

# SF Journal of Material and Chemical Engineering

## A Review of Biochar Derived from Pyrolysis and Its Application in Biofuel Production

Zhu L<sup>1</sup>, Lei H<sup>1\*</sup>, Zhang Y<sup>1</sup>, Zhang X<sup>1</sup>, Bu Q<sup>1,2</sup>, Wei Y<sup>1,3</sup>, Wang L<sup>1,4</sup>, Yadavalli G<sup>1</sup> and Villota E<sup>1</sup>

<sup>1</sup>Department of Biological Systems Engineering, Washington State University, Richland, WA 99354-1671, USA

<sup>2</sup>Institute of Agricultural Engineering, Jiangsu University, Zhenjiang 212013, China

<sup>3</sup>School of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310023, China

<sup>4</sup>School of Biological and Medical Engineering, Hefei University of Technology, Hefei 230009, China

### Abstract

Increasing energy demand, environmental pollution, and soaring CO<sub>2</sub> emissions necessitate the exploitation of renewable sources of energy. Lignocellulosic biomass is a naturally abundant resource that can be considered as one of the promising environment-friendly renewable energy options. Biochar is a carbon-rich, porous solid produced by the thermal decomposition of biomass under anoxic conditions and at moderate temperatures; it is suitable for soil remediation and with some functionalization can be converted into functional materials, finding applications in catalysis for biofuel production. Biochar can be produced on a scale ranging from large industrial facilities to individual farms since it is a solid residue formed in the pyrolysis of biomass. How to use it effectively is a critical question for improving economic viability and environmental sustainability of biomass conversion technologies. Biochar production and applications for soil remediation and pollutant removal has been discussed and reviewed extensively. However, there are limited critical reviews on the biochar formation mechanism, functionalization of biochar materials for catalysis and biofuel production applications. Therefore, this study reviewed the current literature on the activities and advantages of biochar derived materials used in biofuel production. The preparation methods and prevailing reaction conditions affecting the catalytic activity of the biochar derived material along with their reusability aspect are discussed in this review.

**Keywords:** Biochar; Biofuel; Pyrolysis; Biomass; Biochar-based materials

### Introduction

Fossil fuels like coal, oil, and gas are good and convenient sources of energy, and they meet the energy demands of society very effectively. However, those fossil fuel resources are finite and not renewable. With growing evidence of global warming, decreasing crude-oil reserves, enhanced worldwide demand for fuels, increased concerns of climate change and air pollution from the use of fossil-based energy carriers, and political commitment, the focus has recently turned towards development and improved utilization of low-carbon energy technologies.

The low-carbon energy technology is an umbrella term used to describe a wide variety of energy technologies that produce significantly less CO<sub>2</sub> than traditional fossil fuel-based systems and that are compatible with stabilizing global atmospheric CO<sub>2</sub> concentration [1]. Biomass, on the other hand, has special appeal in this regard, as it is an abundant alternative solid fuel to the conventional fossil fuel and has an impact on the carbon emission that is close to neutral [2]. The plants uptake the CO<sub>2</sub> from the atmosphere, producing large amounts of biomass, which can be converted into bio-oil and biochar. The bio-oil, following upgrading treatments, is converted to various biofuels and used as an alternative to fossil fuels. It should be noted that the emission of CO<sub>2</sub> from biofuels can be fixed by the plant again. Meanwhile, as a recalcitrant form of carbon, the biochar itself can be regarded as a carrier for long-term carbon storage [3-4].

Biochar has been generated from a range of agricultural and organic materials; it is the intermediate solid residue, which can be formed by several thermochemical processes including pyrolysis. Biochar is a carbon-rich, fine-grained, porous substance, but it can also contain some oxygen and hydrogen. It has a high porosity and surface area, high chemical stability, and is cost-effective [5-7]. Besides the intrinsic nature of the biomass feedstock, pyrolysis process conditions could greatly affect the biochar quality and determine its resultant properties. Biochar contains

### OPEN ACCESS

#### \*Correspondence:

Lei H, Department of Biological Systems Engineering, Washington State University, Richland, Washington, USA.

**Tel:** +1 509 372 7628

**Fax:** +1 509 372 7690

**E-mail:** hlei@wsu.edu

**Received Date:** 20 Mar 2018

**Accepted Date:** 25 Apr 2018

**Published Date:** 30 Apr 2018

**Citation:** Zhu L, Lei H, Zhang Y, Zhang X, Bu Q, Wei Y, et al. A Review of Biochar Derived from Pyrolysis and Its Application in Biofuel Production. *SF J Material Chem Eng.* 2018; 1(1): 1007.

**ISSN 2643-8100**

**Copyright** © 2018 Lei H. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

a high quantity of minerals and functional groups anchored on the surface, which make it suitable for soil remediation and with some functionalization can be converted into functional materials, finding applications in catalysis, energy storage and conversion, and environmental protection [3,8].

Biochar production and applications for soil remediation and pollutant removal have been discussed and reviewed extensively [9–12]. However, there are limited critical reviews on the biochar formation mechanism, functionalization of biochar materials for catalysis and biofuel production applications. With the development of biomass pyrolysis, increasing amount of biochar will be produced for applications. Therefore, the specific aim of the present study is to review and analyze the current literature and studies related to biochar produced from pyrolysis, characterization, and the activities of biochar derived material used in biofuel production.

## Biochar from Biomass Pyrolysis

“Biochar” is a recently coined term emerging along with the growing interests in renewable fuel, soil amendment, and carbon sequestration. It is a high-carbon, fine-grained, porous substance, which is produced by thermal decomposition of biomass under oxygen-limited conditions and at relatively low temperatures (<700°C) [11,13]. That is the most standardized definition of biochar so far regulated by the International Biochar Initiative (IBI) guidelines.

It furthermore specifies the need for purposeful application of this carbonaceous material to the soil for both agricultural and environmental gains. This fact distinguishes biochar from charcoal, which is a carbon-rich solid product prepared via charring biomass and is used as a fuel source for producing energy, as an adsorbent material, or as a reducing agent in metallurgical processes [14–15]. Typically, biochar is produced as a solid by-product material in a dry carbonization process like pyrolysis. The properties of given biochar strongly depend on the characteristics of each process and also on the material to which the process is applied.

### Biochar production

The most common method to produce biochar is pyrolysis, which can be dated to thousands of years ago. Pyrolysis is the thermochemical decomposition of biomass at a temperature between 350–700 °C in the absence of oxygen. The decomposition process releases volatile species, while the carbon-rich solid, non-volatiles are collected as biochar. A portion of the gas-phase volatiles condenses into dark brown, viscous liquid phase termed bio-oil [16], and the remaining low molecular weight volatile compounds (e.g., CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and light hydrocarbons) remain in the gas phase called “non-condensable” gas. The physical process and chemical reactions occurring in pyrolysis are very complex and depend on the reactor conditions, heating rate, and the nature of the biomass.

