Journal of Cleaner Production 297 (2021) 126645

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Review on biomass feedstocks, pyrolysis mechanism and physicochemical properties of biochar: State-of-the-art framework to speed up vision of circular bioeconomy

Gajanan Sampatrao Ghodake [a], Surendra Krushna Shinde [a], Avinash Ashok Kadam [b], Rijuta Ganesh Saratale [b], Ganesh Dattatraya Saratale [c], Manu Kumar [d], Ramasubba Reddy Palem [e], Hind A. AL-Shwaiman [f], Abdallah M. Elgorban [f], Asad Syed [f], Dae-Young Kim [a, *]

[a] *Department of Biological and Environmental Science, Dongguk University-Seoul, 32 Dongguk-ro, Ilsandong-gu, Goyang-si, 10326, Gyeonggi-do, South Korea*

[b] *Research Institute of Biotechnology and Medical Converged Science, Dongguk University-Seoul, 32 Dongguk-ro, Ilsandong-gu, Goyang-si, 10326, Gyeonggi-do, South Korea*

[c] *Department of Food Science and Biotechnology, Dongguk University-Seoul, 32 Dongguk-ro, Ilsandong-gu, Goyang-si, 10326, Gyeonggi-do, South Korea*

[d] *Department of Life Science, Dongguk University-Seoul, 32 Dongguk-ro, Ilsandong-gu, Goyang-si, 10326, Gyeonggi-do, South Korea*

[e] *Department of Medical Biotechnology, 32 Dongguk-ro, Ilsandong-gu, Goyang-si, 10326, Gyeonggi-do, South Korea*

[f] *Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455 Riyadh, 11451, Saudi Arabia*

ARTICLE INFO

Article history:
Received 23 July 2020
Received in revised form
1 March 2021
Accepted 3 March 2021
Available online 9 March 2021

Handling editor: Prof. Jiri Jaromir Klemeš

Keywords:
Biomass feedstocks
Pyrolysis mechanisms
Carbon sequestration
Biochar properties
Agronomic applications

ABSTRACT

The biochar is a solid carbon-rich, porous material produced by the thermochemical conversion of a diverse range of biomass feedstocks under an inert atmosphere (i.e., in the absence of oxygen). We can produce the biochar at all likely scales, ranging from the industrial to the domestic level and even at individual farms, thus, the biochar industry is leading as a most appropriate at different socioeconomic settings. The possibility of sustainable biochar production practices and multi-functionality features make it a promising candidate to fulfill an increasing demand in the fields of soil amendment, agricultural sustainability, environmental protection, cutting-edge materials, and to achieve circular bioeconomy and mitigation of climate change. An available fraction of waste biomass (agroforestry waste, biomass crops, agricultural residues, mill residues, and animal manure, and many more) can be used efficiently in pyrolysis and converted into desired biochar materials, besides this alternative energy products, such as syngas, bio-oil, electricity generation, and process heat. This report emphasizes the fate of biomass composition, pyrolysis mechanisms, and applications of modern analytical and characterization techniques that are being adopted, applied, and standardized to improve understandings of molecular, structural, and surface properties characteristics of biochar. To achieve precisely designed biochar, there is a need to understand the latest advances in biochar materialization mechanisms and structure-application relationships to speed up their agronomic applications and to achieve a zero-waste dream. This report also summarizes a wide range of literature published on feedstocks, pyrolysis, and biochar and suggests several practical recommendations appropriate to implement and bring together specific details on the thermochemical conversion of biomass, desired biochar properties, organic and inorganic phases, and the significance to the agronomic applications.

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* Corresponding author.
E-mail address: sbpkim@dongguk.edu (D.-Y. Kim).

https://doi.org/10.1016/j.jclepro.2021.126645
0959-6526/

1. Introduction

Among the critical environmental concerns facing the global community at present is the dumping of pollutants and global warming (Flandroy et al., 2018). Climate change and the energy crisis are the big environmental problems that causing great concern across the world (Jacobson, 2009). Many research groups and government policymakers determined to find eco-friendly, simple, and cost-effective solutions addressing environmental concerns. There is an increasing need to find out environment-friendly and economically workable renewable energy sources that will support the achievement of sustainable development goals and build a better and more sustainable future blueprint for all (Owusu and Asumadu-Sarkodie, 2016).

An inefficient biomass resource management resulting in substantial economic losses owing to the wastage of a sizeable amount of biomass, natural resources (Fu and Jiang, 2019), and municipal waste (Tian et al., 2012), as a result, most of them being preferred to either dump out or incinerate (Chen, J. et al., 2017). Thus, emissions and infiltrations are the significant aspects causing environmental pollution and speeding up global warming (Tripathi et al., 2019). The incineration of biomass also results in severe air pollution (Beydoun and Klankermayer, 2020), increases the possibility of dispersing pollutants into the environment (Ahmed and Hameed, 2020). A large area required to construct most of the waste biomass landfill sites (Johnston et al., 2019), which leads to potential pollution risk (Brand et al., 2018) and severe groundwater contamination with a diverse range of pollutants (micropollutants (Umar, 2016), volatile organic compounds (Randazzo et al., 2020), heavy metals (Jambeck et al., 2008), methane gas (Singh et al., 2018), ammonium ions (Yi et al., 2021), nitrates (Liu, H. et al., 2019), and many more). Therefore, myriads of environmental and health risks are linked to the residents living in close proximity to landfill sites (Njoku et al., 2019). Therefore, thorough management of most of the accessible feedstocks and their types worldwide is recommended (Zhao et al., 2019), their systematic conversion into one or the other, compost (Mihai and Ingrao, 2018), engineered biochar (Kazemi Shariat Panahi et al., 2020), biogas (Pawar et al., 2020), and/or bio oil (Mohan et al., 2006), pyrolysis technologies are prevalent to prevent resulting secondary pollution and ensure establishing circular bioeconomy (Yaashikaa et al., 2020). Economically viable technologies and environmentally sustainable alternatives must be employed to perform industrial-scale pyrolysis and production of biochar, thus ease to success in the commercialization of biochar-based products and potential applications (Manyà, 2012).

Presently, various types of biochemical processes and agrochemical processes are being accustomed to exploiting conversion of lignocellulosic waste into value-added products, such as microbial delignification combined with pretreatments and hydrolysis (Tsegaye et al., 2019) to enhance biofuel production includes ethanol (Zabed et al., 2016), methanol (Eichler et al., 2015), butanol (Li, J. et al., 2019), methane (Xu et al., 2019), biodiesel (Yousuf, 2012), fuel briquettes (Sette et al., 2018), and hydrogen production (Zhang et al., 2018). However, microbe-mediated conversion of lignocellulosic biomass involves controlling a series of complex metabolic pathways, such as acidogenesis, methanogenesis, acetogenesis, and hydrolysis (Putro et al., 2016). Most of those are exciting but, at the same time challenging to operate at a large-scale and while practicing green chemistry principles, since they require experts, and also are time and energy-intensive (Schievano et al., 2019).

Organic materials of biomass feedstocks are clean and renewable energy source that can be made available from various fragments including, agricultural residues, forest biomass, algae biomass, organic fraction of sludge, cardboard waste, paper pulp waste, slaughterhouse waste, food waste, municipal solid waste, and some other organic waste (Carpenter et al., 2014). The quantity of biomass available globally anticipated to increase constantly; thus, pyrolysis of waste biomass has huge potential to produce biochar or charcoal-based products and supplement renewable energy sources (Zhai et al., 2015). However, establishing an efficient economically viable thermochemical conversion facility is still a challenging task because of the inconsistency over availability of biomass, uncertainty over profits, and strict regulations from policymakers (Tanger et al., 2013).

As a renewable alternatives, biomass-based biorefineries (Kumar and Verma, 2021), and modern thermochemical technologies to convert biomass feedstocks into biochar or biofuels can be a sustainable route if it is made simple and efficient to perform worldwide (Mathimani et al., 2019). Biomass pyrolysis (Fahmy et al., 2020), waste valorization (Nayak and Bhushan, 2019), biomass cogeneration (Sipilä, 2016), hydrothermal carbonization (Kwon et al., 2012), hydrothermal liquefaction (Gollakota et al., 2018), torrefaction rotary kilns and kiln reactors (Mei et al., 2015), and catalytic gasification (Mandal et al., 2019) are the leading thermochemical technologies for biomass conversion into biochar, biogas, and bio-oil (Rago et al., 2018). Precise control over the heating in the pyrolysis process is the key factor to produce good-quality biochar (Jiang et al., 2019), and this method has several benefits besides low energy consumption (it uses about 10% of the energy used by other energy-intensive conventional methods) (Uzakov et al., 2018). Furthermore, the emissions of harmful gases in biomass pyrolysis are relatively low, and the scale-up plants are more simple, convenient, and portable, which allows them to move from one site to another, unlike incineration plants adopted by most of the urban municipal plants (Czajczyńska et al., 2017).

Biochar is a stable porous carbon-rich material formed by the pyrolysis of biomass feedstocks with a slow heating rate and at a relatively low temperature (400–700 °C) (Tomczyk et al., 2020). The International Biochar Initiative (IBI) defined biochar as the solid stable form of carbon material resulting from the thermochemical transformation of biomass feedstocks in the absence of oxygen (Pourhashem et al., 2019). As illustrated in Fig. 1, it is important to integrate biochar production, functionalization, and the development of potential applications in various sectors. There is a need to differentiate biochar from the activated carbon and charcoal (Liang et al., 2019), charcoal is also a carbon-rich solid material traditionally derived from biomass feedstocks (Hagemann et al., 2018), but we normally use it for cooking-heating or as an alternative reducing agent in the metallurgical process (Wiinikka et al., 2018). Alternatively, popular type carbon-rich solid material called activated carbon typically derived from various biomass feedstocks (Ahmed et al., 2019) and also from various types of carbonaceous materials, including lignite, coal, and tar pitch (Saleem et al., 2019). In this process, carbonaceous materials are “activated” by additional treatment processes that significantly improve the surface chemistry, and increase surface area and porosity, facilitating them to use in preparing multifunctional carbon materials (Yan et al., 2019). Its high adsorption properties (Saha and Grappe, 2017), makes it effective for air purification (Gwenzi et al., 2021) and remediating contaminants from soil and water (Zheng et al., 2020), which is why activated carbon specially intended for water purification and potential environmental protection applications. Pyrolysis of biomass feedstocks is a “carbon-negative” energy strategy, warrants profound research and development (R&D) activities globally (Lu et al., 2019) in the field of climate mitigation (Gurwick et al., 2013), environmental pollution control (Wang and Wang, 2019), and renewable energy alternatives (Kim et al., 2019); footstep towards sustainable agriculture, food security, and progress of human civilization (Marmiroli et al., 2018).

This report aims to describe recent developments in biochar production and characterization inorganic content, and the relationship between the resulting desirable properties and the biomass composition (Li, S. et al., 2019). Various factors and operational settings (e.g., type of carbonization process, temperature, time, type of feedstock, and so on) can influence biochar production (Uroić Štefanko and Leszczynska, 2020). Depending on the temperature conditions, the pyrolysis process gets categorized into three main types: fast pyrolysis (over a short time, fast heating rate,

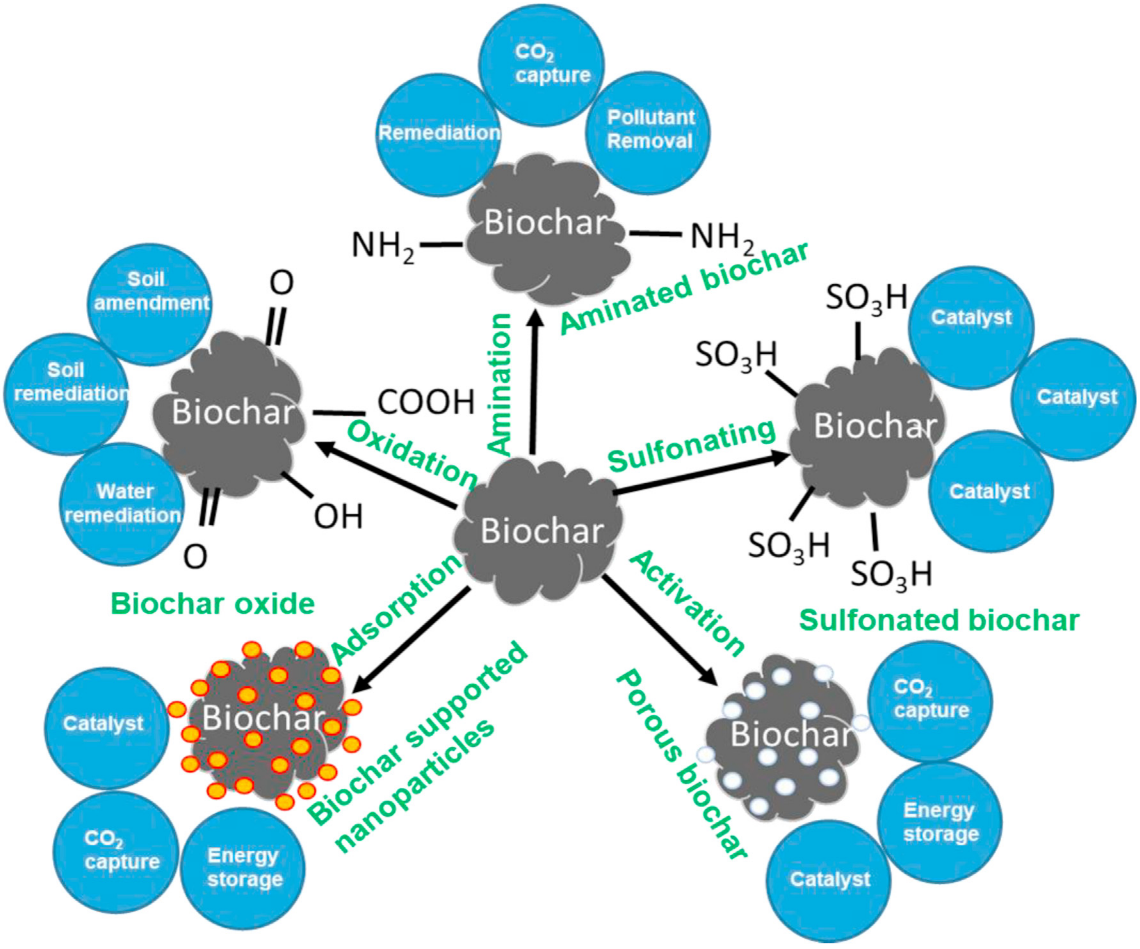


Fig. 1. Biochar as a potential material for the production of different functionalized products and their potential applications in various sectors.

temperature >500 °C), slow pyrolysis (over a long time, slow heating rate, temperature <300 °C), and moderate pyrolysis (average time, moderate heating rate, temperature 300–500 °C) (Zhao et al., 2018). A recent study showed that during biomass waste pyrolysis, the primary step is cracking, and the second step wherein the decomposition of biomass components occurs together with the formation of oxygen-rich functional groups at about 400–500 °C (Wang, Q. et al., 2020). The pyrolysis temperature mainly influences the molecular structure (Singh, S. et al., 2020) and physicochemical properties of biochar materials, such as surface area, functional groups, pore structure, and elemental composition (Tag et al., 2016). The influence on such properties has to be tuned precisely by the pyrolysis temperature, and it can also attribute to the release of volatile organic compounds, particularly at high-temperature settings (Sun et al., 2014). Several other reports have also confirmed that pyrolysis at high temperatures leads to an increased surface area (Zhang et al., 2015a), higher pH (Peiris et al., 2019), and lower N% content but higher C% content (Zhang et al., 2017). Thus, the precise selection of the appropriate pyrolysis temperature is a tradeoff between the chemical and surface properties, normally, 500–800 °C is thought to be the optimal range for the operating pyrolysis temperature to produce desired biochar materials (Wang, Y. et al., 2013).

In the last decade, it has reflected rapid progress in the scientific literature and patents covering both the production of biochar-based functional materials, comprehensive characterization, and discovery of potential applications (Liu et al., 2015). However, the results from many studies suggest that R&D activities on biochar production and its molecular and structural characteristics are currently under serious investigation (Kazemi Shariat Panahi et al., 2020). Developments of functional materials based on biochar is emerging as a sustainable platform of carbon materials (Liu et al., 2015), while speed up biochar production, feasible technologies, and climate change-related practical achievements (Xiao et al., 2018). Thus, worldwide efforts have to be implemented on producing biochar at a different scale, pyrolysis for biochar (Manyà, 2012), production and utilization (Cha et al., 2016), multifunctional biochar-based products (Liu et al., 2015), agroecosystem–sustainability (Nair et al., 2051), soil-water remediation (Guo et al., 2020), and emerging applications (Liu, W.-J. et al., 2019), and collective efforts in biochar research (Wu, P. et al., 2019). However, most of these reviews have stressed certain aspects related to biochar materials, biochar production, and their specific applications. There is also a need for new reports aiming at critical and comprehensive review of biochar's materialization mechanisms, its molecular and structural characterization, and functionalization for emerging applications.

