic acid (BCSA)	Cellulose	100 <sup>a</sup>	2	DMA-LiCl/water	—	30.4 (HMF)	61
Bamboo biochar	1.2 IL-Zn functionalized BCSA	Cellulose	80	3	Water	—	27.9 (HMF)	76
Bamboo biochar	1.1 biochar sulfonic acid (BCSA)	Cellulose	80	3	Water	—	—	—
Commercial activated carbon	1.2 IL-F <sub>1-3</sub> s functionalized BCSA Containing weak acid sites	Glucose	200	3	Water	~55	23 (HMF)	75

<sup>a</sup> Microwave XOS: xylooligosaccharides, TRS: total reducing sugar, FF: furfural, HMF: 5-hydroxymethylfurfural.





Table 2 Biodiesel production under the catalysis of various biochar-based acid or base catalysts<sup>a</sup>

Biochar	Functionalization condition	Feedstock	Reaction conditions	Biodiesel yield (%)	Ref.
Oat hull biochar	None	Waste cooking oils	140 °C, 30 min (microwave), MeOH/oil (10 : 1)	0.5	84
Oat hull biochar	Sulfonated with H <sub>2</sub> SO <sub>4</sub> in microwave reactor at 100 °C for 30 min	Waste cooking oils	140 °C, 30 min (microwave), MeOH/oil (10 : 1)	28	84
Oat hull biochar	Sulfonated with H <sub>2</sub> SO <sub>4</sub> in microwave reactor at 140 °C for 30 min	Waste cooking oils	140 °C, 30 min (microwave), MeOH/oil (10 : 1)	72	84
Biochar from Dynamotiv Inc.	Sulfonated with fuming H <sub>2</sub> SO <sub>4</sub> at 150 °C for 15 h	Canola oil and oleic acid	150 °C, 3 h, MeOH/oil (10 : 1)	48	85
Biochar from fast pyrolysis of different feedstocks	20 g of biochar sulfonated with 200 mL of H <sub>2</sub> SO <sub>4</sub> at 150 °C for 24 h	Vegetable oils	60 °C, 3 h, EtOH/oil (18 : 1)	77–89	86
Biochar from peanut hulls, pine pellets, and wood chips	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 100 °C for 12–18 h or gaseous SO <sub>3</sub> at room temperature for six days	5% palmitic and stearic acid	65 °C, 3 h, MeOH/oil (20 : 1)	>80 (FFA conversion)	83
Wood biochar	Sulfonated with fuming H <sub>2</sub> SO <sub>4</sub> at 150 °C for 15 h	Canola oil	65 °C, 12 h, MeOH/oil (15 : 1)	44.2	87
Biochar from glucose	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 160 °C for 12 h	Palm fatty acid	65 °C, 134 min, MeOH/oil (12.2 : 1)	92.4 (FAME yield)	88
Biochar from glucose	4 g of biochar sulfonated with 100 mL of H <sub>2</sub> SO <sub>4</sub> at 150 °C for 15 h	Palm fatty acid	75 °C, 2 h, MeOH/oil (10 : 1)	94.5 (FFA conversion)	89
Sulfonated starch solid acid	5 g of biochar sulfonated with 200 mL of H <sub>2</sub> SO <sub>4</sub> at 160 °C for 12 h	Palm fatty acid	75 °C, 3 h, MeOH/oil (10 : 1)	92.3 (FAME yield)	90
Rice husk biochar	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 90 °C for 0.5 h	Waste cooking oils	110 °C, 15 h, MeOH/oil (20 : 1)	95.4 (FFA conversion)	53
Rice husk biochar	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 70–150 °C for 0.25–4 h	Oleic acid	110 °C, 2 h, MeOH/oil (4 : 1)	94.6 (FFA conversion)	91
Corn straw biochar	Sulfonated with fuming H <sub>2</sub> SO <sub>4</sub> at 180 °C for 4 h	Oleic acid	110 °C, 2 h, MeOH/oil (4 : 1)	87.6 (FAME yield)	92
Biochar from glucose–starch mixture	Sulfonated with H <sub>2</sub> SO <sub>4</sub> at 150 °C for 5 h	Cotton seed oil containing 55.2 wt% of FFA	60 °C, 4 h, MeOH/oil (7 : 1)	>80	93
Douglas fir biochar	20 g of biochar sulfonated with 150 mL of H <sub>2</sub> SO <sub>4</sub> at 150 °C for 24 h	Crude microalgal oil	80 °C, 12 h, MeOH/oil (20 : 1)	>80	94
Douglas fir biochar	1.1 Douglas fir biochar	Crude microalgal oil	100 °C, 60 min, MeOH/oil (20 : 1)	98.6 (FFA conversion)	94
Palm kernel shell biochar	1.2 CaO	Crude microalgal oil	1.1 100 °C, 60 min, MeOH/oil (20 : 1)	99	94
Palm kernel shell biochars	Loaded with CaO at a total basicity of 0.516 mmol g <sup>-1</sup>	Sunflower oil	1.2 65 °C, 60 min, MeOH/oil (10 : 1–20 : 1)	99	95
Peat biochar	Loaded with 50.6% of CaO	Sunflower oil	65 °C, 300 min, MeOH/oil (9 : 1)	99	63
Peat biochar	None	Palm oil	65 °C, 1.5 h, MeOH/oil (8 : 1)	10.5	81
Flamboyant pods biochar	Loaded with 20–40 wt% of K <sub>2</sub> CO <sub>3</sub>	Palm oil	65 °C, 1.5 h, MeOH/oil (8 : 1)	95.2–98.6	81
Biochar from maize residue	Impregnated in KOH solution	<i>Hevea brasiliensis</i> oil	60 °C, 1 h, MeOH/oil (15 : 1)	89.3	96
	None	Waste cooking oils	300 °C, 1 h, MeOH/oil (50 : 1)	~90	82