Depending on the reaction time, temperature, and heating rate the pyrolysis process is sub-divided to four categories: slow pyrolysis, intermediate pyrolysis, fast pyrolysis, and pyrolytic gasification. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters. Lower process temperatures and longer vapor residence times favor the production of biochar. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures and short vapor residence time are optimum for producing liquids. Figure 1 shows the product distribution obtained from different modes of pyrolysis, showing the considerable flexibility achievable by changing

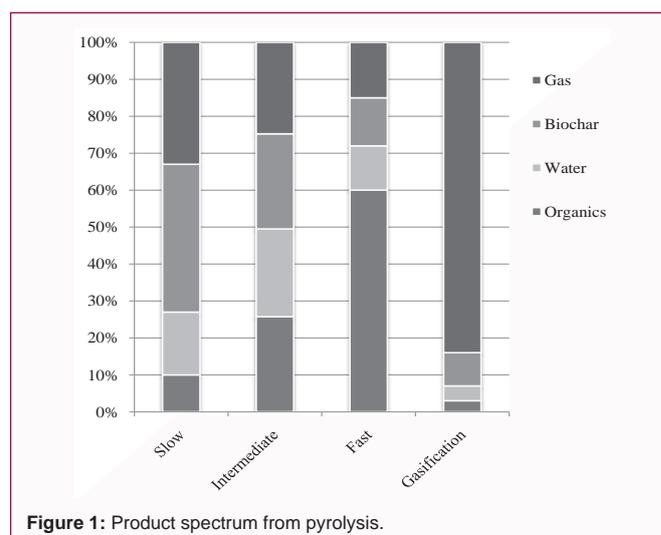


Figure 1: Product spectrum from pyrolysis.

Table 1: Characteristics of different pyrolysis processes and typical yields of biochar in these processes.

	Slow pyrolysis	Fast pyrolysis	Pyrolytic Gasification
Heating rate (°C / min)	5–7	300–800	-
Temperature (°C)	300–800	400–700	750–1000
Vapor residence time	>1h	0.5–10 s	< 2s
Main product	biochar	bio-oil	syngas
Biochar yield (wt %)	35–50	15–30	20–Oct

process conditions [17].

The two most common methods of pyrolysis are “fast” pyrolysis and “slow” pyrolysis. As shown in Table 1, slow pyrolysis, also called conventional carbonization, produces biochar by heating biomass at a low heating rate for a relatively long residence time. On the other hand, fast pyrolysis yields 60–75% bio-oil, 15–30% biochar and 10–20% non-condensable gas, and can be done in seconds, whereas slow pyrolysis has the advantage that can retain up to 50% of the feedstock carbon in stable biochar [18], but takes up to several days to complete. Furthermore, the bio-oil and gas co products of these technologies can be produced on a large scale and they should find their applications in many fields.

Alternatively, microwave technology has recently been used to efficiently convert organic matter to biochar on an industrial scale, producing up to 50% biochar. Microwave-assisted pyrolysis has been explored as an effective tool to improve the quality of bio-oil, biochar and syngas for different biomass materials such as wood wastes, wheat straw, corn stover and sewage sludge [19–24]. Biochar produced from microwave-assisted pyrolysis has been reported to have higher surface area and pore volume than those from conventional heating processes [25–27].

### Characterization of biochar

Pyrolysis process condition (principally temperature, heating rate, pressure, and residence time at the final temperature), and any post-pyrolysis changes caused by aging or treatment greatly effect on the biochar production, hence resulting in the formation of a final product with different physical and chemical characteristics. In addition to this, the intrinsic nature of the biomass feedstock also interacts with the rest of the variables in determining the properties of the produced biochar [28–29].

It is critically important to characterize biochar because its characterization will play a vital role in determining their importance and application in the industry and environment. However, the relationships between biochar properties and their effects on enhancing performance in various applications are still not well-understood. Although many papers have reported relationships between biochar properties and its respective production conditions, no universal relationship between the properties and process conditions has been well established. Biochar properties can be divided into chemical (such as proximate and elemental analysis, mineral content, polar surface functional groups and heating value) and physical (such as specific surface area, pore-size distribution, and morphology) [12].

#### **Chemical properties and characterization of biochar:**

Concerning the chemical properties of biochar obtained by pyrolysis, the proximate analysis includes contents of volatile matters (VM), moisture, ash and fixed carbon (FC). The volatile content can be determined following ASTM D 3175-11 [30]. Energy content or higher heating value (HHV) is determined using a bomb calorimeter. The biochar pH is determined following ASTM D4972-01 [31].

Several analytical techniques can be applied to characterize the inorganic species of biochar: inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), and X-ray diffraction (XRD). ICP-AES is able to determine the absolute concentration of inorganic elements (P, Al, Ca, Cr, Ni, Cu, Fe, K, Mg, Mn, Na, etc.) [32]. XRF spectrometry is used to determine the ash compositions in terms of weight fraction of oxides [33]. However, molecular-level analysis on the chemical structure of biochar organic matters is very limited. Most information on biochar organic structure is acquired by Fourier transform infrared (FT-IR) and Raman spectroscopy. FT-IR analyzes the chemical properties of biochar by assigning peaks of interest to functional groups based on characteristic absorption regions [34].

Biochar can be generated by pyrolysis of pure biomass components (cellulose, hemicelluloses or lignin) and whole biomass; it is theorized that lignin would undergo partial decomposition and hemicellulose and cellulose would undergo a series of thermal homolysis, hydrolysis, dehydration, and molecular rearrangement reactions to form a polymerized aromatic structure.

High-temperature biochars tend to have greater concentrations of condensed aromatic carbon, while biochar produced by lower-temperature pyrolysis may contain remnants of biopolymers. From a chemical composition point of view, biochars obtained at high heating rates are characterized by high oxygen content and low calorific value, probably as a result of the relatively short particle residence time [35]. Usually, the carbon content of a typical biochar is in the range of 45–60 wt %, the hydrogen content 2–5 wt %, and the oxygen content about 10–20% [36–37].

The ash content of biochar depends substantially on the feedstock. Some sources of biomass, such as corn stover, rice husks contain relatively high levels of Si, and after pyrolysis, the Si is concentrated in the biochar. Combustion of high Si biochars will cause scaling on the walls of combustion chambers and decrease the usable life of those chambers. Generally, softwood biochars tend to have low ash content; hardwood biochars have intermediate ash content, and biochars derived from corn or wheat stover typically have higher ash content. Low-ash biochars are also used in metallurgy and as a feedstock for

production of activated carbon, which has many uses, such as an adsorbent to remove odorants from airstreams and both organic and inorganic contaminants from waste-water streams.

Pyrolysis temperatures also greatly influence the final inorganic element content of the biochar. It has been reported that the P, Ca, Mg, K, Fe, and Al content in the biochar derived from wheat straw increased significantly with increasing temperature [38]. This can be explained as follows: with the increase in the pyrolysis temperature, more volatile matter is formed and released into the bio-oil and gas phases. In contrast, most of the less-volatile inorganic species remain in the solid biochar phase [3].

Freshly made biochar is hydrophobic and contains few polar surface functional groups; however, on exposure to water and oxygen in soil environments, the surfaces of biochar oxidize, forming carboxyl and other oxygen-containing functional groups. The main contribution to the reactivity of biochar is the fact that the surface usually exhibits a range of hydrophilic and hydrophobic functional groups both acidic and basic [14].