More specifically, critical assessment of the sustainability over availability of biomass feedstocks, which plays a key role in achieving sustainable biochar production and agronomic applications of biochar-based materials, would be useful. We see this as an opportunity to articulate recent developments systematically, current challenges, and future perspectives on pyrolysis of biomass to biochar and some alternative products. There is a thoughtful need to evaluate the fate of biomass components, biochar formation mechanisms, physicochemical characteristics, and their miscellaneous applications in the agronomic field, and related fields. In this report, we thus attempt to cover the biochar formation mechanism in relation to biomass components, and pyrolysis temperature, potential characterization techniques, molecular aspects behind tuning surface functionality, and some sustainability insights.

2. Biochar production

2.1. Choice of feedstocks

To achieve multiple biochar production goals, including fine-tuning of properties, improving economic aspects, reducing environmental emissions, and increasing co-products in biochar production (Czajczyńska et al., 2017), significant feedstock resource supply factors must be considered carefully, such as feedstock type, collection, comminution (size reduction), storage facilities, automation in handling/feeding, and analysis of its composition (Stone et al., 2010). The uncertainty over the cost and availability of biomass feedstocks varies significantly across the world (Speirs et al., 2015). Thus, the blending, pelleting, comminution, cost-effective transport, and formulation of various available feedstocks, combined with chemical pretreatment (Carpenter et al., 2014) and thermochemical procedures, would facilitate a reliable, lower-cost, and high-volume biomass supply for the emerging biochar industry (Yazan et al., 2016). However, there are several other critical factors involved in achieving sustainability in the pyrolysis process (Homagain et al., 2016). Accordingly, the biomass feedstock choice and pretreatment methods used do affect biochar yield and quality (Gai et al., 2014a), and the potential implications of the pyrolysis environment are yet to be fully understood. This review describes the broad literature currently available to the author's knowledge regarding the choice of feedstocks and the effect of pretreatments on the yield, product improvement, and distribution of inorganic elements in biochar materials.

As shown in the graphical abstract, when the conversion of biomass into biochar has to be executed sustainably globally, it has enormous potential to achieve climate change mitigation (Woolf et al., 2010), environmental protection (Kazemi Shariat Panahi et al., 2020), and soil amendment (Woolf et al., 2010). Biochar is a viable alternative to manage solid waste and it can be produced sustainably from the various biomass feedstock materials accessible (Gezae and Chandraratne, 2018), agricultural residues (Colantoni et al., 2016), agro-industrial waste (Dahal et al., 2018), hard-wood forestry biomass (Lu and El Hanandeh, 2019), food waste (Elkhalifa et al., 2019), and livestock manure (Gunamantha and Widana, 2018). To be precise, a wide range of feedstock resources have to be undertaken predominantly (Hassan et al., 2020). These include agricultural lignocellulosic biomass residues (sugarcane bagasse (Raul et al., 2021), banana peduncle (Karim et al., 2015), corn stover (Zhu, L. et al., 2015), wheat straw (Junna et al., 2014), rice straw (Li, J. et al., 2018)), forest residues (thinning (Puettmann et al., 2020) and logging residues (Campbell, J.L. et al., 2018)), aquatic biomass (Mokrzycki et al., 2020), cardboard waste (Ghorbel et al., 2015), paper waste (paper mill sludge (Yoon et al., 2017), paper mill waste (Van Zwieten et al., 2010), municipal solid waste (Jayawardhana et al., 2016), wastewater organic sludge (Bolognesi et al., 2019), and dedicated energy crops (Blanco-Canqui, 2016) (switchgrass (Koide et al., 2018), high biomass sorghum (Kotaiah Naik et al., 2017), hybrid poplars. The utilization of woody biomass to manufacture value-added products, particularly using residual biomass harvesting and wood thermochemical conversion, increases the feasibility of biomass processing and reduces the vulnerability of tragic wildfires and incidences of disease and insects in forests (Luo et al., 2016). Feedstocks, particularly from industrial or landfill waste, sewage sludge, and biomass from phytoremediation, must be examined before being used for biochar production and must not contain elevated levels of heavy metals because they end up in the final product (Zhao et al., 2019). A significant consequence of biochar R&D activities has raised serious attention among scientists, production industries, and farmer communities. The potential negative impacts of increasing competition for agricultural land include rising food prices, threats to biodiversity, and greenhouse gas emissions (Tisserant and Cherubini, 2019). Fixing socioeconomic and socioecological factors can be a potential framework to address land-related limitations and examine the roles of policymakers in accelerating biomass conversion movement, sustainable biochar production, and expected carbon sequestration.

It is important to consider all possible channels of feedstock supply with a sustainability approach from local communities and local businesses prior to the establishment of a biochar production unit (Homagain et al., 2016). To ensure this, there is need into put serious efforts on featuring the significance of sustainable aspects. Thus, there is a need to use a stringent set of standards to consume most of the available biomass feedstocks in pyrolysis. Biomass availability in the immediate area also affects the feedstock choice and is of primary significance in terms of conversion of the land site to generate feedstocks at a reasonable price (Torres et al., 2011). In developing countries, biomass is often consumed as a cooking and heating fuel; however, nursery production worldwide with ecosystem conservation is a potential alternative with added sustainability (Overend, 2017).

Biomass-crop production, residual feedstock, such as cropping residues (Li, Z. et al., 2019), municipal sludge (Sun et al., 2017), and agro-industrial byproduct bagasse (Vimal et al., 2019) are sustainable sources of feedstocks available globally to achieve next-level production of biochar. Cattle manure and chicken litter are traditionally used as a direct bio-fertilizer in organic farming practices (Sikder and Joardar, 2019), but in some sites, they also considered waste, and their disposal is a costly and challenging task (Dróżdż et al., 2020). However, there are tradeoffs, and there is the possibility of nutrient value loss from the use of such feedstocks (Woolf et al., 2019) in the production of biochar (Jeffery et al., 2015). An important step is that the particular feedstock must be adequately dehydrated prior to the pyrolysis, and we can acquire alternative energy needed for dehydration can be acquired from the pyrolysis process itself of the previous batch of feedstock (Kim and Kang, 2012). Depending on the feedstock choice, the dehydration process, and careful storage, a series of interventions that include labor, energy utilizers, and dehydrators are necessary (Whittaker and Shield, 2017). Mill and forest residues are potential sources of biomass feedstocks applicable in the production of biofuels, bioenergy, and solid biochar (Simangunsong et al., 2017). However, most of the time, these biomass materials are considered waste and left on the site to decompose or pile burned to avoid wildfire risk (Corona et al., 2015). The transportation cost of such biomass feedstocks is very high, when the feedstock is located far from the processing unit (Searcy et al., 2007), the densification of the feedstock biomass by pelletizing or chipping is a sensible approach (Thornley et al., 2015). Thus, some alternative practices can be sustainable and economically feasible in terms of resourcing biomass feedstocks; includes installing preprocessing onsite units to increase portability and generate high-density biomass (Homagain et al., 2016).

Renewable fuels from biomass feedstocks have the potential in reducing CO_2 emissions and transform the current fuel supply scenario globally. Lignocellulosic biomass, the most widely researched and used materials, is mostly being favored in thermochemical processing because of its high-quality biochar, and bio-oil with low ash-content produced. However, the ease of use and price of biomass feedstocks (e.g., agricultural residues, forest residues, energy crops) vary significantly by area, and these are key factors in approximating the economic viability of a pyrolysis process (Dhyani and Bhaskar, 2018). A comprehensive techno-economic examination of various thermochemical conversion paths has to be conducted for all possible biomass feedstocks to investigate the effects of overall cost and other variable factors in terms of financial performance (Carrasco et al., 2017). The thermochemical conversion of wood biomass to energy alternatives can be more economically viable if value-added byproducts used in the production of biochar-based materials (Campbell, R.M. et al., 2018). Furthermore, blending or formulation of different feedstocks, combined with chemical and/or thermal pretreatments prior to pyrolysis, would facilitate steady, low-cost, high-volume biomass supplies to develop a sustainable biofuel and biochar industry. However, the influence of biomass choice and pretreatment methods on biochar and other product properties, and yield, and the pyrolysis process effects, are yet to be fully understood. This review further summarizes the literature on the current state of understanding regarding the influence of feedstock and pretreatment choice on the quality, product yield, organic/inorganic phases, and structure—application relationship of biochar.

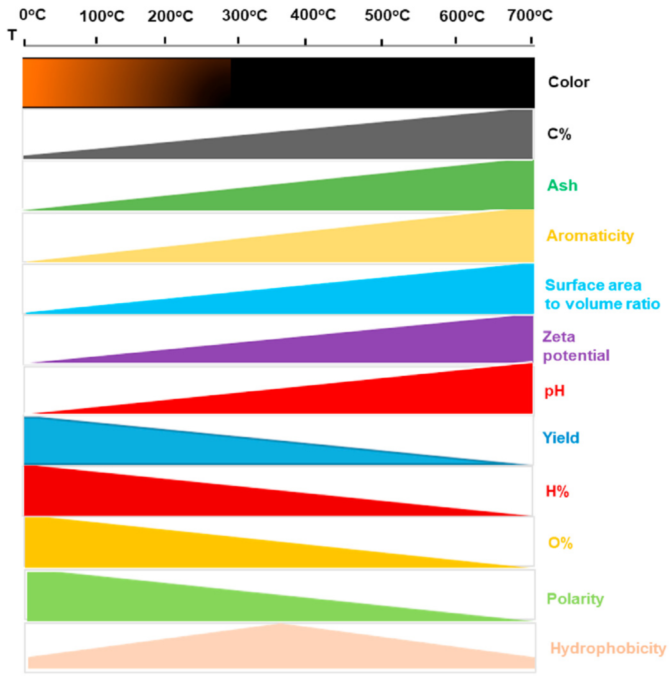
2.2. Production of biochar

According to reports on historical forest sites at the Amazon basin (Chen, W. et al., 2019) and other literature reports, the traditional production of biochar by pyrolysis of biomass dates back to several thousands of years (De Gisi et al., 2014). However, pretreatment methods for biomass are emerged recently (Roberts and de Nys, 2016) and pyrolysis at a slow rate (termed slow pyrolysis) are advantageous and most often recommended for producing biochar products with desired properties (Ronsse et al., 2013). Therefore, this report emphasizes the significance of pretreatment procedures before the pyrolysis of biomass; for instance, biomass alkali treatments (e.g., potassium hydroxide) help to “soften” the biomass tissues through the breakdown of lignocellulosic compounds (Veksha et al., 2014). It also suggests pretreatment of biomass with chemicals like phosphoric acid to reduce the pH and to increase the functional groups involves in the slow-release of phosphate fertilizer (Yao, C. et al., 2015). Other methods of biomass pretreatment are also effective, such as varying the base and acid content using mixed clay, salts, or minerals (e.g., rock phosphate), which helps to reduce the rate of pyrolysis and increase the quantity of nutrient-rich inorganic particulate matter in the porous structures and on the biochar surfaces (Joseph et al., 2018). Furthermore, such pretreatments can be used to increase yields of liquid products, gas as well as biochar (Wang et al., 2015). One of the report revealed the effects of freeze-drying and silver staining on the cellulose fibers to enhance the yield of the carbon nanofibers while keeping their original structures intact (Kim and Im, 2012). The review of Putro et al. has discussed various aspects of the chemical and physical pretreatment and thermochemical conversion of lignocellulosic materials to improve the production of valuable biochar, chemicals, and biofuels (Putro et al., 2016).

Dry torrefaction has recently received extensive attention; this process needs an external heat input to speed up the dehydration of biomass and breakdown of molecular bonds simultaneously (Gronnow et al., 2013). Acetic acid, methanol, and other volatile, oxygenated, and organic compounds are expected to be released during this pretreatment (Carpenter et al., 2014), along with the emission of CO_2 and CO owing to the breakdown of the molecular bonds present in hemicellulose and cellulose materials (Pahla et al., 2017). Torrefied biomass is more brittle than that of fresh biomass, thus making the powder of the resultant biochar is much easier and less energy-intensive downstream processing (Chen, 2015). It is often recommended to use dry torrefaction treatment to biomass before the production of biochar to improve surface properties, water uptake, stability against biological degradation, and long-term storage of biochar products (Restuccia et al., 2019).

Whereas, wet torrefaction is one of the important and emerging pretreatment processes typically recommended to convert lightweight biomass to energy-dense solid fuel using a uniform biomass method. The fuel value of such solid biomass produced is much higher than that of the pristine biomass. In the procedure, pristine biomass is treated with boiling water to compress at the temperature of 200–260 °C (Yan et al., 2010), as reported mass and energy balances of wet torrefaction of lignocellulosic biomass (Yan et al., 2010). However, few of them addressed the aspects to estimate precise energy and mass balance involved. In particular, energy and mass balance are the most significant factor to ensure precise optimization and an economically feasible design (Tzanetis et al., 2017). A comprehensive assessment was reported on wet torrefaction covering two types of biomass fuels as feedstock softwood and hardwood, wherein they examined the effects of parameters such as temperature, pressure, holding time, reaction settings, and feedstock size on the properties and yield of the solid biochar products (Bach et al., 2013). Furthermore, there is a need for further investigations to establish precise energy and mass balance that would aid in energy production, estimate its commercial feasibility, and facilitate technical and economic analysis of the emergent biomass torrefaction technologies (Mamvura and Danha, 2020).

The properties of biochar differ according to the pyrolysis temperature, as shown in Scheme 1. As the pyrolysis temperature increases (200–700 °C), the biomass color turns from brown to black, and the biochar yield varies typically from 15 to 40% and polarity values get decrease (Tomczyk et al., 2020). The hydrogen content (H%) ranges from 1.4 to 6.1%, and the oxygen content (O%) ranges from 11 to 41% for biochar derived from pine needles (Chen et al., 2008). The fixed carbon content (C%) for this biochar typically ranges from 50 to 85%, and the ash percentage varies from 13 to 49% for biochar derived from rice straw (Xiao et al., 2014). The aromaticity, pH, zeta potential (ζ), and surface area for biochar derived from pine needle biomass increases with an increase in pyrolysis temperature from 200 to 700 °C (Chen et al., 2008).



Scheme 1. Variation in biochar properties with an increase in pyrolysis temperature conditions.

The biomass undergoes the pyrolysis process in the absence of O_2 at a temperature above 300 °C, causing the organic components to decompose thermally and release the vapor phase, finally forming residual solid-phase biochar materials (Mohan et al., 2006). When cooled down, the vapor phase produces bio-oil, wherein the mixture of polar and high-molecular-weight organic compounds gets condensed, while the low-molecular-weight volatile compounds (CO, C_2H_2, CH_4, and H_2) remain as gas-phase (Chua et al., 2019; Laird et al., 2009). The liquid condensate of pyrolysis is called wood vinegar or smoke water, depending on the temperature conditions and the concentration during production (Lu et al., 2019). We can use wood vinegar as a plant growth promoter, biofungicide, seed germination aid, and composting stimulator; it can also be used to improve the characteristics of biochar (Fagernäs et al., 2015).

As shown in Table 1, we can categorize the pyrolysis processes into three main types (i.e., flash, fast, and slow pyrolysis) based on the reaction duration, heating rate, and main product yield (Onay and Kockar, 2003). Fast pyrolysis technology has received global attention as a potential platform for the production of sustainable drop-in biofuels, biogas, and several chemicals as well as some important commercial products (Bridgwater, 2012). A previous review report by Mohan et al. was dedicated on wood pyrolysis and detailed characteristics of the bio-oils as a main product of fast pyrolysis (Mohan et al., 2006). We usually prefer low energy density biomass for the production of biofuels by fast pyrolysis reactor systems. This process is frequently considered as a thermal decomposition route (heating value ~10–11 MJ kg^{-1}) at a medium temperature range (400–600 °C) in the absence of oxygen with a higher heating rate (>200–300 °C/min) and shorter vapor residence time (VRT) (0.5–10 s) (Czernik and Bridgwater, 2004). In the fast pyrolysis process, a fast heating rate with high temperatures and short VRTs are advantageous for higher bio-oil yield (Garcia-Nunez et al., 2017). Fast pyrolysis method can yield high-energy-density fuels (heating value about ~15–17 MJ kg^{-1}), however, syngas with a relatively low-energy-density (heating value ~ 5–6 MJ kg^{-1}), and a minor yield of solid biochar materials (heating value about ~15–18 MJ kg^{-1}) (Bergvall et al., 2020).

To make biochar the major product, a carbonization process called slow pyrolysis is recommended for almost all sorts of biomass feedstocks (Cong et al., 2018). It involves a broad range of temperatures from 300 to 800 °C with a slow heating rate from 5 to 7 °C/min and with a longer VRT (normally > 1 h) (Higashikawa et al., 2016). In the slow pyrolysis process, a slow heating rate with low temperatures and long VRTs are appropriate for the formation of stable carbonaceous solid biochar materials (Hodgson et al., 2016). In this process, the yield of other pyrolysis products, bio-oil, and biogas is dependent on parameters, including temperature, VRT, and heating rate (Mahinpey et al., 2009). The third process called flash pyrolysis is for feedstock with a very small

Table 1
Yields and characteristics of biochar are prepared with four different pyrolysis methods.