<sup>a</sup> FFAs: free fatty acids, FAME: fatty acid methyl ester.



and hydrodenitrogenation (HDN) processes. Both oxygenates and nitrogenates in the bio-oil were sharply reduced after the catalytic upgrading process, indicating the high activity and selectivity of the Ni/biochar catalyst.<sup>62</sup>

Additionally, the presence of numerous inorganic compounds in the biochar matrix can also catalyze the pyrolysis or gasification of biomass.<sup>100,101</sup> Specifically, Lei *et al.*<sup>100</sup> and Ren *et al.*<sup>101</sup> investigated the catalytic performance of biochar from corn stover in biomass pyrolysis and bio-oil upgrading. Their results showed that the biochar catalyst could improve the quality of syngas and bio-oil to some degree, and high-quality syngas enriched in H<sub>2</sub>, CO, and CH<sub>4</sub> was achieved from the catalytic pyrolysis of sawdust in the presence of the biochar catalysts with a high mineral content, such as K, Ca, Mg, *etc.*<sup>100,101</sup>

## 5. Conclusions and prospects

In this review, the formation of two typical biochar (pyrochar and hydrochar) is proposed. Due to the limited surface area, porosity, and surface functional groups of the biochar, an activation and/or functionalization process is always required for the biochars intended to be used as catalysts. The physico-chemical properties of the biochar, especially the surface area and porosity, can be improved to varying degrees according to the activation methods. Functional groups or substances can be further introduced into the activated biochar to endow it with specific properties, such as selective adsorption and catalysis. The activated and functionalized biochars show great potential to be used as versatile catalysts and/or catalyst supports in biomass upgrading, which have been successfully applied in carbohydrate hydrolysis and dehydration, biodiesel production, biomass pyrolysis, gasification, and bio-oil upgrading. However, the physicochemical properties of the biochars vary significantly with the biomass type, production conditions, and activation or functionalization conditions. Further investigations on the industrial scale production of biochars with stable properties should be conducted in the future. In addition, combination of the biochar production with the biomass upgrading process has not received much attention so far. More efforts should be devoted to the co-production of biochars and biofuels or biochemicals from biomass upgrading, which will be beneficial for the further utilization of biochars and the development of the biomass upgrading industry.

## Conflicts of interest

There are no conflicts of interest to declare.

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