Many properties of biochar are significantly influenced by the chemisorption of oxygen onto the carbon surface. Oxygen in the surface oxides can be found in the form of various surface organic functional groups. The surface functional groups are mainly derived from activation process, precursor, heat treatment, and post chemical treatment. Some studies already demonstrated that the surface functional groups anchored on/with carbon were found to be responsible for the variety in catalytic and physicochemical properties of the matter considered [39], [40]. Surface functional groups could be quantified by means of titrimetric techniques; the method was first proposed and established by Boehm [41].

Surface functionality can be investigated by means of Fourier transform infrared (FTIR) spectroscopy. There is an alteration in the aromatic structure of biochar samples in comparison with biomass samples. The peaks between 680 and 900  $\text{cm}^{-1}$  corresponding to an aromatic C-H stretching vibration that indicates the presence of adjacent aromatic hydrogen in biochar samples which is not seen in biomass samples [6,42].

The FTIR spectra of both biomass feedstock and biochars obtained at different pyrolysis peak temperatures are used to analyze the gradual loss of lignocellulosic functional groups (change in the O-H stretch peak around 3400  $\text{cm}^{-1}$ , which dominates the feedstock's spectrum) [43]. Assignment of other spectral peaks of interest for biochar samples, including the aliphatic C-H stretch at 3000–2850  $\text{cm}^{-1}$ , the aromatic C-H stretch around 3060  $\text{cm}^{-1}$ , and the various aromatic ring modes at 1590 and 1515  $\text{cm}^{-1}$ , was proposed by Sharma et al. [44]. The peaks characteristic of the carbonyl groups should appear in the range 1660–1725  $\text{cm}^{-1}$ . The exact position of the peaks depends on whether the carbonyl groupware in conjunction with the aromatic ring (position below 1700  $\text{cm}^{-1}$ ) or not (position above 1700  $\text{cm}^{-1}$ ) [15,44].

Surface functional groups also play an important role in the application of biochars as functional materials, e.g., catalysts, adsorbents, and electrode materials. Due to its highly heterogeneous composition, the surface chemistry of biochar is very variable [3].

**Physical properties and characterization of biochar:** Concerning the physical properties of biochar obtained by biomass pyrolysis, the structure of biochar can be analyzed using a broad suite of analytical

techniques. Regarding the morphological characterization, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the most common techniques used to analyze the biochar particle structure and surface topography [45-46].

Surface area and pore structure can be analyzed using the Brunauer, Emmett and Teller (BET) method, in which  $N_2$  is the most widely used sorbate gas. If the biochar contains a large number of micropores, the surface area is estimated using  $CO_2$  isothermal adsorption method at  $0^\circ C$ . These methods are well-developed and used routinely for the characterization of the biochar textural features, such as surface area and porosity [46-47].

The physical properties and the surface morphology of biomass samples changed after carbonization. Biochar samples enriched in carbon contain several cracks and holes formed because of the evolution of volatile matter during carbonization. The extent of devolatilization has a significant effect on the characteristics of the produced biochar. As known, higher volatile matter release produces biochars with lower densities, higher porosities and significantly different pore structure [48].

Boateng and co-workers, and Mullen et al. reported relatively low BET surfaces areas ( $3.10-21.6 \text{ m}^2/\text{g}$ ) for biochars formed from switch grass and corn stover in a fluidized bed reactor [49-51]. This result is expected because of the short residence time of solid particles. In addition to this, Brewer and co-workers also observed a very small particle size for biochar obtained from fast pyrolysis of switch grass [43]. This fact is mainly due to the small particle size of the feedstock (averaging around 1mm) usually required in fast pyrolysis systems, and probably, to the hypothesis that fast devolatilization might create very fragmented char structures [52].

The heating method also had a significant effect on the morphology of the biochar structure. Biochar produced from microwave-assisted pyrolysis has a significantly higher BET surface area (up to  $76.3 \text{ m}^2/\text{g}$  compared to  $0.33 \text{ m}^2/\text{g}$  for a sample from conventional heating), micropore area and pore volume than those produced from conventional heating. Zhu and co-workers studied the corn stover biochar generated from different pyrolysis conditions using microwave-assisted heating. The results showed the surface functional groups of biochar were significantly influenced by the pyrolysis temperature and residence time [53-54].

In microwave-assisted pyrolysis, moisture is vaporized from the depth of the particle prior to the organic contents being volatilized. The steam from vaporized water is swiftly released, and not only sweeping volatiles from the pores, but also creates preferential channels in the biochar, which in turn increases the biochar porosity [27]. In conventional pyrolysis, volatiles produced during pyrolysis are released from outer layer first, and the thermal decomposition of volatiles released from the sample is expected to increase as the reaction develops toward the center of the particle because of the slow heating rate [55]. Because of the cracking volatiles, it will deposit inside the pores and block them. However, the micropores of biochar produced from microwave-assisted pyrolysis are clean and have more pores due to the uniform release of the volatile matters across the whole article [19]. At low heating rate during pyrolysis, the inherited porosity of feedstock would allow volatiles to release without morphological changes [55]. However, higher heating rates quickly release the volatiles and modify the pore structure of biochar associated with increased yield of liquid and gas fractions [26,56].

Therefore, microwave-assisted pyrolysis can provide a new strategy for creating more porous biochars, which can be used in sorption applications or as a precursor for producing activated carbon [27].

## Biochar used for Biofuel Production

The most appealing feature of biochar is the fact that it represents an inexpensive, sustainable and easy-produced process allowing the production of materials with extensive applications at a lower cost compared to materials from petrochemical or other chemical processes. Even though most of the applications are still in their infancy, biochar is already being used in many applications with extraordinary effects [12]. Initial studies for the application of biochar was primarily focused on using it as a source of soil amendments and pollutant removal, which has been discussed and reviewed extensively [15]. However, the recent revolutions brought by the advancement in research and technology for the field of pyrolysis have broadened its applications. There are many applications of both the products including but not limited to energy production, catalysis, water purification, and biorefinery. In recent decades, the carbonaceous material has been widely used as a catalyst support due to its high chemical stability and easily modified structural and surface properties. However, the solid product of the biomass thermochemical conversion, biochar, has rarely been exploited and is often discarded or burnt as a fuel. Biochar has properties similar to activated carbon and its surface chemistry can be modified [3].

Recent studies showed that the biochar could be developed and used as a catalyst in biodiesel production, catalytic esterification, biomass hydrolysis, bio-syngas reforming, and bio-oil upgrading [57-59].

### Biodiesel production

Biodiesel (mono-alkyl esters of long chain fatty acids) is a promising alternative (or extender) to conventional petroleum-based diesel fuel. Biodiesel is produced from the reaction of a vegetable oil or animal fat (which are composed of complex mixtures of triglycerides and free fatty acids depending on the quality of the oil or tallow) with a low molecular weight alcohol, such as methanol, ethanol or propanol. Methanol is most frequently used as it is the least expensive alcohol [60]. Heterogeneous and homogeneous acid catalysts are commonly used for esterification and transesterification of vegetable oil or animal fat for biodiesel production. Heterogeneous solid acid catalysts showed lower production costs and easier operational processes as opposed to homogeneous acid or alkali catalysis in biodiesel production from waste cooking oil [61]. With appropriate treatment, biochar has proven to be a good precursor for producing heterogeneous acid catalysts (also called solid acid catalyst) [58,60,62]. Since 2006, carbon-based solid acid catalyst (e.g., d-glucose-based) gained much attention in esterification of fatty acids and transesterification of vegetable oils as two separate reactions [63-66]. Recently the carbon-based catalyst has also been investigated for simultaneous transesterification and esterification of oil and free fatty acids (FFA) mixture [67].