	Slow	Flash	Fast	Gasification
Temperature (K)	300–800	400–1000	400–600	750–1000
Heating rate (K/min)	5–7	~1000	300–800	~1000
VRT	>60 min	2–3 s	1–10 s	10–20 s
Major Products	Biochar	Fuel gas	Fuel oil	Fuel gas
Biochar yield (wt %)	30–55	11–22	16–37	14–25

[a]The tabular data were collected and amended from different references (Babu, 2008; Bridgwater, 2012; Liu et al., 2015; Liu, W.-J. et al., 2017).

particle size (e.g., <0.5 mm) (Urban et al., 2017), which reaches high reaction temperatures (600–1200 °C) within 2 s, owing to the high heating rate and temperature (Di Blasi, 1996), yields biogas as the main product (Song and Watkinson, 2004).

Some other thermochemical conversion platforms like liquefaction are gasification are useful besides pyrolysis to convert pretreated biomass into fuels. Biogas produced from gasification technologies is currently standing at third position after ethanol, suggesting syngas could be a potential alternative to gasoline fuels (Colmenares et al., 2016). Since nonrenewable gasoline rates are anticipated to surge, renewable alternative fuel sources, such as conventional or cutting-edge biodiesel technologies, do not appear to be economically cost-effective (Misra et al., 2016). The gasification of biomass seems to be a versatile and exciting technology to process various biomass resources (energy crops, agricultural residues, urban waste, industrial and food processing waste), after adaptation of traditional coal gasification equipment's developed in the course of the industrial revolution (Couto et al., 2013). However, the high density of oxygen-functionalized organic compounds present in various types of biomass poses a major challenge to improve the conversion of biomass into fuel (Mohan et al., 2006). The gasification of biomass yields syngas, which can be also converted into liquid hydrocarbon, high-density fuel, by using the Fischer–Tropsch method and other oxochemical reactions in conversion procedures (Klimkiewicz, 2014). Thus, gasification technologies have potential to get rid of quality control issues; in addition, it offers incredible plasticity to employ syngas for different other purposes. Therefore, the production of syngas from the gasification of biomass is now emerging as the most favorable technique to exploit renewable fuel sources (Sikarwar et al., 2017).

The gasification of biomass is normally achieved in the temperature range from 750 to 1000 °C (Basu, 2018) and the pressure range from 1×10^5–3×10^5 Pa with or without catalytic agents (Liakakou et al., 2019). Recent reports covered techno-economic comparison (Anex et al., 2010), catalytic reactions occurs during the biomass gasification (Hashaikeh et al., 2006), dual fluidized bed systems for biomass gasification (Hanchate et al., 2021), low-temperature gasification technology (Hayashi et al., 2014). Advances in biomass gasification can be achieved by range of reactor structure designs (Sikarwar et al., 2016), shapes (Schulzke, 2019), and configurations (Erakhrumen, 2012) embraced for fixed bed with downdraft or updraft (Alarcón-Gaete and Elicer-Cortés, 2016), circulating fluidized beds (Grace and Lim, 2013), and gasifier with dual fluidized bed (Kern et al., 2013), and most of them are appropriate to employ in commercial scale operations. These technologies allow more precise control over temperature, pressure, ash removal, and suitable to ease scale-up practices. However, to make biomass gasification a more profitable technology, adaptability and pretreatments are essential to introduce a wide variety of lignocellulosic-rich biomass (Yousuf et al., 2020). In the same vein, the production of high value-added products, chemicals, and high-quality biofuels for power and heat generation, whenever required as those markets are promising with profitable prospects.

Furthermore, this review emphasized on the slow pyrolysis. This process involves an exothermic reaction; thus, the released energy is attributed to the breakdown of biopolymers present in the biomass (Blasi et al., 2019). During this process, the oxygen within the biomass materials gets released, which in turn influences the energy-releasing oxidation processes besides the yield of both biochar and biogas (Bacskai et al., 2019). The released energy creates sufficient heat to breakdown the remaining chemical bonds present in the biomass (Gumisiriza et al., 2017). We thus consider this process as a self-sustaining, and it continues on its own to a temperature of approximately 400 °C, eventually resulting in stable carbon-enriched biochar in the oxygen-deficient environment (Crombie and Mašek, 2014). We can establish such a setting to obtain the maximum yield of biochar before ending the exothermic step; however, there is a possibility of a resulting unstable state of carbon (Restuccia et al., 2019). As the heat from the pyrolysis reaction declines, it require additional heat input to maintain or increase the temperature throughout the slow pyrolysis process to increase the yield of biochar and percentage of fixed carbon (Cong et al., 2018).

Pyrolysis reactors for slow pyrolysis processes are further classified into kilns, converters, and retorts (Garcia-Nunez et al., 2017). Thermally insulated reactors are traditionally known as kilns, which are primarily known to produce self-sufficient temperatures during biochar formation from wood logs (Heredia Salgado et al., 2020). Industrial reactors are being developed for recovering biochar and other products from volatile fractions (liquid and syngas), are called converters and retorts (Garcia-Nunez et al., 2017). More specifically, retort reactors are being developed for large-scale industrial processes and the pyrolysis of large wood logs (over 20 cm in diameter and over 30 cm in length) (Antal and Grønli, 2003). Converters produce biochar by carbonizing biomass particles such as wood chips or wood pellets under conditions similar to those of intermediate pyrolysis, as described previously by Garcia-Nunez (Garcia-Nunez et al., 2017). Wood biomass is most widely researched and commonly used for high-quality biochar production (Domingues et al., 2017), and also preferred for thermochemical conversion owing to its low ash content (De Souza et al., 2020).

Exothermic reactions with wood biochar also turn into ash content typically around 1.5–5%, while biochar with a fixed carbon content is 60–70% and the volatile matter (VM) varies from 20 to 35% by weight ratio (Ronsse et al., 2013). The biochar produced at the exothermic reaction stage contains considerable amounts of VM (Panwar et al., 2019); thus, it has to be further processed to remove such content, improve porosity, and recover a sizable amount of syngas. That report further reveals that additional heating is essential to increase the fixed carbon content, surface-area-to-volume ratio, and biochar porosity through emitting and disintegrating the residual volatile compound content. The yield of biochar from oven-dry wood feedstocks may vary from 25 to 30% (w/w) at temperature of 550–600 °C with a fixed carbon content of about 80–85% and volatile compound content of about 10–12% (Antal and Grønli, 2003). Thus, the fixed carbon content and stability of biochar normally increase with the pyrolysis temperature (Crombie et al., 2013). This phenomenon is due to the further release of volatile compounds and gaseous content from the biomass with an increase in the pyrolysis temperature, forming biochar with large pores and increased surface area (Tomczyk et al., 2020). That report provided detailed information about the fixed carbon, volatile matter (VM), weight fractions of moisture, and ash content in biochar. These observations suggest that with the careful tuning of the pyrolysis temperature (Liu et al., 2020) and choice of biomass feedstock, is likely to be transformed into highly desired biochar having multifunctional physicochemical properties (Table 2). Similarly, it is liable to produce biochar with a “fine design” that has specific characteristics for emerging potential applications.

McBeath et al. recently examined the impact of feedstock choices on the quality of biochar, their stability, and yield of biochar under an inert H_2 atmosphere (McBeath et al., 2015). They revealed a trade-off between improved stability of aromatic polycyclic carbon content and reduced biochar yield as temperature increases, ranging from 500 to 700 °C, for most common feedstocks (wood, grass biomass, paper mill waste, domestic animal manure, macroalgal biomass, etc.). Biochar obtained from wood feedstocks (pinewood and hardwood) is known for its high recalcitrance of

Table 2
Pyrolysis of different types of feedstocks and physicochemical properties of biochar samples from manufacturers.

Biomass	T (°C)	Total carbon (%)	Carbon sequestration (%)	Fixed carbon (%)	Yield (%)	Ash (%)	VM (%)	CEC (cmol kg^{-1})	Surface area (m^2 g^{-1})	pH
Wheat straw	500	62.9	26.4	63.7	29.8	18.0	17.6	95.5	33.2	10.2
Grass	500	62.1	28.0	59.2	27.8	20.8	18.9	84.0	3.33	10.2
Sawdust	500	75.8	28.5	72.0	28.3	9.94	17.5	41.7	203	10.5
Peanut shell	500	73.7	34.4	72.9	32.0	10.6	16.0	44.5	43.5	10.5
Waterweeds	500	25.6	47.1	3.84	58.4	63.5	32.4	509	3.78	10.3
Chlorella	500	39.3	33.0	17.4	40.2	52.6	29.3	562	2.78	10.8
Waste paper	500	56.0	24.7	16.4	36.6	53.5	30.0	516	133	9.88
Wastewater sludge	500	26.6	21.1	20.6	45.9	61.9	15.8	168	71.6	8.82
Shrimp hull	500	52.1	34.3	18.9	33.4	53.8	26.6	389	13.3	10.3
Pig manure	500	42.7	26.6	40.2	38.5	48.4	11.0	82.8	47.4	10.5
Cow manure	500	43.7	41.8	14.7	57.2	67.5	17.2	149	21.9	10.2

[a]Volatile matter (VM), Cation exchange capacity (CEC). The tabular data were adopted with significant changes from the references (Zhao et al., 2013), copyright 2013 Elsevier B.V.

carbon (Domingues et al., 2017), with a relatively low ratio of total organic carbon to stable polycyclic aromatic carbon. However, biochar derived from agriculture residues or grass biomass has low carbon content, but relatively with a high ratio of total organic carbon phase to stable polycyclic aromatic carbon phase (Jindo et al., 2014). It has also been revealed that biomass feedstocks with high moisture content (45–65%) can be an attractive option for preparing biochar with increased yield, particularly under high-temperature and -pressure conditions (Wang, L. et al., 2013).

A comprehensive report by Zhao et al. also reported that biochar characteristics and their functionalities more relative to the pyrolysis temperature, the biomass choice, and structural heterogeneity features (Zhao et al., 2013). It was also demonstrated that the pyrolysis temperature can influence the pH of biochar and its surface area (Pariyar et al., 2020). Furthermore, the mineral distribution, stable carbon, potential sequestration capacity, organic carbon, and ash content of biochar materials are mainly influenced by the choice of biomass feedstock and its composition (Zhao et al., 2019). The peak temperature is the most significant factor influencing the features of the final biochar prepared by the slow pyrolysis process (Zhang, H. et al., 2020). Moreover, an increase in the peak temperature enables the rapid formation of biochar with a higher content of fixed carbon, aromatic characteristics, and higher porosity (Tomczyk et al., 2020). These properties are important to increase the stability of the fixed carbon in the biochar and thus improve the nutrient and water retention capacity when applied for soil amendment purposes (Hagemann et al., 2017). The chemical reactions and physical changes in biomass materials during the pyrolysis process are multifarious and likely dependent on the reactor type, settings, heating rate, and composition of the biomass, as described in the subsequent section. The primary basis for this phenomenon is illustrated in Fig. 2: specifically, the enhanced release of VM and its relation with a decrease in the yield of biochar during the pyrolysis stage (Becidan, 2007). We recommend further detailed studies on the influence of the peak temperature in the pyrolysis process on both biochar characteristics and applicability to confirm these preliminary findings.

3. Biochar formation mechanism

Since the main precursor of biochar from pyrolysis is biomass, during biochar production, its mechanism and composition/structural characterization are important aspects to understand the pyrolysis process (Babu, 2008). An understanding of the biochar-formation mechanism is essential (Keiluweit et al., 2010), since full information on the chemical reactions and physical conversions occurring is important to consider controlling the surface area and porosity (Leng et al., 2021), surface morphology (Komnitsas and Zaharaki, 2016), chemical and physical structure (Sun et al., 2012), and surface functionalities of the resultant biochar materials (Liu et al., 2015). Lignocellulose-rich biomass mainly comprises cellulose, hemicelluloses, and lignin, and the respective components pyrolysis at a particular temperature condition and via various pathways, reactions, and mechanisms (Yang et al., 2006). For instance, during the pyrolysis process, decomposition of hemicelluloses occurs primarily at a lower temperature range from 200 to 250 °C, cellulose decomposes at the moderate temperature range from 250 to 350 °C, and lignin converts at the higher temperature range from 300 to 500 °C (Chen et al., 2018). The degree of thermochemical conversion also depends on several other operating parameters (Deng et al., 2016) (e.g., heating rate (Onsree et al.,

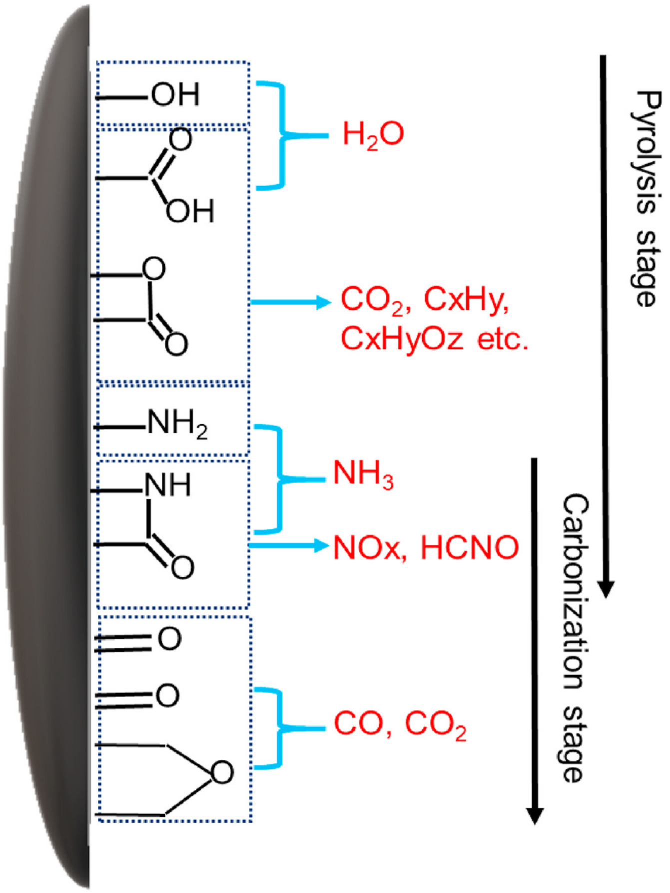


Fig. 2. Relation of pyrolysis temperature increase with biomass decomposition.

2018)), residence time (Zhang and Zhang, 2019), peak temperature (Ramesh and Somasundaram, 2020), reactor type (Resende, 2014), biomass size/composition (Klinger et al., 2018). Furthermore, intrinsic features, most key components of the biomass (e.g., hemicelluloses, cellulose, lignin, and inorganic content), also define biochar properties and thus should be taken into account (Kwapinski et al., 2010).

The molecular mechanism for biochar materialization is indirectly governed by feedstock choice and the pyrolysis temperature kinetics of the major components of biomass, namely, hemicellulose, cellulose, and lignin as well as inorganic catalysts (Chen, T. et al., 2017). It causes the pyrolysis mechanism for cellulose by a reduction in the polymerization ratio, which can occur through two primary reactions (Chen, L. et al., 2019). The primary reaction involves the disintegration and charring of cellulose components at a slow heating rate and low pyrolysis temperature (Dieguez-Alonso et al., 2015), as typically occurs in slow pyrolysis (Amini et al., 2019). The second reaction, like fast pyrolysis, involves the rapid volatilization and simultaneous formation of organic compounds with rapid heating rates at high pyrolysis temperature settings (Tsubaki et al., 2020). Furthermore, cellulose depolymerizes into oligosaccharide chains during the pyrolysis process, resulting in the production of d-glucopyranose owing to the cleavage of the glycosidic bonds (Fang et al., 2018). These compounds in turn undergo secondary reactions like an intramolecular rearrangement reaction (Ronsse et al., 2012) and forms a vital intermediate compound called levoglucosan (Wang, Q. et al., 2020). As shown in Scheme 2, biochar formation pathways are multifarious, including exsiccation, dehydration, aromatization, decarboxylation, polymerization, intramolecular condensation, and rearrangement reactions resulting in solid carbon-rich biochar (Wan et al., 2020). On the other hand, levoglucosan undergoes a chain of rearrangement reactions and a dehydration process to produce hydroxyl-methylfurfural, which can further yield volatile products, like syngas and bio-oil (Mettler et al., 2012).