From Dehkhoda's group study, the biochar based catalyst was successfully produced through chemical activation of biochar followed by sulfonation with fuming sulfuric acid [60]. The prepared catalyst was tested for the simultaneous alkali-ester formation from a mixture of canola oil and oleic acid to mimic the waste vegetable oil feedstock. The catalyst showed promising yields (up to 48.1%) in three hour reaction time a high temperature/pressure conditions

(150°C/1.52MPa). The biochar-based catalyst can be recycled and reused successfully with a slight decrease in reaction yield (8%).

Joylene et al. studied the biochar-based catalyst for transesterification of canola oil. The results showed that the catalyst carbonized at 675°C gave the highest catalytic performance, as evidenced by the yield from the transesterification reaction. The increasing rigidity of the carbon sheets activated at 875°C makes the incorporation of sulfonic acid groups more difficult [68]. However, the biochar-based catalyst showed poor reusability for transesterification of canola oil using methanol under high temperature/pressure conditions.

Dehkhoda et al. further explored the use of biochar as the support for a heterogeneous acid catalyst for biodiesel production leading to a green catalyst. Carbon-based solid acid catalysts were prepared by sulfonating pyrolysis biochar with concentrated or fuming sulfuric acids. Prepared catalysts were studied for their ability to catalyze transesterification of vegetable oils and esterification of free fatty acids. Results showed the catalyst with the highest surface area and acid density has the highest catalytic activity for the production of biodiesel from canola oil in the presence of methanol as the reagent [60]. Sulfonated biochar shows considerable potential for use as a catalyst in biodiesel production, especially in a context used to reduce the free fatty acid content of a vegetable oil feedstock.

### Catalytic esterification

Glycerol is the main by-product in biodiesel synthesis by the transesterification of oil with methanol or ethanol. Glycerol is a renewable feedstock, which can be converted into valuable chemicals [69–70]. Glycerol is a highly functional molecule and can undergo oxidation, carbonylation, hydrogenolysis, esterification and etherification yield useful commodity chemicals [71–76].

The esterification of glycerol with acetic acid is one of the important reactions to synthesize glycerol acetins, which are known for their fuel additive properties. Glycerol acetylation has been studied widely using different heterogeneous catalysts, such as Amberlyst and niobic acid, or heteropoly acids [77–78].

Mahammad and co-workers studied the biochar from pyrolysis of Karanja (*Pongamiapinnata*) seed shells [79]. The catalytically active biochar was used directly as an acid catalyst without any functionalization/treatment for the esterification of glycerol with acetic acid. The acidity of the biochar depended on the carbonization temperature. The biochar obtained at 400°C possessed moderate to strong acidic sites. These catalysts showed an excellent activity for the esterification of glycerol under mild reaction conditions, and the catalyst carbonized at 400°C showed the highest activity among all the catalysts. The conversion and selectivity for glycerol acetylation depended on the reaction parameters. The biochar catalyst can be reused with consistent activity.

### Biomass hydrolysis

Glucose is expected as a renewable feedstock molecule, which can be efficiently converted into various chemicals, fuels, foods, and medicines [80–82]. Therefore, the cellulose hydrolysis into glucose is a key process for the beneficial use of cellulose. Biochar-based solid acid materials also act as efficient catalysts for the hydrolysis of biomass [83–85].

The application of carbon solid acids in cellulose hydrolysis was first reported in 2008 [86]. The catalytic hydrolysis of cellulose with

carbon solid acids is similar to saccharification using concentrated  $H_2SO_4$  but different from enzymes that hydrolyze cellulose consecutively. Carbon solid acid attacks both the chain ends and the random inter-chain components of cellulose molecules [83,87]. Although carbon solid acids are similar to sulfuric acid in catalysis mechanisms, the carbon solid acid catalysts show a significantly higher yield of glucose than sulfuric acid. Besides property parameters of carbon solid acid catalysts, other factors affect the hydrolysis process including the amount of water, temperature, biomass amount, catalyst amount, and the ratio of biomass to the catalyst.

A new carbon solid acid based on the biochar from the pyrolysis process of biomass and sulfuric acid was developed by Li and co-workers' group. The biochar solid acid showed higher hydrolysis activity as well as selectivity of xylose and glucose than sulfuric acid. The biochar solid acid also generated less soluble lignin-derived products than sulfuric acid [88].

Hemicellulose can be used as a bio/chemical building block but requires hydrolysis of monomeric carbohydrates. Hemicellulose does not have as tight crystal structure as cellulose. As a result, hemicellulose in biomass is easier to hydrolyze to reducing sugars such as xylose and galactose with carbon solid acid [89]. In Ormsby and Kastner's study, solid acid carbon catalysts generated from slow pyrolysis biochar were demonstrated to hydrolyze hemicellulose [90]. An 85% conversion of xylan was observed within 2h using the biochar catalyst, compared to 57% at 24h for activated carbon (7.7g/L, 120°C).  $H_2SO_4$  was used to activate the biochar via sulfonation process, increasing surface area and pore structure, and attached sulfonic acid groups that were responsible for catalytic hydrolysis. These results demonstrated the potential of using solid acid catalysts derived from biochar to replace expensive and unrecoverable enzymes in the lignocellulosic biorefinery, targeted at hemicellulose hydrolysis if catalytic deactivation can be prevented.

Jiang and co-workers reported that lignocellulosic biomass (from corn crops) can be effectively hydrolyzed to yield soluble sugars using solid acids based on corn crop biochar [91]. At mild temperatures (110–140°C) under microwave irradiation, the cellulose and hemicellulose in the corncob biomass can be decomposed into the corresponding sugars. The maximum yields of glucose, xylose, and arabinose reached 34.6%, 77.3% and 100%, respectively. The catalyst could be reused three times without a significant decrease in catalytic activity.

### Tar decomposition

Biomass gasification produces syngas which can be utilized for fuels and power production. One of the major problems in utilizing syngas for industrial applications is the presence of high concentrations of tars formed during gasification.

Tars can be defined as the large aromatic hydrocarbons produced under thermal or partial-oxidation regimes having a molecular weight higher than benzene [92]. Although the compositions and amount of tar compounds vary with the type of gasifiers, gasification conditions and feedstock type, the most commonly reported tar compounds in syngas are benzene, toluene, naphthalene, styrene, phenol and other polyaromatic hydrocarbons (PAH) [93–94]. The traditional methods of hot syngas cleaning include filtration, water scrubbing, thermal cracking and catalytic cracking [95–96]. Catalytic removal or transformation of tar to synthesis gas components is the most practical method of solving this problem compared to physical

separation or thermal treatment of the tar. A wide range of catalysts has been studied for tar removal including, Ni supported catalysts (Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>), dolomite, olivine, zeolites and carbon supported catalysts [97].

Biochar reportedly removes tar components via a catalytic mechanism [98]. Biochar generated from slow pyrolysis of pine bark at 950°C was studied by Mani's group as a potential low-cost catalyst to decompose a model tar compound, toluene [93]. A fractional conversion of 94% toluene was achieved via the biochar catalyst and the activation energy was reduced by four-fold compared to thermal cracking. Benzene was detected as an intermediate compound during catalytic cracking of toluene with a selectivity of up to 28% at 900°C.

Abu El-Rub et al. compared the activity of a biomass-derived biochar to other catalysts that are commonly used for tar decomposition, including calcined dolomite, olivine and nickel catalyst [98]. The biochar was produced by pyrolysis of pine wood at 500°C. Pheno land naphthalene were used as tar models and the tests were carried out in the presence of CO<sub>2</sub> (6 vol. %), H<sub>2</sub>O (10 vol. %) and N<sub>2</sub> (balance) at 700 and 900°C. The biochar was found to be more active for naphthalene conversions than other catalysts tested [99].

Recent research indicates that biochar catalytically removes tar components partly due to the presence of surface alkali metals such as Na, Ca, K and potentially Fe [93,98]. However, tar removal rates using biochar are lower than metal supported catalysts, such as Ni/olivine and Ni/dolomite [99]. Attaching an active metal to the biochar surface may improve biochar catalytic performance. Kastner and co-workers reported iron supported biochar catalysts were used to decompose toluene, a model tar compound, over a temperature range of 600-900°C. Toluene conversion and decomposition rates increased linearly with increasing temperature and catalyst loading from 600 to 700°C [97].

### Bio-Syngas reforming

The gaseous product of biomass thermochemical conversion is bio-syngas, a composite gas consisting of CO, H<sub>2</sub>, CO<sub>2</sub> and volatile hydrocarbons. Recently, there has been considerable research towards converting bio-syngas into alcohol, hydrocarbons, and ethers for use as a fuel [100–103]. It is crucial to select the correct catalyst to promote the syngas reforming process. In recent decades, the carbonaceous material has been widely used as a catalyst support due to its high chemical stability and easily modified structural and surface properties [104]. Biochar is a low cost and renewable carbon source that has great potential for application as a catalyst support. Yan et al. used biochar as the support material for the synthesis of carbon-encapsulated iron nanoparticles. And it showed a high activity for the Fischer–Tropsch synthesis from bio-syngas [105].

Wang and his co-workers reported the utilization of the gaseous and solid products of biomass thermochemical conversion for a methanation process [106]. Biochar derived from the fast pyrolysis of lauan was activated to develop its pore structure and used as a catalyst support in the methanation of bio-syngas. Experimental results showed that the activated biochar provided a large BET surface area to ensure the high dispersity of Ru on the catalyst support.

To study the possibility of directly converting biogas to syngas, Dominguez et al used pyrolyzed bio-char pellets from coffee hulls as a potassium-rich catalyst during gasification of a mixture of CH<sub>4</sub> and CO<sub>2</sub> (1:1 ratio) [25]. The study indicated that the gasification of CH<sub>4</sub> to H<sub>2</sub> increased with high conversion of CH<sub>4</sub> being achieved. In

addition, the addition of biochar may potentially lead to hydrogen formation during pyrolysis as it contains catalytic inorganic minerals [107–110].

### Catalytic pyrolysis and bio-oil upgrading

In recent years, increasing attention has been focused on upgrading the composition and qualities of the bio-oil product by means of the addition of a catalyst (*in situ* upgrading) [111–112]. Catalytic upgrading the volatiles prior to their condensation is currently considered as the most promising method to minimize the negative characteristics of bio-oil [113]. During the catalytic upgrading process, the moisture and oxygen contents of bio-oil are minimized; the molecular weight is reduced, and some bio-oil mass is reduced in favor of char and gaseous species [114]. The ideal catalyst should be highly active, selective to particular products, resistant to deactivation, readily recycled and cheap.

Jinet al. investigated the potential for upgrading pyrolysis vapors from raw wood chips using bio-chars (from red oak bark and switch grass) and its effects on the yield and composition of various pyrolysis products. The vapor-upgrading process significantly decreased the carbon yield in the bio-oil when switch grass biochar was used for co-processing. The lost mass of bio-oil ended-up in the gaseous phase as reflected in an increased content of carbon dioxide and carbon monoxide [107].

Ren and his co-workers investigated the influences of biochar as a catalyst in biomass pyrolysis and bio-oil upgrading using microwave assisted heating [47]. The biochar catalyst enhanced the syngas and improved the bio-oil quality in biomass pyrolysis. The bio-oil chemical profile from catalytic pyrolysis and bio-oil upgrading over biochar catalysts was simplified to phenols and hydrocarbons, and their concentrations were increased with the increase of biochar catalyst loadings. High-quality syngas richened in H<sub>2</sub>, CO, and CH<sub>4</sub> was also obtained for biomass catalytic pyrolysis over biochar catalysts. These results indicated that biochar might be a potential cheap catalyst in biomass conversion and bio-oil upgrading

### Conclusions

Recent studies on biochar formation, characterization, functionalization of biochar materials for catalysis and biofuel production applications, are discussed. Pyrolysis derived biochar-based functional materials exhibit favorable catalytic performance in different reactions for biofuel production including catalytic transesterification/esterification, biomass hydrolysis, tar decomposition, biogas reforming and bio-oil upgrading. However, the performance of biochar-based catalysts is still greatly limited in terms of catalytic selectivity and stability due to the complex surface chemistry and heterogeneity. The relationship between the chemical and physical properties of biochar and biochars' applicability in different fields is still poorly understood and it is still difficult to establish process conditions to produce biochars with desired characteristics.

Expanded research efforts will provide solutions to those problems in the near future. To help advance the application of biochar for advanced biofuel production, it is critical that details about the properties of the biochar, the feedstock type and conditions used for making the biochar are reported to establish the appropriate process conditions for producing biochars with more desirable characteristics.

Challenges related to the application of biochar on biofuel production remain and have to be addressed in the future research. It believes that the rapidly growing and strong interest in biochar will bring biochar research and application into a new stage.

## Acknowledgment

This study was supported by The Agriculture and Food Research Initiative of National Institute of Food and Agriculture, United States Department of Agriculture (Award Number: 2016-67021-24533, and 2018-67009-27904) and the Chinese Scholarship Council.