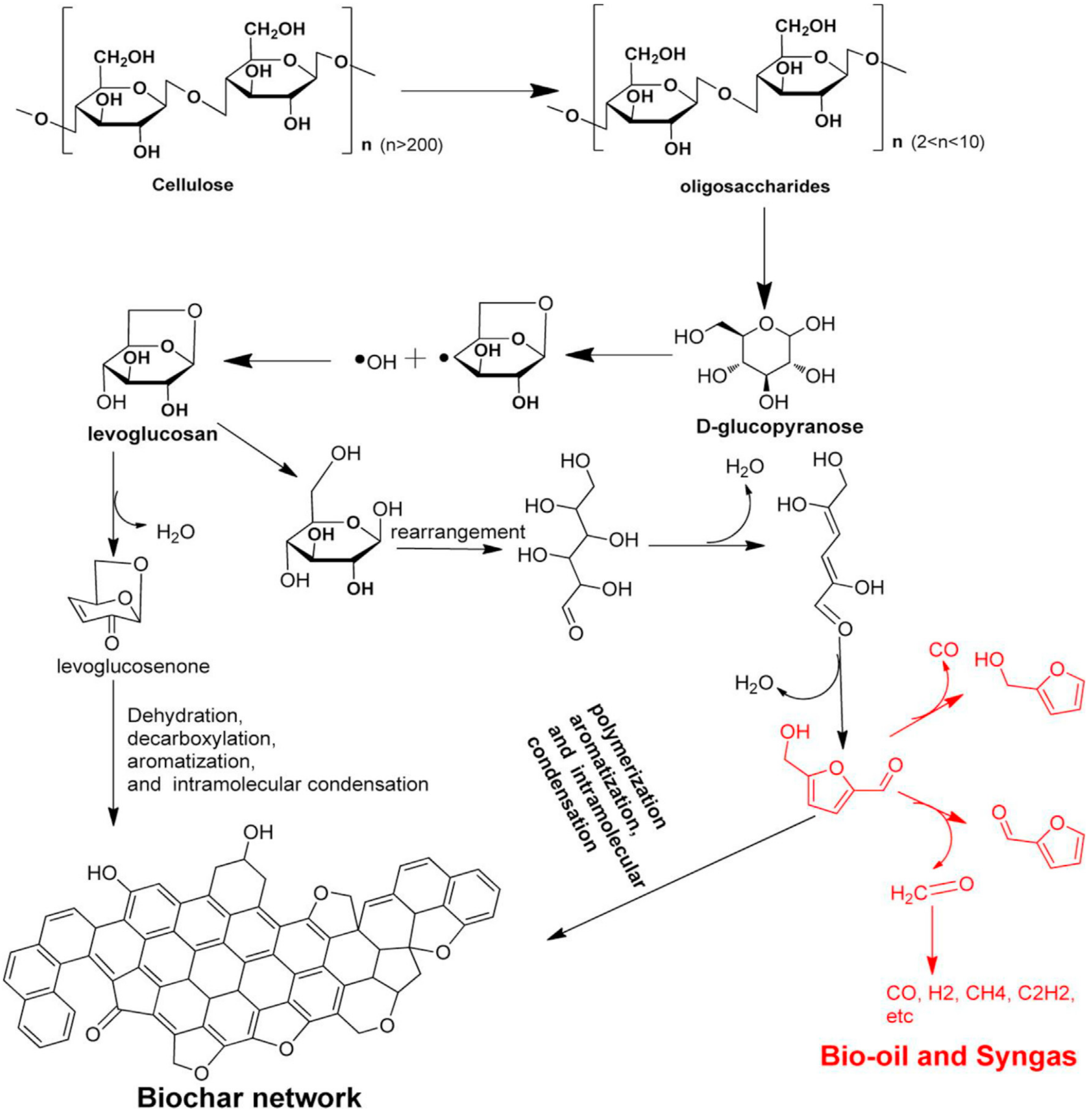
Hydrodeoxygenation of lignocellulosic fast pyrolysis into bio-oil as the main product (Benés et al., 2019), which can be further processed and integrated with crude oil products (Talmadge et al., 2014). The yield and composition of bio-oil can be dependent on the type of biomass choice and molecular structures of the biomass components (Mullen and Boateng, 2008). In general, biofuel resulting from the woody biomass pyrolysis often has high viscosity and heating values and low water content (Papari and Hawboldt, 2015). In contrast, bio-oil resulting from agricultural biomass (bagasse (Rabiu et al., 2018), rice straw (Maguyon-Detras et al., 2020), rice husks (Cai et al., 2018)) is typically known to have low viscosity, low heating values, and high water content (Isahak et al., 2012).

From a chemical point of view, bio-oil contains water and multiple types of organic compounds, including oxygenated chemicals (e.g., ketones, phenols, aldehydes, carboxylic acid), long-chain hydrocarbons, and lignin compounds (Oyebanji et al., 2018). Some of these components are primarily responsible for the low-quality bio-oil (e.g., strong corrosivity, low stability, low viscosity, low heating value), which restricts its long-term storage and utilization (Yang, Z. et al., 2015). Its main compounds, particularly oxygenated ones including aldehydes, ketones, and carboxylic acids, were found to be primarily accountable for such negative features (Ruddy et al., 2014). We need further advancement in the production processes and pathways to increase the quality of pyrolytic bio-oil and make it more appropriate for additive ingredients or bio-fuels as illustrated in Fig. 3.

Improving bio-oil production mainly involves tuning the pyrolysis process for catalytic cracking (Ibarra et al., 2016), hydrogenation (Reddy Kannapu et al., 2015), and steam reforming (Gil et al., 2016). The series of chemical reactions that can be employed for bio-oil quality improvements comprise, hydro-deoxygenation, catalytic cracking, aromatization, ketonization, and/or aldol condensation (Li, H. et al., 2018). It primarily involves these mechanisms in transforming the oxygenated compounds present in bio-oil into low-molecular-weight hydrocarbons and aromatic compounds, as well as syngas and hydrogen gas (Ro et al., 2018). Catalytic cracking strategies for bio-oil has to mainly designed for cracking C—C bond cleavage, scission of aromatic compounds' side chains, H-transfer, and deoxygenation in addition to isomerization reactions, such as dehydration, de-carbonylation, and decarboxylation (Shen and Fu, 2018). There is a need to anticipate the future for the biofuel industry that would be based on biomass gasification coupled with hydrogen enrichment like potential synergisms between biomass gasification and hydrogen production technologies (Patra and Sheth, 2019).

Hemicellulose accounts for around one-third of the total dry biomass, and it slightly differs from cellulose owing to its heterogeneous polysaccharide chains. However, pyrolysis behavior (Ben et al., 2019), mechanism (Yang, H. et al., 2020), and reaction pathways for hemicellulose (Huang et al., 2016), is quite analogous with those of cellulose according to a recent investigation (Yang, H. et al., 2020). As shown in Scheme 3, the pyrolysis of hemicellulose begins with the depolymerization of chemical structures, resulting in the formation of oligosaccharides (Shen et al., 2010). Then, the glycosidic bonds in the xylan chain are cleaved, which produce depolymerized compounds after rearrangement reactions (Li, L. et al., 2013). This finally turns into 1,4-anhydrous-d-xylopyranose and furfural, which act as intermediate products (Li, S. et al., 2020). These products undergo further rearrangement reactions through several complex pathways (e.g., dehydration, aromatization, decarboxylation, condensation, and finally, intramolecular rearrangement) (Liu et al., 2014). Yang et al. recently reported detailed reaction pathways for hemicellulose and their pyrolysis mechanism after studying the evolution patterns of the functional groups by using infrared spectroscopy equipped with two-dimensional perturbation correlation (Yang, H. et al., 2020).

Lignin is a third important component, a phenolic polymer that provides much mechanical strength and embedding structures; its structure made with lignin—carbohydrate complexes is more complex than hemicellulose and cellulose (Tarasov et al., 2018), which makes the pyrolysis mechanism complex (Kumar and Bhaskar, 2020). Unlike other components of biomass (hemicellulose and cellulose), the lignin pyrolysis mechanism needs free radical reactions are leading pathways (Custodis et al., 2014), and is the most prominent mechanism involved in the transformation lignin into either syngas, bio-oil, and biochar (Jiang, X. et al., 2018). As shown in Scheme 4, free radicals are formed by cleavage of β-O-4 linkages present in the lignin component (Chu et al., 2013), and this is the first stage in a lignin decomposition mechanism (Liu et al., 2015). Furthermore, generated free radical reactions captures protons from each organic species having weak O—H/C—H bonds (C_6H_5—OH) (Erfani Jazi et al., 2019), thereby generating organic products, such as 2-methoxy-4-methyl phenol, catechol, syringol, and vanillin (Kibet et al., 2012). In the time course of the reaction, it transports free radicals onto the rest of the organic species, thus leading to a series of chain propagation reactions (Kim et al., 2015). Lastly, such chain propagation reactions get terminated once two radicals collide with some other and form stable organic compounds (Shen, Y. et al., 2017). Though detecting such free radicals reactions during the lignin pyrolysis process is quite challenging (George et al., 2014), thus illustrating the lignin pyrolysis mechanism with great precision remained an interesting task. Therefore, a clear understanding of the free radical mechanism in the pyrolysis process is yet to be established (Meng et al., 2014), by uncovering



Scheme 2. The molecular mechanism proposed for cellulose pyrolysis and formation of biochar. Reprinted with permission from the reference (Liu et al., 2015). Copyright (2015) American Chemical Society.

minute details of the lignin pyrolysis mechanism.

Along with the three major components of biomass, inorganic content can also significantly influence the pyrolysis of biomass and the formation of biochar materials (Boscagli, 2018). On the other hand, Ca and Mg are bound to bind either covalently or ionically with complex organic molecules and to be lost in a later stage by vaporization at high-temperature conditions (Bourke et al., 2007). During pyrolysis, covalent bonds form among P, N, and S elements with organic compounds in the biomass, and the decomposition process subsequently occurs at low pyrolysis temperatures (Shen, Y. et al., 2017). The pyrolysis of biomass with inorganic constituents is also characteristically termed an autocatalytic process (Ferreira et al., 2019), particularly for alkaline earth and alkali metals Mg, K, and Ca, which cause important catalytic reactions during biochar formation (Jiang, Z. et al., 2018). Furthermore, potassium-containing biomass undergoes secondary cracking reactions, causing the subsequent breakdown of volatile organic compounds produced in the pyrolysis process (Bridgwater, 2012). The K-mediated catalytic reactions increase the formation of gaseous products, including carbon monoxide, carbon dioxide, hydrogen, methane, and ethylene, which facilitate the further cracking of biochar (Nuth et al., 2016).

On the other hand, in the case of lignocellulosic complex feedstocks, the autocatalytic pyrolysis process based on its intrinsic inorganic elements alone is not adequate to produce desired properties in biochar materials (Xiao et al., 2018). Using added catalytic agents or inorganic catalysts can enable the pyrolysis process at low-temperature conditions and short residence times (Santosa et al., 2020), and in effect, it also enables the direct preparation of nanocomposites or advanced hybrid materials useful in energy storage devices (Leng, J. et al., 2019). Further R&D is required to explore effective catalysts during the conversion of biomass components by tuning catalytic mechanisms to biochar materials with the desired porous structures and functional groups.

Thus, several studies have been devoted to the evaluation of catalysts in biomass pyrolysis (Imran et al., 2018), catalytic fast

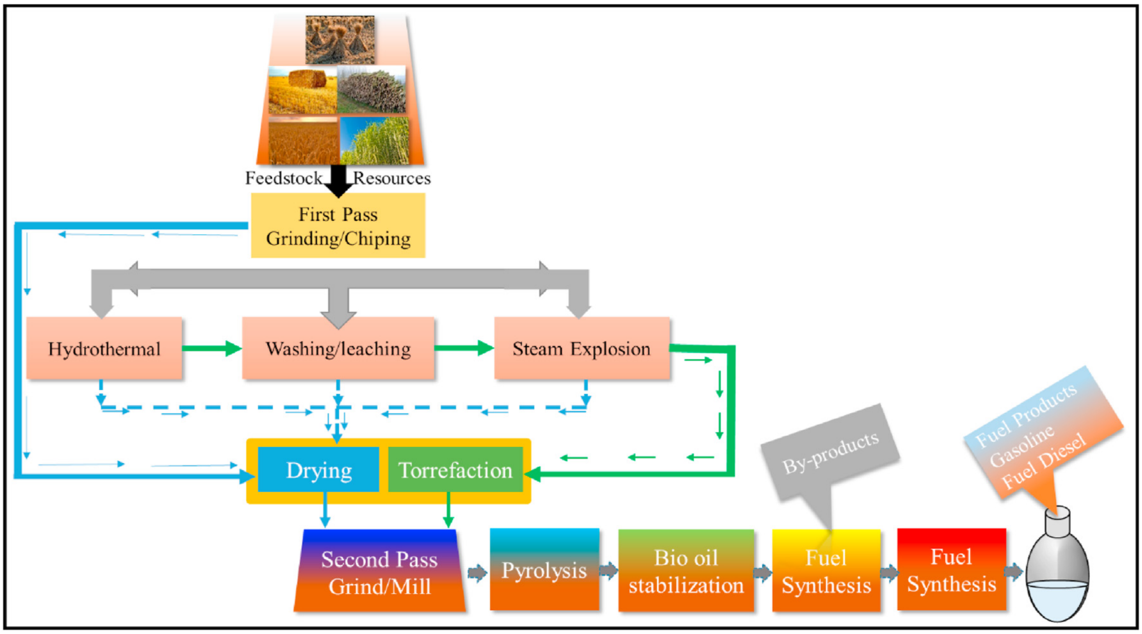
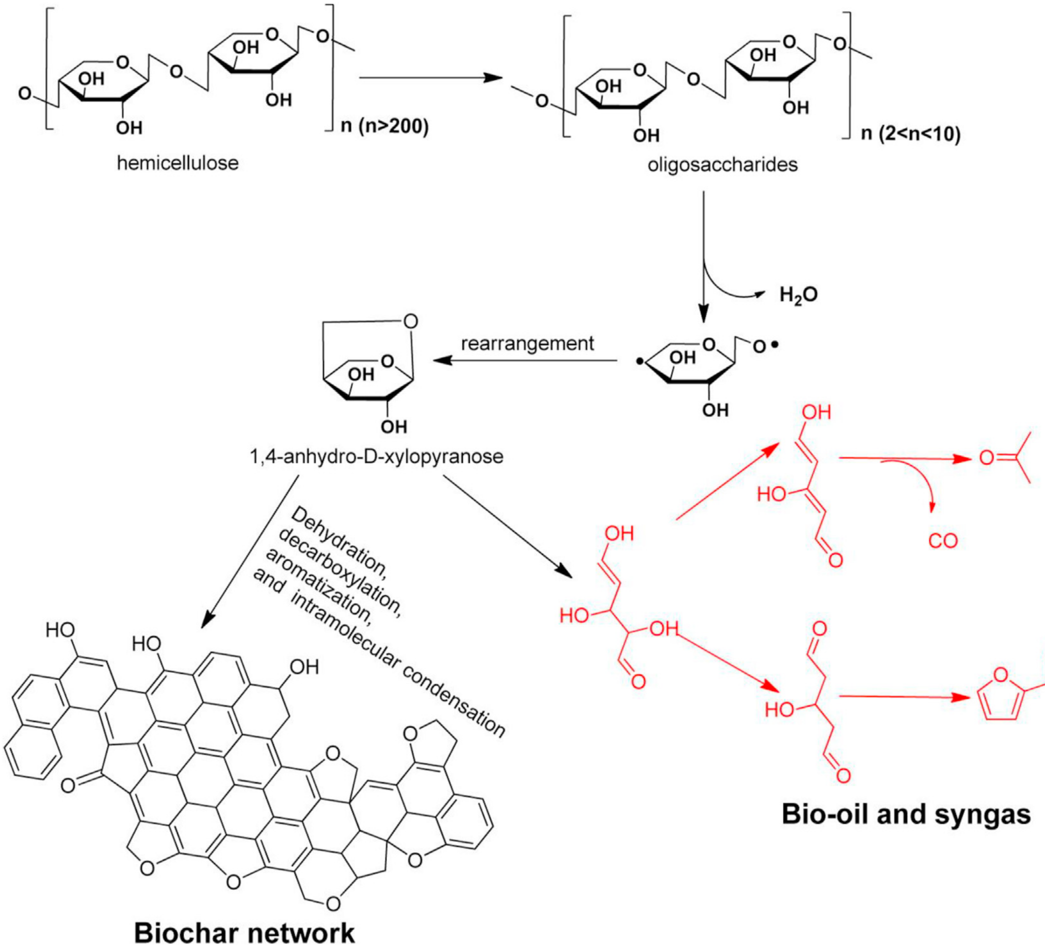
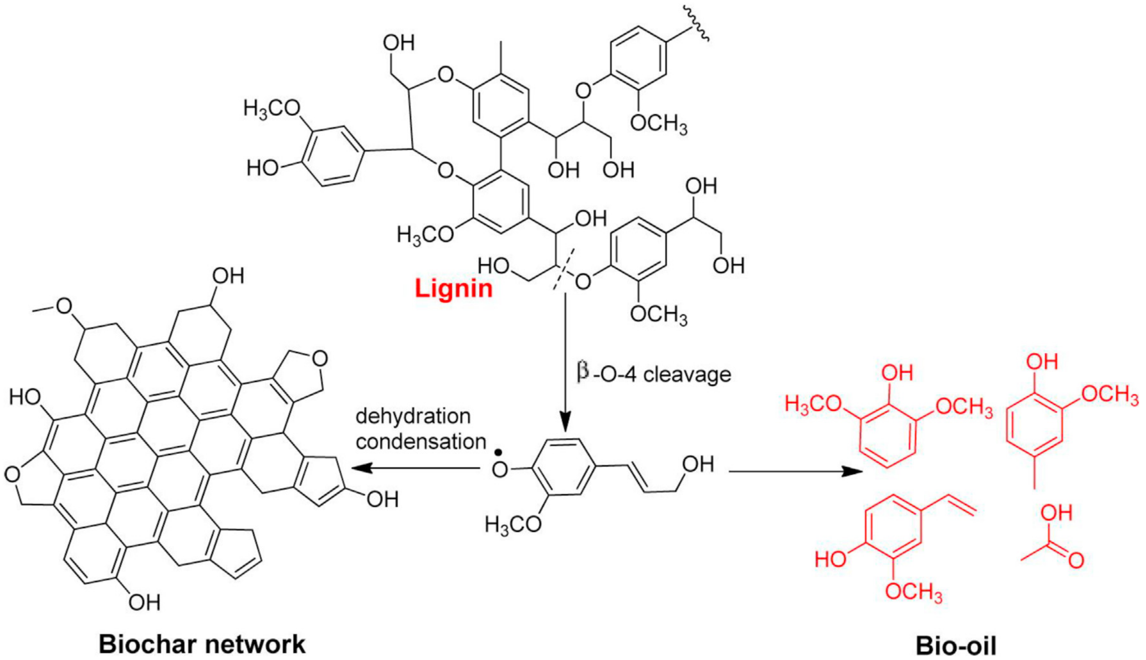


Fig. 3. Different pathways to produce renewable fuels from various biomass resources including harvesting, grinding or chipping or pelleting, pretreatments, drying, torrefaction, pyrolysis, upgrading, and fuel purification.