## References

1. T Roberts, P Upham, S Mander, C McLachlan, P Boucher, C Gough, and Da Ghanem *Low-carbon energy controversies* Routledge 2013
2. P Basu, B Prabir, and P Basu *Biomass Gasification and Pyrolysis: Practical Design and Theory* Academic Press 2010
3. W-J Liu, H Jiang, and H-Q Yu. "Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material." *Chem Rev.* 2015.
4. GW Huber, S Iborra, and A Corma. "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering." *Chem Rev.* 2006; 106: 4044–4098.
5. S-H Kong, S-K Loh, RT Bachmann, SA Rahim, and J Salimon. "Biochar from oil palm biomass: A review of its potential and challenges." *Renew Sustain Energy Rev.* 2014; 39: 729–739.
6. D Özçimen and A Ersoy-Meriçboyu. "Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials." *Renew Energy.* 2010; 35: 1319–1324.
7. M Garcia-Perez and E Al. *Methods for Producing Biochar and Advanced Biofuels in Washington State.* 2013.
8. YS Ok, SX Chang, B Gao, and HJ Chung. "SMART biochar technology-A shifting paradigm towards advanced materials and healthcare research." *Environ Technol Innov.* 2015; 4: 206–209.
9. SP Sohi, E Krull, E Lopez-Capel, and R Bol. "A review of biochar and its use and function in soil." *Adv Agron.* 2010; 105: 47–82.
10. S Meyer, B Glaser, and P Quicker. "Technical, economical and climate related aspects of biochar production technologies: A literature review." *Environ Sci Technol.* 2011; 45: 22, p 110930141845009.
11. DA Laird, RC Brown, JE Amonette, and J Lehmann. "Review of the pyrolysis platform for coproducing bio-oil and biochar." *Biofuels, Bioprod Biorefining.* 2009; 3: 547–562.
12. K Qian, A Kumar, H Zhang, D Bellmer, and R Huhnke. "Recent advances in utilization of biochar." *Renew Sustain Energy Rev.* 2015; 42: 1055–1064.
13. JJ Manyà and JJ Manyà. "Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs." *Environ Sci Technol.* 2012; 46: 7939–7954.
14. J Lehmann and S Joseph. *Biochar for environmental management: science and technology.* Earthscan. 2009.
15. JJ Manyà. "Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs." *Environ Sci Technol.* 2012; 46: 7939–7954.
16. S Yaman. "Pyrolysis of biomass to produce fuels and chemical feedstocks." *Energy Convers Manag.* 2004; 45: 651–671.
17. aV Bridgwater. "Review of fast pyrolysis of biomass and product upgrading." *Biomass and Bioenergy.* 2011; 38: 1–27.
18. JL Gaunt and J Lehmann. "Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production." *Environ Sci Technol.* 2008; 42: 4152–4158.
19. M Miura, H Kaga, A Sakurai, T Kakuchi, and K Takahashi. "Rapid pyrolysis of wood block by microwave heating." *J Anal Al Pyrolysis.* 2004; 71: 187–199.
20. VL Budarin, JH Clark, BA Lanigan, P Shuttleworth, SW Breeden, AJ Wilson, et al. "The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw." *Bioresour Technol.* 2009; 100: 6064–6068.
21. Q Bu, H Lei, L Wang, and J Tang. "Renewable phenols and fuel production from catalytic pyrolysis of lignin using microwave irradiation heating." 2013.
22. Y Wan, P Chen, B Zhang, C Yang, Y Liu, X Lin, and R Ruan. "Microwave-assisted pyrolysis of biomass: Catalysts to improve product selectivity." *J Anal Al Pyrolysis.* 2009; 86: 161–167.
23. Q Lu, X Zhu, W Li, Y Zhang, and D Chen. "On-line catalytic upgrading of biomass fast pyrolysis products." *Chinese Sci Bull.* 2009; 54: 1941–1948.
24. Q Lin, G Chen, and Y Liu. "Scale-up of microwave heating process for the production of bio-oil from sewage sludge." *J Anal Al Pyrolysis.* 2012; 94: 114–119.
25. JA Menéndez, A Domínguez, Y Fernández, and JJ Pis. "Evidence of Self-Gasification during the Microwave-Induced Pyrolysis of Coffee Hulls." *Energy & Fuels.* 2007; 21: 373–378.
26. R Luque, JA Menéndez, A Arenillas, and J Cot. "Microwave-assisted pyrolysis of biomass feedstocks: the way forward?." *Energy Environ Sci.* 2012; 5: 5481.
27. Ba Mohamed, CS Kim, N Ellis, and X Bi. "Microwave-assisted catalytic pyrolysis of switchgrass for improving bio-oil and biochar properties." *Bioresour Technol.* 2016; 201: 121–132.
28. C Di Blasi, G Signorelli, C Di Russo, and G Rea. "Product distribution from pyrolysis of wood and agricultural residues." *Ind Eng Chem Res.* 1999; 38: 2216–2224.
29. JJ Manyà, J Ruiz, and J Arauzo. "Some peculiarities of conventional pyrolysis of several agricultural residues in a packed bed reactor." *Ind Eng Chem Res.* 2007; 46: 9061–9070.
30. ASTM. "D3175-11 standard test method for a tile matter in the analysis sample of coal and coke." 2011.
31. ASTM. "ASTM Standard E1755-01(2007). Standard test method for pH of soils." West Conshohocken. PA. 2007.
32. C Liao, C Wu, and Y Yan. "The characteristics of inorganic elements in ashes from a 1 MW CFB biomass gasification power generation plant." *Fuel Process Technol.* 2007; 88: 149–156.
33. F Suarezgarcia, A Martinezalonso, M Fernandezllorente, and J Tascon. "Inorganic matter characterization in vegetable biomass feedstocks I." *Fuel.* 2002; 81: 1161–1169.
34. K Qian, A Kumar, K Patil, D Bellmer, D Wang, W Yuan, and LR Huhnke. "Effects of Biomass Feedstocks and Gasification Conditions on the Physiochemical Properties of Char." *Energies.* 2013; 6: 3972–3986.
35. G Duman, C Okutucu, S Ucar, R Stahl, and J Yanik. "The slow and fast pyrolysis of cherry seed." *Bioresour Technol.* 2011; 102: 1869–1878.
36. TR Brown, MM Wright, and RC Brown. "Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis." *Biofuels, Bioprod Biorefining.* 2011; 5: 54–68.
37. CA Mullen, AA Boateng, NM Goldberg, IM Lima, DA Laird, and KB Hicks. "Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis." *Biomass and Bioenergy.* 2010; 34: 67–74.
38. L Zhao, X Cao, O Mašek, and A Zimmerman. "Heterogeneity of biochar properties as a function of feedstock sources and production temperatures." *J Hazard Mater.* 2013; 256–257: 1–9.

39. MS Shafeeyan, WMAW Daud, A Houshmand, and A Shamiri. "A review on surface modification of activated carbon for carbon dioxide adsorption." *J Anal Al Pyrolysis*. 2010; 89: 143–151.
40. S Biniak, G Szymański, J Siedlewski, and A Świątkowski. "The characterization of activated carbons with oxygen and nitrogen surface groups." *Carbon NY*. 1997; 35: 1799–1810.
41. H Boehm. "Chemical identification of surface groups." *Adv Catal*. 1966; 16: 179–274.
42. Y Guo and R Bustin. "FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals." *Int J Coal Geol*. 1998; 37: 29–53.
43. CE Brewer, K Schmidt-Rohr, JA Satrio, RC Brown, and K Schmidt-Rohr. "Characterization of biochar from fast pyrolysis and gasification systems." *Environ Prog Sustain Energy*. 2009; 28: 386–396.
44. RK Sharma, JB Wooten, VL Baliga, X Lin, W Geoffrey Chan, and MR Hajaligol. "Characterization of chars from pyrolysis of lignin." *Fuel*. 2004; 83: 1469–1482.
45. Ka Spokas, JM Novak, CE Stewart, KB Cantrell, M Uchimiya, MG Dusaire, et al. "Qualitative analysis of atile organic compounds on biochar." *Chemosphere*. 2011; 85: 869–882.
46. D Wang, W Zhang, X Hao, and D Zhou. "Transport of Biochar Particles in Saturated Granular Media: Effects of Pyrolysis Temperature and Particle Size." *Environ Sci Technol*. 2013; 47: 821–828.
47. CA Masiello, Y Chen, X Gao, S Liu, H-Y Cheng, MR Bennett, et al. "Biochar and Microbial Signaling: Production Conditions Determine Effects on Microbial Communication." *Environ Sci Technol*. 2013; 47: 11496–11503.
48. H Haykırı-Açma, A Ersoy-Meriçboyu, and S Küçükbayrak. "Effect of mineral matter on the reactivity of lignite chars." *Energy Convers Manag*. 2001; 42: 11–20.
49. Boateng. "Characterization and thermal conversion of charcoal derived from fluidized-bed fast pyrolysis oil production of switchgrass." *Ind Eng Chem Res*. 2007; 46: 8857–8862.
50. Mullen and AA Boateng. "Catalytic pyrolysis-GC/MS of lignin from several sources." *Fuel Process Technol*. 2010; 91: 1446–1458.
51. Day, RJ Evans, JW Lee, and D Reicosky. "Economical CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub> capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration." *Energy*. 2005; 30: 2558–2579.
52. F Scala, R Chirone, and P Salatino. "Combustion and attrition of biomass chars in a fluidized bed." *Energy & fuels*. 2006; 20: 91–102.
53. L Zhu, H Lei, L Wang, X Zhang, Y Wei, Y Liu, and G Yadavalli. "Characterization of Surface Functional Groups in Corn Stover Biochar Derived from Microwave-assisted Pyrolysis." in 2014 Montreal, Quebec Canada. 2014.
54. L Zhu, H Lei, L Wang, G Yadavalli, X Zhang, Y Wei, et al. "Biochar of corn stover: Microwave-assisted pyrolysis condition induced changes in surface functional groups and characteristics." *J Anal Al Pyrolysis*. 2015; 115: 149–156.
55. E Cetin, B Moghtaderi, R Gupta, and T Wall. "Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars." *Fuel*. 2004; 83: 2139–2150.
56. a Dominguez, B Fidalgo, Y Fernandez, J Pis, and J Menendez. "Microwave-assisted catalytic decomposition of methane over activated carbon for CO<sub>2</sub>CO<sub>2</sub>-free hydrogen production." *Int J Hydrogen Energy*. 2007; 32: 4792–4799.
57. R Azargohar and a K Dalai. "Biochar as a precursor of activated carbon." *Al Biochem Biotechnol*. 2006; 131: 762–773.
58. M Dehkhoda, A H West, and N Ellis. "Biochar based solid acid catalyst for biodiesel production." *Al Catal A Gen*. 2010; 382: 197–204.
59. S Ren, H Lei, L Wang, Q Bu, S Chen, and J Wu. "Hydrocarbon and hydrogen-rich syngas production by biomass catalytic pyrolysis and bio-oil upgrading over biochar catalysts." *RSC Adv*. 2014; 4: 10731.
60. M Dehkhoda and N Ellis. "Biochar-based catalyst for simultaneous reactions of esterification and transesterification." *Catal Today*. 2013; 207: 86–92.
61. PK Swain, LM Das, and SN Naik. "Biomass to liquid: A prospective challenge to research and development in 21st century." *Renew Sustain Energy Rev*. 2011; 15: 4917–4933.
62. M Li, Y Zheng, Y Chen, and X Zhu. "Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk." *Bioresour Technol*. 2014; 154: 345–348.
63. K Nakajima, M Hara, and S Hayashi. "Environmentally benign production of chemicals and energy using a carbon-based strong solid acid." *J Am Ceram Soc*. 2007; 90: 3725–3734.
64. M Toda, A Takagaki, M Okamura, JN Kondo, S Hayashi, K Domen, et al. "Green chemistry: biodiesel made with sugar catalyst." *Nature*. 2005; 438: 178.
65. M Okamura, A Takagaki, and M Toda. "Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon." *Chem*. 2006; 5: 3039–3045.
66. L Peng, A Philiaerts, X Ke, J Van Noyen, F De Cliel, G Van Tendeloo, et al. "Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids." *Catal Today*. 2010; 150: 140–146.
67. Y-S Lien, L-S Hsieh, and JCS Wu. "Biodiesel Synthesis by Simultaneous Esterification and Transesterification Using Oleophilic Acid Catalyst." *Ind Eng Chem Res*. 2010; 49: 2118–2121.
68. JT Yu, AM Dehkhoda, and N Ellis. "Development of Biochar-based Catalyst for Transesterification of Canola Oil." *Energy & Fuels*. 2011; 25: 337–344.
69. Behr, J Eilting, K Irawadi, J Leschinski, and F Lindner. "Improved utilisation of renewable resources: New important derivatives of glycerol." *Green Chem*. 2008; 10: 13–30.
70. J Yu, A Corma, SI Zones, S Elomari, ME Davis, AW Burton, et al. "Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils." *Science (80-)*. 2010; 330: 1222–1227.
71. P McMorn, G Roberts, and GJ Hutchings. "Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts." *Catal Letters*. 1999; 63: 193–197.
72. S Demirel-Gülen, M Lucas, and P Claus. "Liquid phase oxidation of glycerol over carbon suorted gold catalysts." *Catal Today*. 2005; 102–103: 166–172.
73. E Maris and R Davis. "Hydrogenolysis of glycerol over carbon-suorted Ru and Pt catalysts." *J Catal*. 2007; 249: 328–337.
74. T Miyazawa, S Koso, K Kunimori, and K Tomishige. "Glycerol hydrogenolysis to 1,2-propanediol catalyzed by a heat-resistant ion-exchange resin combined with Ru/C." *Al Catal A Gen*. 2007; 329: 30–35.
75. MA Dasari, P-P Kiatsimkul, WR Sutterlin, and GJ Sues. "Low-pressure hydrogenolysis of glycerol to propylene glycol." *Al Catal A Gen*. 2005; 281: 225–231.
76. HJ Lee, D Seung, KS Jung, H Kim, and IN Filimonov. "Etherification of glycerol by isobutylene: Tuning the product composition." *Al Catal A Gen*. 2010; 390: 235–244.
77. P Ferreira, I Fonseca, A Ramos, J Vital, and J Castanheiro. "Esterification of glycerol with acetic acid over dodecamolybdophosphoric acid encaged in USY zeolite." *Catal Commun*. 2009; 10: 481–484.