Scheme 3. The biochar formation mechanism for hemicellulose pyrolysis. Reprinted with permission from the reference (Liu et al., 2015). Copyright (2015) American Chemical Society.



Scheme 4. The biochar formation mechanism in lignin pyrolysis. Reprinted with permission from the reference (Liu et al., 2015). Copyright (2015) American Chemical Society.

pyrolysis (Lu et al., 2018), catalytic biomass pyrolysis (Samolada et al., 2000), and pyrolysis of biomass impregnated with inorganic metals (Lu et al., 2018). However, the main goal of this approach is the improvement of the effective and long-term stability of catalysts that are compatible with the vast range of intermediate decomposition compounds resulting in lignocellulosic biomass (Huang et al., 2017). It documents catalytic reactions in fast pyrolysis of organic materials as an effective and flexible method to transform available lignocellulosic materials into bio-fuel (Liu et al., 2014). Additional studies are essential for the development of effective catalysts appropriate for the transformation of organic materials into biochar with desired properties, including nanocomposites with high porosity and surface functional groups.

With the increasing demand for renewable energy and chemicals, alternative biomass sources have to be explored, and we should blend renewable fuels with the depleting petroleum-derived fuels and chemicals (Levi and Cullen, 2018). The emerging cellulose-to-ethanol industry can create large amounts of lignin-rich biomass called hydrolyzed lignin, which may be further utilized as raw biomass for pyrolysis and fuel formation (Kalyani et al., 2017). We consider lignocellulosic biomass is the most promising feedstock for sustainable fuels and biochemical products (Den et al., 2018). Hydrocarbon materials obtained from lignocellulosic materials are the most interesting products owing to their relationship with prevailing technologies and higher energy density (Liu et al., 2014). Therefore, converting lignocellulosic biomass into renewable and sustainable energy and fuels through fast catalytic pyrolysis has attracted much attention recently (Yaman, 2004).

4. Physicochemical characteristics of biochar

4.1. Structural and morphological characteristics of biochar

First, various waste produced in the manufacturing of beer, wine, sugar, flour, and vegetable oil and in the processing of wood, it must be characterized prior to pyrolysis to examine the composition/micronutrients (Islam et al., 2018), characterization of biomass wastes (Kwoczynski and Čmelík, 2021), and contamination of heavy metals and metalloids in biomass (Yan et al., 2020) and it may hampers the use of biochar in many sectors (Yao, Yan et al., 2015). The comprehensive structural and functional characterization of biochar materials have to be performed using different instrumentations, including field-emission scanning electron microscopy (FE-SEM) (Ma et al., 2016b), high-resolution transmission electron microscopy (HR-TEM) (Santhosh et al., 2020), inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Pourret and Houben, 2018), energy-dispersive X-ray (EDX) spectroscopy (Ma et al., 2016), Raman spectroscopy (Xu et al., 2020), Fourier-transform infrared spectroscopy (FTIR) (Singh et al., 2016), X-ray diffraction (XRD) (Shaaban et al., 2013), and many others as illustrated in Fig. 4. Recent advancements in characterization techniques and mathematical modeling (Ranzi et al., 2017), including dynamic TEM, aberration-corrected TEM, electron tomography, and *in-situ* XRD, have helped researchers to reveal the physicochemical characteristics of biochar, inorganic content stability, and the fate of biochar materials (Ranzi et al., 2017). Many other physical and chemical characterization techniques, including the X-ray photoelectron spectroscopy (XPS) (Singh et al., 2014b), Brunauer, Emmett, and Teller (BET) method (Angin and Sensöz, 2014), FTIR, and ICP-AES (Wang, J. et al., 2018), are possibly useful to characterize the surface area and porosity of biochar materials as summarized in Table 3. These methods can also be employed to examine the composition of surface functional groups, comprising OH, NH_2, COOH, and C=O (Fahmi et al., 2018), and mineral content (N, P, K, Mg, Ca, and S, etc.) (Xu, X. et al., 2014). Thermogravimetric analysis, micro gas chromatography, the BET method, and the use of N_2 as a sorbate gas are recommended for the characterization of surface texture and permeability features, including the porous structures (Yang, J. et al., 2020) and biochar surface area (Rafiq et al., 2016b). As an alternative to N_2 gas, CO_2 can also result better features at higher temperatures; thus, CO_2 adsorption-desorption isotherms are found to be more accurate values (Gargiulo et al., 2018), as the BET analysis of biochar (Castilla-Caballero et al., 2020).

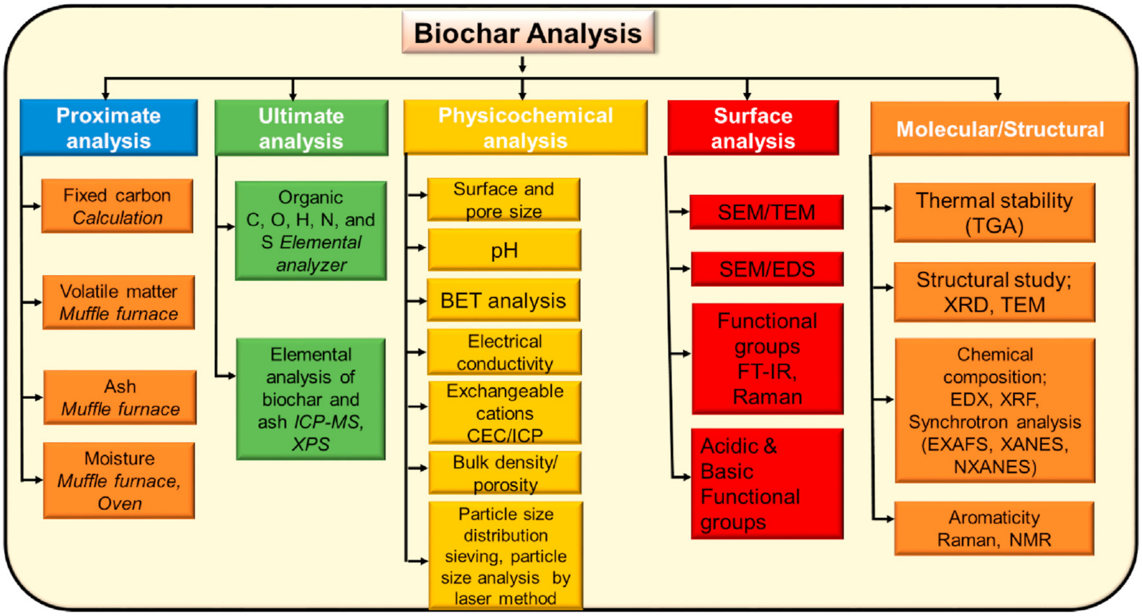


Fig. 4. Different instrumentation and methods used in physicochemical analysis including molecular structures, surface chemistry, proximate and ultimate analysis of biomass and biochar samples.

The BET equation can determine the surface area, while the microporous volume can be determined using the Dubinin Radushkevich (DR) equation to calculate the narrow microporous volume (Silvestre-Albero et al., 2012). The surface area of about 81 m^2/g of biochar produced using slow pyrolysis was found to be much higher than biochar produced using fast pyrolysis (Tomczyk et al., 2020), with well-developed pores with diameters of about 5–40 μm (Liu, Z. et al., 2017). In contrast, the fast pyrolysis of switchgrass resulted in biochar with a typical surface area of 7.5–8.1 m^2/g without a significant presence of porosity. For instance, the surface areas for biochar produced at a heating rate from 30 to 1000 °C/h were about <10 m^2/g at low-temperature about 450 °C. However, an increase in the surface areas of biochar was evidenced sharply by more than 400 m^2/g after the temperature reached 750 °C (Brown et al., 2006). They have reported the BET surface area values to range between 250 and 600 m^2/g as the pyrolysis temperature increases. The biochar materials surface area gets considerably influenced by the pyrolysis temperature but not totally dependent on the heating rate, as reported recently (Gai et al., 2014). These results showed that the high temperature during pyrolysis can cause the broadening of the microporous structures owing to the breakdown of adjacent wall pores, thus resulting in a reduction in microporous volume but an increase in overall surface area and porosity volume.

The biochar prepared using the wood logs of *Phyllostachys nigra* species was reported to have a lower surface area than that of cellulosic fibers owing to the differences in the precursor's biomass composition (Giudicianni et al., 2013). Indeed, this report further revealed that wood has two major components (i.e., hemicellulose and lignin) besides cellulose, which might inhibit the formation of porosity during pyrolysis (e.g., the cellulose fraction is likely to be entrapped in the compact matrix). Thus, surface analysis of activated biochar using BET can be used to reveal the total pore volume, microporous surface, and formation mechanism (Zhu et al., 2018). The results for empty fruits of oil palm indicated that fine particles showed a higher surface area than large biomass particles (Fahmi et al., 2018). Furthermore, this report described the “bottleneck phenomenon” where micropores enable the removal of possible obstructions present in the macroporous structures, like volatile compounds or ash materials. Similarly, the role of the ash content in the lowering surface area cannot be ignored, since it expresses this degree per gram of material (Giudicianni et al., 2014). Furthermore, to reveal this mechanism, a biochar sample was used to remove alkali-soluble inorganic species using 1 M NaOH solution. The washed biochar material showed the presence of negligible ash content, and despite an increase in the over-all pore volume and total surface area by ca. 30%, but values seem to be lower than those of biochar materials prepared using pure cellulose fibers (Gargiulo et al., 2018).

The first systematic structural analysis of carbon material was executed by (Franklin and Randall, 1951) using an XRD technique to examine different crystallites of carbon categorized into two classes. One was graphitizing carbon characterized as having a combination of sharp and narrow (002) XRD pattern reflection when tested after thermal pretreatment. It identified the other class, as non-graphitizing carbon that showed an XRD pattern with broad (002) reflection when tested after similar treatment. Several other reports have revealed additional details on the development of carbon structures like porous graphene-like carbon (Gomez-Martin et al., 2019), graphitic carbon structures (Harris, 2005), or graphitic carbon from the lignin (Tam et al., 2020), during graphitization and carbonization processes (Vázquez-Santos et al., 2012). A recently developed technique like TEM with the high spatial resolution has the potential to reveal graphitization behaviors precisely at the nanoscale level in non-graphitizing carbon materials (Meier et al., 2012). Subsequent research to determine the graphitization behaviors in carbon materials at the nanoscale supported the notion that there is no possibility of achieving either absolute non-graphitizing carbon or graphitizing carbon materials (Sharma, 2018). Non-graphitizing carbon would be an excellent precursor (biomass) for the synthesis of graphitic carbon crystallites by performing reactions during thermo-catalysis (Hata et al., 2002). For instance, raw biomass having lignocellulosic components converted into nano-structured graphitic carbon using catalytic iron carbide nanoparticles is produced in situ through the carbothermal reduction of the metal precursor iron nitrate (Thompson et al.,

Table 3
Various characterization methods reported in the literature for the analysis of biochar.

Characterization methods	Results	Remarks	References
Thermogravimetric analysis	Proximate analysis	Fixed carbon calculation	Torquato et al. (2017)
Muffle furnace	Proximate analysis	Volatile matter, ash content, moisture content	Domingues et al. (2017)
CHNS/O combustion analyzer	Ultimate analysis	Organic functional groups, O C, H,N, and S analysis, Elemental analysis	Bakshi et al. (2020)
Liquid chromatography	Ultimate analysis	Organic carbon detection	Hagemann et al. (2017)
ICP-MS	Ultimate analysis	Elemental content	Bachmann et al. (2016)
ICP-AES	Ultimate analysis	Elemental content	Mašek et al. (2020)
Potentiometric titrations	Ultimate analysis	Atomic ratios of O/C, H/C, N/C	Bakshi et al. (2018)
X-ray photoelectron spectroscopy	Ultimate analysis	types and contents of the functional groups	(Li, Pengwei et al., 2020)
Volumetric energy density	Ultimate analysis	Calorific value	Abdullah and Wu (2009)
SEM-EDX	Ultimate analysis	Elemental content of biochar	Stella Mary et al. (2016)
FESEM	Surface analysis	Morphology of biochar surfaces	Williams et al. (2018)
XPS	Surface analysis	Surface functional groups	(Singh et al., 2014b)
(Brunauer-Emmett-Teller) method	Surface analysis	BET surface area (m^2/g)	Fahmi et al. (2018)
Polanyi theory	Surface analysis	Pore volume (cm^3/g)	Sigmund et al. (2017)
Dubinin-Radushkevich method	Surface analysis	Micropore volume (cm^3/g)	Hamzenejad Taghlidabad et al. (2020)
(Brunauer-Emmett-Teller) method	Surface analysis	Average pore width (nm)	Kwiatkowski and Kalderis (2020)
FTIR	Surface analysis	Functional group	Stylianou et al. (2020)
Zeta potentials analyzers	Surface analysis	Zeta potentials	Long et al. (2019)
Contact angle system precision tensiometer	Surface analysis	Contact angle measurements	Batista et al. (2018)
13C solid-state nuclear magnetic resonance spectroscopy	Structural analysis	Chemical structures of insoluble materials	Fu and Jiang (2019)
Synchrotron-based techniques	Structural analysis	Oxidation states of biochar	Lombi and Susini (2009)
X-ray Diffraction	Structural analysis	Polyaromatic carbon crystallite analysis	Yoo et al. (2018)
Electron Energy Loss Spectroscopy	Structural analysis	Carbon and nitrogen speciation	Hagemann et al. (2017)
Raman spectroscopy	Structural analysis	Structure stability of carbon	Sousa et al. (2020)
1H solution nuclear magnetic resonance spectroscopy	Molecular analysis	Presence of hydrocarbons, acetic acid, ketones, alcohols, esters and phenolics	Salami et al. (2020)
13 C magnetic resonance spectroscopy	Molecular analysis	aromatic carbon, aliphatic carbon,	Xu, D.Y. et al. (2014)
GC/MS	Molecular analysis	Identification and quantification of pyrolysis products specified for each chemical group.	Rombolà et al. (2016)
Fourier transform ion cyclotron resonance mass spectrometry	Molecular analysis	Molecular characterization of biochar	Zhang, P. et al. (2020)
Excitation-emission matrix fluorescence spectroscopy		Dissolved organic matter released from biochar	Gao et al. (2020)
Electrospray ionization fourier transform ion	Molecular analysis	Molecular characterization of biochar	Smith et al. (2013)
Cyclotron resonance mass spectrometry	Molecular analysis	Characterization of biomass and biochar	Aubriet et al. (2018)

2015). In addition to XRD, TEM and Raman spectroscopy are also sensitive techniques to examine the evolution of structural features from less-ordered to graphitic carbon, and they are most suited to monitoring the growth of tri-periodic order during the graphitization of carbon fibers (Vázquez-Santos et al., 2012).

The characterization techniques that reveal carbon nanostructure, particularly HR-TEM and XRD, are most reflective of such regions where aromatic fringes are assembled (Martin et al., 2019). Furthermore, this report revealed that applications of both mass-spectrum and HR-TEM are typically found consistently with unceasing curved molecular and nanostructures at layer arrangement regions. These techniques are sensitive and useful for understanding aromatic network-like structures regarding the arrangement perspectives and are not applicable for examining single layers (Xiao and Chen, 2017). Onion-like multi-walled graphitic structures of charcoal was also observed (Hata et al., 2000), Raman-

HR-TEM study reported structural analysis of carbonized wood (Deldicque et al., 2016), and microstructure of wood charcoal was by using scanning probe microscopy (Kurosaki et al., 2003). Such curved nanostructure of wood charcoal was also similar to that of sucrose char prepared at 1000 °C in an oxygen-free environment; the morphology and arrangement of fringes were identical to the curved isotropic and low-degree of fringes curvature with an anisotropic arrangement under identical conditions (Harris, 2005). In the HR-TEM, one can see evidence of the assemblage of aromatic layers networking via van der Waals forces. The important observation to be noted that is where a decrease in C—C bond length was reported as the increase in the pyrolysis temperatures from 500 to 700 °C, representing that after the aliphatic-carbon converts into aromatic-carbon (Xiao and Chen, 2017). Thus, such structural characterization techniques are sensitive to examine biochar for quaternary structure, including graphene-like fringes, aromatic clusters (nano-, macro-sized), heterogeneous phases, and atomic arrangement. Such physicochemical characteristics have to be subtly understood to improve our anticipation over molecular structures of biochar, which would upsurge the development of novel functionalities and assist to make a well-defined molecular, structural, and functional guide for developing potential applications for biochar materials.