78. Dosuna-Rodríguez, C Adriany, and EM Gaigneaux. "Glycerol acetylation on sulphated zirconia in mild conditions." *Catal Today*. 2011; 167: 56–63.
79. M Rafi, a Rajashekar, M Srinivas, BVSK Rao, RBN Prasad, and N Lingaiah. "Esterification of glycerol over a solid acid biochar catalyst derived from waste biomass." *RSC Adv*. 2015; 5: 44550–44556.
80. GW Huber, S Iborra, and A Corma. "Synthesis of Transportation Fuels from Biomass : Chemistry , Catalysts , and Engineering." *Science*. 2006; 2: 4044–4098.
81. J Ragauskas, CK Williams, BH Davison, G Britovsek, J Cairney, CA Eckert, et al. "The path forward for biofuels and biomaterials." *Science*. 2006; 311: 484–489.
82. D Klemm, B Heublein, HP Fink, and A Bohn. "Cellulose: Fascinating biopolymer and sustainable raw material." *Angew Chemie - Int Ed*. 2005; 44: 3358–3393.
83. D Yamaguchi, M Kitano, S Suganuma, K Nakajima, H Kato, and M Hara. "Hydrolysis of Cellulose by a Solid Acid Catalyst under Optimal Reaction Conditions." *J Phys Chem C*. 2009; 113: 3181–3188.
84. H Guo, Y Lian, L Yan, X Qi, and RL Smith. "Cellulose-derived superparamagnetic carbonaceous solid acid catalyst for cellulose hydrolysis in an ionic liquid or aqueous reaction system." *Green Chem*. 2013; 15: 2167.
85. Shuai and X Pan. "Hydrolysis of cellulose by cellulase-mimetic solid catalyst." *Energy Environ Sci*. 2012; 5: 6889–6894.
86. Onda, T Ochi, and K Yanagisawa. "Selective hydrolysis of cellulose into glucose over solid acid catalysts." *Green Chem*. 2008; 10: 1033.
87. Kitano, K Arai, A Kodama, T Kousaka, K Nakajima, S Hayashi, and M Hara. "Preparation of a Sulfonated Porous Carbon Catalyst with High Specific Surface Area." *Catal Letters*. 2009; 131: 242–249.
88. S Li, Z Gu, B E Bjornson, and A Muthukumaraan. "Biochar based solid acid catalyst hydrolyze biomass." *J Environ Chem Eng*. 2013; 1: 1174–1181.
89. Mosier, C Wyman, B Dale, R Elander, YY Lee, M Holtzale and M Ladisch. "Features of promising technologies for pretreatment of lignocellulosic biomass." *Bioresour Technol*. 2005; 96: 673–686.
90. R Ormsby, JR Kastner, and J Miller. "Hemicellulose hydrolysis using solid acid catalysts generated from biochar." *Catal Today*. 2012; 190: 89–97.
91. Y Jiang, X Li, X Wang, L Meng, H Wang, G Peng, X Wang, and X Mu. "Effective saccharification of lignocellulosic biomass over hydrolysis residue derived solid acid under microwave irradiation." *Green Chem*. 2012; 14: 2162.
92. Ta Milne and RJ Evans. "Biomass Gasifier 'Tars': Their Nature, Formation, and Conversion." *Constraints*. 1998.
93. S Mani, JR Kastner, and A Juneja. "Catalytic decomposition of toluene using a biomass derived catalyst." *Fuel Process Technol*. 2013; 114: 118–125.
94. S Van Paasen and J Kiel. "Tar formation in fluidised-bed gasification-impact of gasifier operating conditions." *Acknowledgement/Preface*. 2004: 10–14.
95. R Frazier, E Jin, and A Kumar. "Life Cycle Assessment of Biochar versus Metal Catalysts Used in Syngas Cleaning." *Energies*. 2015; 8: 621–644.
96. a Gerber. "Review of Novel Catalysts for Biomass Tar Cracking and Methane Reforming." 2007.
97. JR Kastner, S Mani, and A Juneja. "Catalytic decomposition of tar using iron soorted biochar." *Fuel Process Technol*. 2015;130: 31–37.
98. Z Abu El-Rub, E a Bramer, and G Brem. "Experimental comparison of biomass chars with other catalysts for tar reduction." *Fuel*. 2008; 87: 2243–2252.
99. C Xu, J Donald, E Byambajav, and Y Ohtsuka. "Recent advances in catalysts for hot-gas removal of tar and NH<sub>3</sub> from biomass gasification." *Fuel*. 2010; 89: 1784–1795.
100. M Haider, M Gogate, and R Davis. "Fe-promotion of soorted Rh catalysts for direct conversion of syngas to ethanol." *J Catal*. 2009; 261: 9–16.
101. S Wang, Q Yin, J Guo, B Ru, and L Zhu. "Improved Fischer–Tropsch synthesis for gasoline over Ru, Ni promoted Co/HZSM-5 catalysts." *Fuel*. 2013; 108: 597–603.
102. Y Zhu, S Wang, X Ge, Q Liu, Z Luo, and K Cen. "Experimental study of improved two step synthesis for DME production." *Fuel Process Technol*. 2010; 91: 424–429.
103. V Jiménez, P Sánchez, P Panagiotopoulou, JL Valverde, and A Romero. "Methanation of CO, CO<sub>2</sub> and selective methanation of CO, in mixtures of CO and CO<sub>2</sub>, over ruthenium carbon nanofibers catalysts." *AI Catal A Gen*. 2010; 390: 35–44.
104. RM Malek Abbaslou, J Soltan, and AK Dalai. "Iron catalyst soorted on carbon nanotubes for Fischer–Tropsch synthesis: Effects of Mo promotion." *Fuel*. 2011; 90: 1139–1144.
105. Q Yan, C Wan, J Liu, J Gao, F Yu, J Zhang, and Z Cai. "Iron nanoparticles in situ encapsulated in biochar-based carbon as an effective catalyst for the conversion of biomass-derived syngas to liquid hydrocarbons." *Green Chem*. 2013; 15: 1631.
106. S Wang, H Wang, Q Yin, L Zhu, and S Yin. "Methanation of bio-syngas over a biochar soorted catalyst." *New J Chem*. 2014; 38: 4471.
107. W Jin, K Singh, and J Zondlo. "Co-processing of pyrolysis vapors with bio-chars for ex-situ upgrading." *Renew Energy*. 2015; 83: 638–645.
108. M Chen, J Wang, M Zhang, M Chen, X Zhu, F Min, and Z Tan. "Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating." *J Anal AI Pyrolysis*. 2008; 82: 145–150.
109. JQ Bond, AA Upadhye, H Olcay, GA Tompsett, J Jae, R Xing, et al. "Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass." *Energy Environ Sci*. 2014; 7: 1500–1523.
110. Aho, N Kumar, K Eränen, T Salmi, M Hupa, and D Y Murzin. "Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure." *Fuel*. 2008; 87: 2493–2501.
111. S Czernik and A Bridgwater. "Overview of alications of biomass fast pyrolysis oil." *Energy & Fuels*. 2004; : 590–598.
112. D Mohan, CU Pittman, and PH Steele. "Pyrolysis of wood/biomass for bio-oil: a critical review." *Energy & Fuels*. 2006; 20: 848–889.
113. a V Bridgwater. "Production of high grade fuels and chemicals from catalytic." *Catal Today*. 1996; 5861: 285–286.
114. Y Sekiguchi and F Shafizadeh. "The effect of inorganic additives on the formation, composition, and combustion of cellulosic char." *J AI Polym Sci*. 1984; 29: 1267–1286.