Many scientists have now studied the pyrolysis of biomass and their decomposition on the basis of three main biomass components (Pasangulapati et al., 2012), effect of the biomass components (Burhenne et al., 2013) like lignin, cellulose and hemicellulose (Qu et al., 2011), Thermogravimetric analyzer (TGA) (Ambalae et al., 2006), kinetic analysis (Vuppaladadiyam et al., 2019) and density functional theory are frequently employed techniques (Wang, Q. et al., 2020). Most of them studied the dry weight mass loss characteristic feature in a continuous mode for biomass samples using the TGA to realize pyrolysis mechanisms for various biomass. Alternatively, the mass loss in overall biomass samples determined by TGA analysis usually ranges from less than that of 15—20 mg (El-Sayed and Mostafa, 2015), when the solid waste from municipal and industrial are complex in nature (Abdel-Shafy and Mansour, 2018) and distribution of their components and shapes are also uneven (Zhou et al., 2014). Thus, it may be challenging to keep consistency in TGA results and product quality from such biomass samples. Therefore, kinetics of pyrolysis, thermal decomposition behavior and catalytic pyrolysis studies (Wang, L. et al., 2018), and some other factors have suggested conducting using fixed-bed reactor (Aguiar et al., 2008), for three main components of biomass (Burhenne et al., 2013).

To obtain highly reproducible results for individual biomass samples or in mixtures, a fixed-bed reactor has recently developed by researchers and was equipped weight-function in a real-time analysis called macro-TGA system (Zhou et al., 2015). That report further reveals that the mass loss of a biomass sample determined by macro-TGA can be accurate and was in the range from 0.5 to 4 g, that allows us to examine thermal decomposition pattern of pristine biomass samples also in their mixture similar way to that of conventional TGA measurements. We recommend thermal treatment of biomass samples in addition to some other treatments including combustion, pyrolysis, and gasification with CO_2 for specific biomass components that can be conducted to obtain essential data with or without the simulation system mounted. Field and laboratory-scale experiments with precise focus on ignition and pyrolysis in addition to sufficient depiction of physics-centered modeling and fuel characteristics are required for improved understanding of the combustion process. In future studies, there is a need to focus on the detailed assessment of thermal decomposition in both settings an oxidative atmosphere and an inert environment using macro-TGA.

Besides this further examination of biomass components using series of simulation in a five-component model (cellulose, hemicellulose, pectin, lignin, and starch) and in comparison with three biomass model (cellulose, hemicellulose, and lignin components) needs be directed for vast ranges of biomass samples while comparing and understanding pyrolysis of biomass components' and their combustion behaviors using macro-TGA (Meng et al., 2015) and their pyrolysis characteristics using conventional TGA (Long et al., 2017). Long et al. compared combustion and pyrolysis characteristics with differential thermogravimetric (DTG) (wt %/°C) and thermogravimetric (TG) (wt %) curves of the various biomass components and orange peel, Chinese cabbage, and poplar stem with TGA and macro-TGA, respectively (Long et al., 2017). They revealed the fate of VM, and fixed carbon and finally compared corresponding to the proximate analyses for various biomass samples (Table 4). The fixed carbon and ash are most present in the lignin component is most, while VM is least, and hemicellulose content is in between to those of lignin and cellulose (Demirbaş, 2003). However, proximate analysis of hemicellulose is found to be close to those of the pectin component (Zhou et al., 2017), wherein ultimate analysis shows it to be significantly more like cellulose and starch (Gunnarsson et al., 2008). These results correspond to the alkaline process where sulfur content in lignin components is higher than those in other components (Arapova et al., 2020). Other report revealed that the correlations that are in accordance with proximate analysis, usually offer a cost-effective analysis (Kieseler et al., 2013), however, are liable for less accuracy as compared to the correlations that are based on the ultimate analysis.

Long, Y. et al. report further revealed that the VM is most present in starch and cellulose and that their proximate analyses were identical; results agree with starch and cellulose having identical biomass components, wherein glucose compounds get attributed via $\beta(1 \rightarrow 4)$ and $\alpha(1 \rightarrow 4)$ linkages, respectively. Arapova et al. further described the basic principles involved in the application of microwave technology and their precise stimulation to understand the decomposition of the lignin structure, to ease the conversion of lignin-rich biomass into biogas (Arapova et al., 2020). The proximate and ultimate analysis (weight %) reported for lignin-rich pine biomass and their several biochar samples during the increase of carbonization temperature from 300 to 1000 °C (Yoo et al., 2018). A recent report has developed an analytical technique to perform a proximate analysis of *Chlorella vulgaris* and *Spirulina platensis* algal biomass samples (Jabeen et al., 2020). That report suggested a three-step procedure: a thermogravimetric analyzer (TGA)-based method for the proximate analysis estimating fixed carbon and VM at 600 °C and in the air for determining ash content. The ultimate analysis summarized for various biomass samples corresponds to the aforementioned reports for proximate analysis of various biomass samples (Table 5). The pyrolysis of main biomass components can analyze using TGA curves, however, derivative or DTG curves are highly sensitive than that of the TGA curves. El-Sayed and Mostafa, we can perform the DTGA measurement in either non-isothermal or isothermal settings; the prior method is known for their advantages such as short measurement time, and fewer data sets processing, as well as decomposition kinetics, can be explored over a full temperature range around-the-clock and thus, reduces the experimental errors caused during thermal initiation time. Therefore, most investigators adopt a non-isothermal system to examine the decomposition kinetics of biomass materials. It is thought that, the pyrolysis system will be in a solid—liquid phase when temperature reach higher than that of the melting point called ternary eutectic (~400 °C).

While considering the amplification of the changes in the TGA curves for highlighting the differences in repeated experiments for

Table 4
Proximate analysis (dry basis wt%) reported for various types of biomass.

Sample	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)
Blackbutt wood (Wilson et al., 2018)	5.3	79.5	18.9	1.6
Camellia oleifera shells (Fan et al., 2017)	–	74.68	21.95	3.37
Wheat stem (Wilson et al., 2018)	2.4	71.4	17.7	10.9
Timothy grass (Nanda et al., 2012)	5.6	78.2	12.6	3.6
Rice husk (Yao et al., 2016)	2.3	67.69	16.10	16.21
Cotton stalk (Yao et al., 2016)	4.7	66.04	18.67	2.72
Pruned plum (Voća et al., 2016)	7.10	69.75	21.07	2.10
Pinewood (Nanda et al., 2012)	6.8	71.7	19.2	2.3
Poplar wood (Kieseler et al., 2013)	–	81.9	17.0	1.1
Microalgae (Hossain et al., 2017)	85	67.3	24.8	3.2
Sewage sludge (Gao et al., 2017)	6.30	54.06	7.80	31.84

Table 5
Ultimate analysis (dry basis wt%) reports corresponds to the proximate analysis summarized for various types of biomass.

Sample	C (%)	H (%)	N (%)	S (%)	O[a] (%)
Blackbutt wood	48.9	6.60	0.10	0.3	44.20
Camellia oleifera shells	47.21	5.45	0.43	0.17	46.74
Wheat stem	47.4	6.70	0.20	0.2	45.50
Timothy grass	43.4	6.10	1.30	0.1	45.40
Rice husk	41.76	5.24	0.30	0.08	36.30
Cotton stalk	44.2	5.66	065	0.20	46.49
Pinewood	48.9	6.2	0.10	0.10	42.50
Poplar wood	48.6	6.5	0.1	0.1	43.6
Microalgae	46.3	6.9	7.3	2.3	32.6
Sewage sludge	35.16	5.44	5.61	–	15.64

[a] Oxygen by difference.

different biomass samples (Long et al., 2017). Differential thermal gravimetric analysis (DTGA) is an analytical method that determines the degree the weight gain or weight loss of biomass material as the effect of temperature and also can be used to determine kinetic parameters (El-Sayed and Mostafa, 2014). At this point, overall mass loss is an sign of emission of volatile compounds starts approximately from 230 to 390 °C, which is also known as a devolatilization temperature (Fermoso et al., 2010). Some research accounts provided state-of-art approaches to achieve precise devolatilization of biomass fuels and biomass components (Biagini et al., 2006b), devolatilization of secondary fuels (Biagini et al., 2004), and also devolatilization behavior and pyrolysis kinetics (Jeguirim et al., 2014).

Devolatilization is the initial step and central mechanism in almost all thermal processes and also forms a huge amount and diverse range of gaseous volatile species and the final product called solid carbon residue (Janković et al., 2020). In some of the reports, devolatilization of biomass samples of different composition, properties, and origin suggested studying in a combination of TGA and infrared spectroscopic measurements. Different gas products (including CO_2, CO, CH_4, HCOOH, CH_3OH) are released in addition to these more complex organic compounds (oxygenated and hydrocarbon) since the broad range of volatile species get released simultaneously in a narrow temperature range (Biagini et al., 2006). The basic reasons for mass loss and devolatilization of biomass are greatly dependent on their chemical components; therefore, the validating results and correlation permits us to predict devolatilization behavior, plant designing, handling, and real-world applications, as well as kinetics and modeling of data sets (Grønli et al., 2002). This report further describes that the understanding of the devolatilization kinetics may aid us considerably in improved planning for central industrial processes since pyrolysis mechanisms are not only non-dependent thermos-conversion technologies but also are part of the conventional combustion and gasification processes. Thus, TGA should be systematically employed for the examination of the devolatilization behavior for several kinds of biomass samples, including a range of wood and agroforestry residues (Ballice et al., 2020). However, researchers should consider main objectives in order to quantify the variations between both softwoods and hardwoods (Kim et al., 2007), with different quantities and chemical components, in addition to determining the involvement of particular mechanism, corresponding devolatilization reactions, together with sets of kinetic considerations such as coefficient of reaction rate and activation energy (Pecha et al., 2019). Thus, in-situ or online monitoring of technical data can help researchers discover in-detail the mechanism of pyrolysis, characteristics of complex lignocellulosic biomass, and their performance during the pyrolysis process (Chen et al., 2020). Therefore, future work must focus on *in-situ* or online monitoring systems and characterization techniques using TGA coupled with FTIR–MS (Gao et al., 2013) and pyrolysis equipped with GC/MS (Gu et al., 2013) or other modern characterization methods based on synchrotron-based X-ray absorption includes near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Lehmann et al., 2005), 2D NMR analysis of biomass and biochar (Le Brech et al., 2015) and solid-state 13C NMR spectroscopy (Baccile et al., 2014).

In addition to the techniques mentioned above, some in-depth characterization techniques are now available for researchers (Halleraker et al., 2020) that can be used to identify fine structural differences in biochar (Igalavithana et al., 2017). For instance, a solid-state 13C NMR could be widely applicable for comparing resonance peaks based on the total resonance intensity and provides information about the relative number of individual functional groups in biochar produced at different pyrolytic conditions (Li, X. et al., 2013a). A solid-state 13C NMR technique is likewise useful to examine influence of feedstock and pyrolysis temperature on biochar carbon chemistry (McBeath et al., 2014), differences between the carbon structures and biomass samples at different heating rates and temperature conditions (Cimò et al., 2014). Furthermore, 13C NMR results can be successfully used to demonstrate that carboxyl C structures and O-alkyl C disappear when the temperature approaches from 300 to 400 °C, whereas alkyl C signals turn stronger can be a good indicator of successful pyrolysis (Chen et al., 2014). However, the evolved alkyl C signal has to disappear at higher pyrolytic temperatures (500 °C), and more aromatic carbon structures have to appear studied using fast field cycling NMR relaxometry method (De Pasquale et al., 2012). These studies can be used to reveal that the aromatic carbon structures in the main biochar product form after reaching a pyrolysis temperature higher than that of 500 °C. A solid-state 13C NMR can be similarly applied to analyze biochar stability, especially in natural settings like the soil (Kan et al., 2020), since there is a strong relationship between biochar stability and degree of aromatic carbon condensation and the initial non-aromatic carbon content (Leng, Lee et al., 2019).

In a previous study, stable biochar samples were successfully obtained from a diverse range of biomass feedstocks and validated using a solid-state 13C NMR technique (Singh et al., 2012). They reported the aromatic carbon forms in biochar at 400 °C to be less stable than that of the biochar prepared at 550 °C. After evaluating literature available on 13C NMR data (Ben and Ragauskas, 2011) and the behavior at the interface between the biochar and soil minerals, the average self-life of the carbon in biochar amended soil (Yang, F. et al., 2016) may vary from 90 to 1600 years owing to the degree of aromatic carbon.

Fig. 5 shows the 13C NMR spectral data for biomass materials and their respective biochar produced using increasing pyrolysis temperature conditions. The cross-polarization magic angle spin for biochar obtained at 200 °C revealed the resonance for alkyl C at $\delta = 0-45$ ppm, for C of O-alkyl at $\delta = 45-110$ ppm, and for C of carboxyl at $\delta = 160-190$ ppm, that were normally allocated to lignin, cellulose, and hemicellulose components, respectively (Baldock and Smernik, 2002). These results postulate that the pyrolysis of biomass cannot be accomplished completely in low-temperature condition (200 °C). The C of carboxyl and O-alkyl carbon structures disappears as increases temperature from 300 to 400 °C. Lastly, as the pyrolysis temperature increases further up to 500 °C, the alkyl C structures in the biochar start getting cracked, forming carbon-rich aromatic structures at about $\delta = 128$, ppm (Chen et al., 2014). Thus, the results and previous reports confirm that aromatic C is the major component of stable biochar materials that have to be mass-produced at or above 500−600 °C (Zhao et al., 2013).

The use of various techniques collectively can provide a viable strategy to define pyrolytic parameters more accurately and better clarify the pyrolysis mechanism and performance of complex lignocellulosic biomass during the thermochemical reaction (Mourdikoudis et al., 2018). The clarification of different pyrolysis mechanisms may fill information gaps and provide new scientific understandings regarding the behavior of the specific chemical components (Liu, W.-J. et al., 2017). Thus, researchers need to use these suggestions to establish more effective pyrolysis methods for vigilant and well-organized conversion of biomass feedstocks while simultaneously avoiding the formation of undesired biochar.

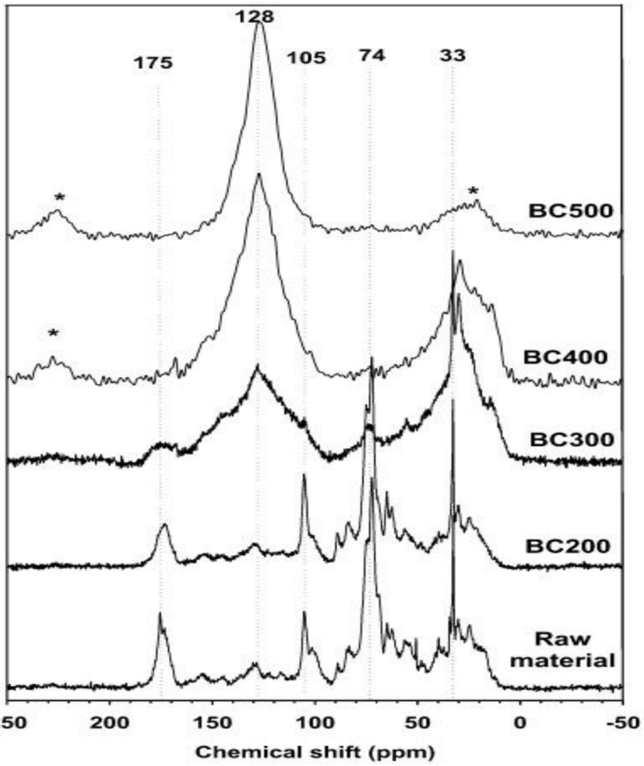


Fig. 5. 13C NMR spectra showing cross-polarization magic angle for biomass materials and biochar produced at increasing pyrolysis temperature. Elsevier B.V Copyright 2014. Reprinted with permission from Reference (Chen et al., 2014).

4.2. *Surface chemistry of biochar*

The main postulation for the desired properties of biochar has been those of large specific surface area (Li, Pengwei et al., 2020), excellent ion exchange capacity (Munera-Echeverri et al., 2018), and resultant surface chemistry prominent to provide high-performance sorption capacity for soil nutrients (Yao et al., 2012), organic and inorganic pollutants (Abbas et al., 2018), and gaseous pollutants (Chen et al., 2015). Biochar formed at higher temperature ranges is likely to have more chemical and biological recalcitrance, which is an important property to present as a potential candidate for carbon sequestration by introducing into the environment or soil (Yang, Gan et al., 2015). However, with pyrolysis at high temperatures, biochar loses its surface functionality owing to more aromatic condensation reactions (Fang, Q. et al., 2014). Therefore, biochar produced at lower and moderate temperatures (400−600 °C) has the possibility of having a diverse range of surface functionalities (Banik et al., 2018). The biochar surface chemistry varies considerably owing to the highly heterogeneous nature of biochar depending on both unstable and stable C composition (Batista et al., 2018). The critical impact of surface behaviors of biochar materials originates basically from the surface chemistry, which typically shows a variety of hydrophobic and hydrophilic functionalities, usually in basic and acidic environments (Ebrahimzadeh Omran et al., 2020). The appearance of chemical bonds in the decomposed biomass during pyrolysis leads to the development of various surface functionalities (Tomczyk et al., 2020), including hydroxyl, $-OH$; amino, $-NH_2$; carboxyl, $-((C{=}O)OH)$; nitro, $-NO_2$; ester, $-(C{=}O)OR$; ketone, $-OR$; aldehyde, $-((C{=}O)H)$. This occurs predominantly on the external surfaces rather than on pore surfaces (Xiao et al., 2018). The heterogeneous nature of biochar surface can be attributed to the complexity of surface chemistry, which in turn, affects its interaction with a broad range of inorganic elements and organic compounds present in the environmental sites (Kharel et al., 2019). In addition, soil nutrients like N, P, K, and S are integrated into the stable C portion and porous structures of biochar materials result into surface heterogeneity because of differences in electronegativity between the aromatic carbon and the heteroelements (Shen, Z. et al., 2017).

Some of other modern techniques are useful for biochar characterization (Amin et al., 2016), surface chemistry of activated carbons includes, potentiometric titrations (Salame, II and Bandosz, T.J., 2001), and temperature-programmed desorption (TPD) studies (Chunfei et al., 2012). To build deep understanding of the surface chemistry of biochar materials (Xiao et al., 2018), physiochemical properties (Jian et al., 2020) and the diverse range of surface functionalities and their composition demands comprehensive studies on biochar materials. TPD and various titration methods are useful for the detection of specific functional groups (Salame, I. and Bandosz, T., 2001), typically for nitro groups that appear deep in the carbon matrix owing to nitration during the oxidation in the presence of HNO_3. The surface functionalities depend on the pyrolysis conditions, the choice of starting biomass, and the use of slow pyrolysis vs. fast pyrolysis (Fahmi et al., 2018). Functional groups containing oxygen, especially carboxylic and hydroxyl functional groups, are known to dominate the biochar surface area produced using fast pyrolysis and are modest for biochar derived by slow pyrolysis (Brewer, C.E. et al., 2009). However, biochar derived from slow pyrolysis is known to result in aromatic C—H functional groups with much greater abundance than that derived from fast pyrolysis. An out-of-plane band characteristic of the aromatic C—H bending mode was also reported between 600 and 1000 cm^{-1} as the pyrolysis temperature progresses further (Keiluweit et al., 2010). If the bands in the FTIR spectra related to oxygen show reduced intensity, this indicates excessive pyrolysis; this is due to the elimination of oxygen-containing groups (labile functional groups), which are typically anticipated at high pyrolysis temperatures (Saha et al., 2019).

Physicochemical properties that can influence the dominance of biochar products as a soil amendment products include surface area, surface charge, porosity (Baltrėnaitė-Gedienė et al., 2020), anion and cation (AEC (Lawrinenko and Laird, 2015) and CEC (Hailegnaw et al., 2019)), and inorganic nutrient content (Mao et al., 2012). The oxygen-containing functional groups present onto the biochar surfaces (Fan et al., 2018), especially carboxyl functional groups (Uchimiya, M. et al., 2012), which are known to play a key role in forming biochar with desired physicochemical properties (Chatterjee et al., 2020), implications for environment (Semida et al., 2019), and soil amendment (Wang, L. et al., 2020), and sustainable agriculture applications (Lee et al., 2010). The carboxyl group density on biochar surface decreases as the pyrolysis temperature increases (Wang, D. et al., 2013), however, the surface carboxyl's content onto various types of biochar remains identical owing to the expansion in surface area at high biochar-producing temperature (Yakout, 2017). Unpredictably, for carboxyl groups, the dissociation pH property covers a broad range of pH values (2—11), on the biochar surfaces owing to the diverse structural micro-environments and chemical phases (Chen, Z. et al., 2015). Various studies have shown that carboxyl groups determine the overall performance of biochar materials as a soil amendment agent (Uchimiya, Minori et al., 2012); these have reported that the surface sites are those involves in ion-exchange, modulation of the release and uptake of inorganic nutrient ions present in the soil (Ding et al., 2016), thus promotes crop growth (Mao et al., 2012). Protonation and/or deprotonation of the existing carboxyl groups (Safari et al., 2019), directly govern the biochar's pH buffering capacity (Chen et al., 2015) and helps to modulate soil pH (Yuan and Xu, 2012). In addition, the dissociation of surface charges from carboxyl groups corresponds to the capacity of particulate biochar to transport in soil and disperse into water (Wang, D. et al., 2013). Several reports specified that the free radicals and redox properties of biochar surfaces (Klüpfel et al., 2014), corresponds to the overall content of oxygen-containing species (quinone moieties and phenolic moieties) (Prévoteau et al., 2016) and condensed aromatics (Faheem et al., 2020), which can thus influence the bio-geochemical cycles (Odinga et al., 2020) and plant-algal toxicity (Liao et al., 2014).

To identify the mechanism of biochar specifically, it is an ongoing necessity to understand the recent developments and fate of carboxylic groups on surfaces of biochar to measure the dissociation constants and chemical states, which are the important factors to optimize the formation and applications of biochar products (Li, J. et al., 2020). The molecular functional groups like oxygen-containing carboxyl and hydroxyl groups and dynamic aromatic structures of biochar are diverse and mainly can be influenced by pyrolysis temperatures (Zhou et al., 2019). Biochar undergoes substantial transitions in terms of physical-chemical reactions as the pyrolysis process progresses (Keiluweit et al., 2010); for example, the lignocellulosic H-bonding (OH···O) network was fragmented, and the primary free hydroxyls groups get oxidized into carboxyls at the pyrolysis temperature of approximately ≤500 °C (Harvey et al., 2012). Biochar materials develop nano-scale pores, with increased surface area and dehydrogenated methylene groups ($R{-}CH_2{-}R = R{=}CH{-}R = R{\equiv}C{=}R$) to make dynamic molecular structures with correspondingly more condensed porosity at high temperatures (Chen et al., 2008). The surface functionalities and nano-scale porous structure present on biochar surfaces may influence carboxylic groups by being involved in making their chemical transitions, dissociation properties, and molecular structural micro-environments (Lian and Xing, 2017). Therefore, it would be quite useful to gain deep comprehensive understanding regarding quantitative characteristics of carboxyl groups on the compositional and molecular structures of biochar products.

So far, it has been a great challenge to identify contents comprehensively, including the dissociation constants (pKa) and chemical transition of carboxyl groups present on the solid biochar surfaces using any single characterization technique. Mukherjee et al. used Boehm titration to investigate the surface chemistry of biochar prepared using wood species like *Pinus taeda*, *Quercus lobata*, and grass species *Tripsacum floridanum* at different temperature conditions, of 250, 400, and 650 °C (Mukherjee et al., 2011). Boehm titration is a characteristic acid-base titration technique specifically established to determine the content of organic acid functional groups organic acids (carboxylic acids, phenols, humic-like substances) present on surfaces, quantifying the amount of NaOH, Na_2CO_3, and $NaHCO_3$ consumed by biochar particles (Tsechansky and Graber, 2014). An acid-base titration is applicable even to quantify the dissociation properties of acid/base groups present on the solid surface, especially activated biochar/carbon, but has some methodological limitations while considering the pH-dependent deprotonation/protonation of acid/base functional groups (Konkena and Vasudevan, 2012; Strelko et al., 2002; Wang et al., 2004). An acid-base titration is applicable to determine specific pKa values of the carboxyl groups present on the biochar surfaces (Li, M. et al., 2014), however, their dynamics with pyrolysis temperature conditions still remained unknown. Moreover, surface characteristics of carboxyl groups are challenging to be understood just by performing acid-base titrations (Xiong et al., 2021). Ex-situ and in-situ infrared spectroscopic studies are also effective for analyzing functional groups present on the solid biochar surfaces (Uchimiya et al., 2013), including COOH, COO−, and some other surface functionalities, such as C—O—C, $-CH_2$, and aromatic bonding C═C (Uchimiya et al., 2013). Attenuated total reflectance (ATR) FTIR of fulvic acid humic acid can be monitored under different pH conditions to identify carboxyl groups present on humic acid substances and also their dissociation pH states (Lumsdon and Fraser, 2005). As carboxyl groups can form ester bonds and/or hydrogen bonds with hydroxyls that usually get broke under alkaline environments (Chen, Wu et al., 2019), monitoring the dissolved organic carbon results from biochar with the influence of pH change (Smebye et al., 2016), may also help to distinguish carboxyl groups present on biochar materials and products (Li, Xu et al., 2013b).

A better understanding of the surface chemistry and functional groups of biochar is also important to identify the pyrolytic transformation with the transformational dynamics and the stability under different environment conditions (Li, X. et al., 2013a). In addition to the simple carbon structures, in most common N/O-containing functional groups, stability, and transformation are of great significance in the development of novel biochar materials and their applications (Oni et al., 2019). Data sets from all possible advanced characterization techniques are also necessary to establish reliable interpretations and implications. Synchrotron-based XAS techniques are now available to investigate dynamic molecular structures by both NEXAFS (Singh et al., 2014a), X-ray absorption near-edge structure (XANES) (Lu et al., 2020), and 3D structure modeling for biochar (Zhao et al., 2017). NEXAFS, XRD, and FTIR were used to investigate the dynamic surface chemistry for two different types of biochar: grass biomass-derived (lignin-poor) and wood chips biomass (lignin-rich) biochar (Keiluweit et al., 2010). This investigation revealed that different biomass materials undertake an analogous route; however, they undergo quantitatively distinct physicochemical transformations as an increase in the pyrolysis temperature from 200 to 700 °C.

The details of such thermal transformations suggest that there are major categories of biochar that include unique combinations of chemical phases and physical states, as depicted in Fig. 6. These categories are as follows: (1) crystalline features of the biomass feedstocks are conserved in the transformation states of biochar, (2) the initial aromatic poly-condensates and heat-transformed compounds are combined arbitrarily in the amorphous phase of biochar, (3) graphene-like structures that are poorly ordered remain ingrained in the amorphous phase of composite biochar materials, and (4) graphitic crystallite structures embedded in a disordered manner dominate this last category. The short-term mineralization of C and N, dynamics of surface molecular structures of biochar amended agronomic soil those are highly weathered also can be studied by using NEXAFS techniques (Chen et al., 2014). It was revealed that both N and C elements get enriched with heterocyclic aromatic structures into the biochar materials as the pyrolysis temperature increases (Yang, Gan et al., 2015). Such structural transition decreases the mineralization rates for both N and C. The NEXAFS spectra revealed that $C{=}C$ $1s-\pi^*$ transition observed at 285.3 eV is consistent with the CH_3-, H-, or aromatic C structures, which are more noticeable for wood than that of the grass biomass; this can be attributed to the lignin content higher in woody biomass material (Urquhart et al., 2000).

Furthermore, researchers still lack sufficient information on the surface charge presents onto the biochar materials. The surface charge makes the biochar candidate either repulsive or attractive to exposed charged organic metal ions (Fan et al., 2020), organic molecules (Singh, R. et al., 2020), environmental organic pollutants (Singh, R. et al., 2020), and with bacteria by forming a structure with electrical double layers (Abit et al., 2012). Thus, biochar materials and activated carbons can show colloidal properties analogous to the soil particulate matter. The foundation of surface charge onto the biochar materials to be from their aromatic/aliphatic surfaces and also from the functional group's dissociation, particularly carboxyl moieties (Harvey et al., 2012). Therefore, the biochar surface charge greatly corresponds to the pH, particularly when used in aqueous media. Furthermore, it can hold a negative charge over a wide range of natural pH, from 4 to 12; however, in intense acidic conditions, the biochar surfaces turn to hold a positive charge. Therefore, when the pH rises above 4, the biochar surfaces start becoming more negatively charged (Fang, Q. et al., 2014). On the other hand, van der Waals interaction and other electrostatic interactions also influence the migration of biochar particles, ions, nanoparticles, and their organic molecules (Wang, D. et al., 2013), and this property influences strongly and is governed by the pH or aqueous phase. The relationships among biochar surface charge, adsorption mechanisms, kinetics, and equilibrium are comprehensively discussed in recent literature (Tong et al., 2019).

Liao et al. has reported the relationship between the biochar surfaces and their free radicals sites (Liao et al., 2014). This report further revealed the significance of the persistent and quite abundant free radicals present within corn stalks-, wheat straws-, and rice straw-derived biochar as detected by electron paramagnetic resonance spectroscopy. Odinga et al. published a detailed account of free radical species evolved from carbon-affiliated radicals to oxygen-affiliated and combined with oxygen-affiliated free radicals density increases with increasing temperatures during pyrolysis (Odinga et al., 2020). This report further reveals the important role of aromatic carbon atoms involved in stabilizing the free radicals present on the surface owing to the generation of aromatic surfaces

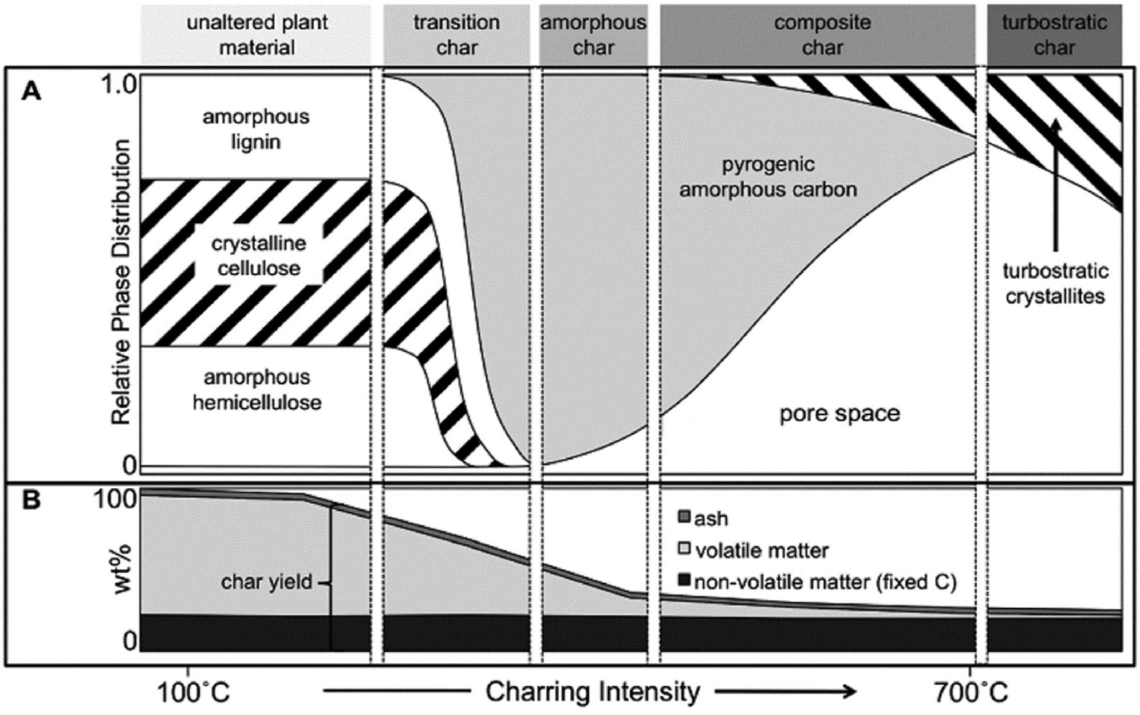


Fig. 6. Dynamic molecular structures and fixed carbon of biochar manufactured at different charring temperature. Graphical illustration of different biochar categories and their discrete phases. Reprint is with permission from reference (Keiluweit et al., 2010). ACS-Copyright, 2010.

that are electron-rich especially at high pyrolysis-temperature conditions. Free radicals thus can be produced during the pyrolysis process (Qiu et al., 2007), and transitions in these free radicals can be monitored simply through observations of in-situ environmentally persistent radicals.

Though it is quite challenging to identify the specific sites for most of the free radicals available, semiquinone and phenoxyl radicals exist as characteristically expected to hold oxygen-affiliated free radicals (Dellinger et al., 2007). Free radicals present in the aqueous phase of the biochar can induce the release of strong $\cdot$OH radicals (Zhu, C. et al., 2015). The free radicals present in the biochar might be the main cause that inhibits the germination of seeds and hindrance shoot and root growth (Liao, Sun et al., 2014), and also may damage the plasma membrane in plants and bacteria (Gorovtsov et al., 2020). Other reports revealed that the abundantly available free radicals of the biochar surfaces react and to activate different chemicals, including hydrogen peroxide (Fang, G. et al., 2014) and persulfate (Fang et al., 2015a). They also help to degrade some various organic pollutants, such as diethyl phthalate species (Fang et al., 2015b), 2-chlorobiphenyls (Fang, G. et al., 2014), and also polychlorinated biphenyl compounds (Fang et al., 2015a). Free radicals present within biochar materials derived at high pyrolysis-temperature are responsible for their electron-accepting capacity, as determined by electrochemical mediated analysis (Klüpfel et al., 2014). More attention from researchers is needed to examine environmentally persistent free radicals (Tao et al., 2020), their toxicity to plant (Liao et al., 2014), neurotoxicity to animals (Lieke et al., 2018) and humans as well as other negative impacts on the environment (Odinga et al., 2020).

5. Bulk elements and inorganic content of biochar

The diverse element species bestow multi-functionality to the biochar, with distinctive structures and functional features. Thus, this section sheds further light on the elemental species, chemical states, functionalities, potential applications, and global geochemical cycling involved within biochar materials. It demonstrates organic fertilizers prepared by biochar as an eco-friendly alternative to the mineral and chemical fertilizers, have better performance, in terms of plant nutrition, plant growth, and overall yield (Glaser et al., 2015). Therefore, it is important to characterize bulk elements and inorganic contents that are composted or existing in biochar and identified to exert considerable influence on the agronomic value of biochar (Xiao et al., 2018). Various analytical methods, including X-ray fluorescence (XRF) (Holden et al., 2018), ICP-AES, and optical emission spectroscopy (ICP-OES) (Buss et al., 2019; Tsai et al., 2018), have been revealed as important for analyzing the inorganic contents of biochar (Clemente et al., 2018). Both ICP-AES and ICP-OES are now being applied for the quantification of the elemental species (Mg, Ca, Na, K, Mn, P, Fe, Mg, Al, Si, etc.) characteristics of inorganic elements in biochar and ash (Liao et al., 2007), and their fate in the soil environment (Low and Zhang, 2012). XRF has been applied to examine the inorganic compositions of biochar in terms of the inorganic elements (Zhang et al., 2015b). As shown in Table 6, the composition and types of inorganic species are dependent on the types of biomass feedstocks (Thy et al., 2013). Recent reports stated that the biochar derived from the herbaceous biomass materials (e.g., wheat straws (Tatarková, V. et al., 2013), sugarcane bagasse (Nwajiaku et al., 2018), chicken manure (Clemente et al., 2018), coffee waste (Tangmankongworakoon, 2019), corn stover (Rafiq et al., 2016a), and grass (Bakshi et al., 2020)) or hydrophytic biomass (water weeds) (Suárez-Garcıa et al., 2002). showed significantly higher content of inorganic elements than that of biochar derived from woody biomass (Domingues et al., 2017). Furthermore, the effect of temperature was also shown to have a significant influence on the final composition of inorganic elements in the biochar materials (Wang et al., 2019a). It was reported that the various metal contents, including Mg, Ca, P, K, Cu, Zn, Fe, and Mn, in biochar, derived from wheat straw and pig manure, noticeably increased with increasing temperature from 200 to 650 °C (Zhao et al., 2013). The key bulk elements in biochar were (C, O, H), as well as N in some of the biochar samples. The fixed carbon content in biochar was typically ranged from 40 to 60 wt %, the oxygen content about 10–20%, and the hydrogen content about 2–5 wt % (Brown et al., 2011). The heteroatoms N, P, K, O, and S get merged into the aromatic carbon structures of biochar materials (Liu, W.-J. et al., 2019), providing unique heterogeneity to the surface chemistry owing to the diversity in electronegativity among these heteroatoms (Zhao et al., 2013) and aromatic carbon atoms of biochar (Mian and Liu, 2018).

The inorganic elements are fundamental building blocks present in the biochar materials. Elements within the biochar undergo different physicochemical changes during the pyrolysis of biomass and form different products and species, and are thus involved in the diversity of biochar materials (Tomczyk et al., 2020). It summarizes the inorganic species and their elemental composition for various biomass samples (Table 6). Most of these inorganic elements are involves in the part of geochemical global cycles and are present in different mass percentage and functionalities in the biochar materials. As described above, among these elemental species, C, O, H, and N are identified as the main element in biomass samples and mostly contribute to the structure and surface function of the biochar. However, inorganic species like Fe, Si, S, and P demonstrate a broad range of mass percentage in particular biochar materials, whereas several of such elements act as potential nutrients for plants and crops (Ding et al., 2016). Some element species (C, O, H, N, and S) in global cycles of geochemistry, are identified as bidirectional in their cycling patterns from the atmospheric source to the soil (Andreae et al., 2002), whereas some specific elements (Si and P) are identified as unidirectional owing to absence in the atmospheric environment.

In addition to carbon, O/N-having functional groups are the typical functional groups in biochar (Duan et al., 2019), which

Table 6
Inorganic content (g/kg) for biochar derived from various biomass samples using fast pyrolysis. Tabular data about the inorganic composition of biochar materials collected from different reports (Brewer, C. et al., 2009; Leijenhorst et al., 2016; Liu et al., 2015; Tatarková et al., 2013; Zhao et al., 2013).

	Sawdust	Corncobs	Corn stover	Grass	Waterweeds	Chlorella	Wheat straw
P	0.061	4.36	12.94	0.59	0.51	4.36	–
Mn	0.009	0.05	0.65	0.01	1.02	0.91	–
K	1.18	43.35	23.46	5.15	3.22	13.67	10.2
Mg	0.34	2.15	14.24	0.53	0.66	0.77	1.3
Ca	2.29	0.97	20.13	5.23	23.13	17.50	3.2
Fe	0.16	0.65	15.95	0.15	0.55	0.40	–
Si	–	73.5	193.23	–	–	–	7.2

intrinsically contributes to their long-term stability (Uchimiya et al., 2013), life cycle assessment of biochar-to-soil system (Matuštík et al., 2020), and series of transitions in the soil environment (Zhou et al., 2020) and in the development of other biochar-based applications (Leng et al., 2020). The volatile compounds are negatively associated with the pyrolytic temperature (Rafiq et al., 2016b), and a high volatile content is an indication of higher biochar reactivity and entails the negligible potential for use as a soil amendment agent (Deenik et al., 2010). Furthermore, VM within biochar forms readily and converts into oil or gas phases as the temperature increases during pyrolysis (Lee et al., 2019). The fate of inorganic species was reported for biochar derived from high-nutrient biomass (Domingues et al., 2017), and mechanism of nutrient retention and release reported for nitrate, phosphate and other nutrient during composting (Joseph et al., 2018), and in other case elements turns to non-volatile and accumulates within biochar materials either as elements or nano-particulate matter (Song et al., 2019).

5.1. Oxygen carbon ratio

The molar percentage of oxygen and carbon content can be used to calculate the molar O/C ratio. A recent report sought to describe the molar O/C ratio of the biochar prior to and after ozonization treatment by performing the elemental analysis (Kharel et al., 2019). Furthermore, that report showed higher carbon content of biochar prior to the ozonization treatment (about 87.0 mol % ± 5.6), while subsequent to the ozonization treatment, the carbon content decreased up to 72.2 mol % ±0.9. On the other hand, ozonization treatment made substantial upsurge of 13.9 mol % ±1.5 in oxygen content wherein non-ozonized control had just 6.6 mol % ±1.3 of oxygen. These observations indicate that the ozonization treatment process increases the O/C molar ratio by a factor of 2–2.5; the O/C molar ratio for non-ozonized pristine was down to 0.07 whereas the dry-ozonized biochar sample O/C molar ratio was about 0.19 (Kharel et al., 2019). Therefore, ozonization treatment has the potential to change the molar ratio for oxygen and carbon in pristine biochar materials. Marmiroli et al. suggested that SEM imaging and EDX analysis can be used to monitor the oxygen to carbon (C/O) ratios and achieve consistency over the results of C/O ratios (Marmiroli et al., 2018a). That report furthermore reveals that the bulk properties may be affected by the ozone treatment of biochar, which implies that dry-ozonization treatment can also change the total oxygen content, as was observed by using SEM-EDS analysis (Ma et al., 2016). That study also suggested that SEM-EDX results were highly consistent to measure carbon, oxygen, and C/O ratios and, thus, should be used in further studies as an effective tool for the characterization of biochar materials and products.

To investigate the premise that the ozonization process generally happens on the surface of the biochar materials, there is a need to compare the changes in between bulk properties before and after the ozonization with biochar with more high surface area and biochar with less surface area (Kharel et al., 2019). Nanoscale particles on surfaces of biochar carbon materials get oxygenated; thus surface oxygenation can be measurable even for both bulk biochar (O/C) ratio analysis (Huff et al., 2018). Therefore, maybe the overall functional groups of oxygen present onto the biochar surfaces can be noteworthy enough to alter the overall percentage of oxygen owing to its extremely more BET surface area; thus, the average carbon content and thickness may vary among the porous spaces.

Qualitative assessment of the VM content of biochar, which is also a useful and labile component to perform quality control measures can describe proximate analysis and elemental results. The dynamic molecular structure of biochar derived from plant biomass corn stover samples showed high ash-content (58%) but comparatively low % of O about 5–8% and %C (ca. 33%), in comparison to wood biochar at identical temperature conditions (Keiluweit et al., 2010). That report further reveals that biochar with higher fixed carbon is characteristic for >600 °C, entailing the possibility of forming thermally stable, and highly condensed biochar materials at higher temperature settings (Pastorova et al., 1994). These reports, in addition to the work of Budai et al., suggested that the atomic ratios for O/C (Ippolito et al., 2020) or H/C (Xiao et al., 2016), and VM contents (Caillat and Vakkilainen, 2013), are important signs to examine the degree of pyrolysis process but are poor forecasters of the biochar applicability in agronomic fields (Budai et al., 2014). Likewise, the lower O/C ratio and lower O% content of biochar materials may suggest dehydration and condensation reactions, respectively. This observation also corroborates the FTIR results, where the O–H stretching vibration band is located at region 3200–3600 cm^{-1}, C=C, and C=O at 1600–1740 cm^{-1} bands which are more strong (Lee et al., 2010). This report determines that the CEC values may vary dependably on the biochar sample types; it seems that the CEC values also corroborate with the O/C ratios as the higher the CEC value the higher the O/C ratio. It has been also established that there is an intense relationship between the O/C ratio and CEC value of biochar samples (Huff et al., 2018), which is owing to the innate negative charge on the oxygen-based functional groups which are able to create an electrostatically attractive force to collect cations (Huff et al., 2014). Though a high O/C ratio is desired for better CEC value when consuming biochar materials as a soil amendment agent, it must also be agreed on when the higher O/C ratio, the largely half-life for such biochar thought to be shorter (Santín et al., 2017). Particularly biochar products with O/C ratios if higher than that of 0.2 have an overall half-life ≥of 1000 years (Spokas, 2010). If O/C ratios are higher (about ≥0.5 to 0.6), then the predictable half-life drops sharply to < 100 years. Thus, precisely designed biochar materials for use as both as carbon sequestration and soil amendment agent will be needed to wisely increase the O/C ratio only on the biochar surface, thus giving a greater CEC value, while such settings even uphold the poly-aromaticity with preferably lesser O/C ratio in the hardcore region of the biochar for long-term carbon sequestration stability (Bakshi et al., 2020). The determined CEC values correspond well with higher ratios of the oxygen to carbon ratios (O/C) thus, higher O/C ratios directly correspond to the presence of abundant carbonyl, hydroxyl, and carboxylate functional groups present on the biochar surfaces (Lee et al., 2010).

5.2. Carbon

The analysis of chemical species of carbon both organic and inorganic phase is an important factor in developing applications in the carbon sequestration, agronomic field, and ecosystem sustainability since the chemical species governs both reactivity and stability of the carbon in the biochar materials (Hernandez-Soriano et al., 2016). Carbon is the most abundant and the most important element, acting as the backbone of biomass and biochar materials. The carbon species present within biochar materials are typically categorized in its inorganic phase as bicarbonate, and carbonate in addition to its aromatic carbon, aliphatic carbon, and surface functional groups of carbon in its organic phase (Faheem et al., 2020). It is quite challenging to accurately distinguish these carbon species and their phases. The inorganic form of carbon may go through a transition to bicarbonate from hydrated carbonate while the pyrolysis process progresses; carbonate, depending on the phase, may be released into the environment as CO_2 gas, and also depending on its fate in the type of inorganic crystals present in the biochar materials. The carbon in its organic phase transforms their carbon from hemicellulose/cellulose/lignin components of the biomass, thus, turns into an aliphatic carbon within biochar at the middle of pyrolysis temperature, and also forms an aromatic carbon species at high temperatures during pyrolysis immediately after complete dehydration, cracking reactions, and then aromatization (Wang et al., 2014). Such transitions can be examined by FT-IR (Chen et al., 2008), Raman spectroscopy (Chia et al., 2012), magic angle spinning coupled with cross-polarization (Baccile et al., 2014), solid 13- C NMR spectroscopy (Jindo et al., 2014), and also by using some other characterization techniques. Furthermore, recently developed techniques called solid-state high-resolution two-dimensional 13-C NMR was also used to collect detailed information on about the status of both carbon species and chemical states within biochar (Le Brech et al., 2015). Most of these characterization techniques can differentiate between alkyl and atomic carbons, but it is quite challenging to distinguish such functionalization present in the carbon atoms of biochar materials.

5.3. Nitrogen

Nitrogen is the main element that contributes to forming peptide bonds present in the protein content of biomass. Generally, biomass feedstocks e.g., wood and plants are reported as nitrogen-poor biomass owing to their somewhat low content of proteins; however, other biomass samples such as manure, chicken litter, plant leaves, food waste, or grass contains rather higher protein content thus are nitrogen-rich biomass materials (Ou et al., 2015). For instance, wood, grass, and casein -derived biochar were reported as containing ~0.3—1%, ~6—7%, and 12 to 15 wt % of nitrogen, respectively (Ou et al., 2015). Nitrogen fraction is an important factor in estimating the recalcitrance of carbon materials (Knicker, 2010). Even though numerous researchers have considered nitrogen-rich biochar in their studies: nitrogen functionalized biochar (Bamdad et al., 2018), nitrogen-doped microporous biochar (Zhang et al., 2016), nitrogen-rich biomass-derived biochar (Zhang et al., 2014), however, only a few studies have emphasized the speciation of nitrogen inside the biochar (Liu et al., 2018). Furthermore, Zhang et al. revealed that micro-porous structures perform a vital role in influencing CO_2 capture at the lower temperature conditions, whereas physicochemical properties, particularly from the nitrogen-rich functional groups perform better to CO_2 capture at higher temperature conditions (Zhang et al., 2016). The structures associated with nitrogen contain various groups including pyridine, pyrrole, imine, amine, nitroso, acrylamide, and nitro functional groups, as summarized in tabular form (Xiao et al., 2018). Some of the reports specify that the total nitrogen content present within biochar materials increases in the initial stage and consequently decreases marginally as the pyrolysis temperature increases (Cantrell et al., 2012). Knicker et al. further revealed biochar materials having N species are mostly from amide-N, pyridine-N, and pyrrole-N. The peptide-N bonds transform into the C base of N-hetero-aromatic compounds during the progress of pyrolysis; however, it was suggested that some of the amide-N groups within biochar decrease with the increase of the pyrolysis temperature (Knicker, 2010). Pietrzak et al. reported nitrogen-enriched activated carbons preparation protocol using reactions with urea or ammonia and suggested that the N can be introduced into biochar/charcoal at temperature from 500 to 700 °C in the forms of pyrrolic-N, pyridinic-N, imine-N, amide-N, amine-N etc. (Pietrzak et al., 2006). Furthermore, Pietrzak et al. revealed products having microporous structures having nitrogen-enriched (1.0—8.5 wt%) activated carbon samples with a fully-grown surface area ranging from 1500 to 2500 m^2/g (Pietrzak et al., 2010). Several reports on pyrrolic-N and pyridinic-N conducted to prepare N-doped carbon arrays are appropriate for developing “electronic band structures” performing as conductive sites during electrochemical applications (Tian et al., 2020). Another report also explained that the N-rich biochar materials applicable to demonstrate a good heat resistance but less stability over chemical-oxidation than that of N-poor biochar materials (Liu, W.-J. et al., 2019).

The fate of extractable nitrogen sources became a subject of interesting research owing to their application to agronomic soils. Various nitrogen species are extractable by applying various extraction methods (Matsumoto and Ae, 2004), including from amino sugars, ammonia, hydrolyzable nitrogen forms, and total amino acids; it seemed their content levels to decrease as the increase in pyrolysis temperatures (Krounbi et al., 2020). Fundamentally, there was found uncertainty over whether extractable nitrogen source originates either from inorganic or organic matter present within biochar (Dempster et al., 2012). Nitrito- and nitro-N were also detected in rice husk-derived biochar, forestry sawdust biomass, and aquatic biomass (*Acorus calamus*) hydrolyzed at 650 °C (Wang et al., 2017). Wang et al. comprehensively described the influence of biochar properties on the various crop yield and their growth (Wang, D. et al., 2020). It is important to note that the intrinsic nitrogen content of biochar is typically low and, thus, can be considered as a nitrogen fertilizer if not treated or co-composted with nitrogen-rich fertilizers (Zafar-ul-Hye et al., 2020).

The biochar-amended compost or co-composted biochar was reported to promote crop growth and also compared with pristine biochar combined with both pristine biochar or mineral fertilizer (Hagemann et al., 2017). However, it has been suggested that biochar with higher C/N ratios those have limited nitrogen availability (Liao et al., 2020), addition of nutrient enriched biochar to soil is increases microbial activity (Azeem et al., 2020) and crop yield (Prommer et al., 2014). For instance, it was described that 5% of biochar materials amended with mineral fertilizer with 0.0134% of nitrogen source showed extraordinarily higher growth promotion of oat crop than pristine biochar (Schulz and Glaser, 2012). Biochar materials are suggested as potential candidates for improving nitrogen recycling in agronomic plant-soil systems (Liao et al., 2020). The application of biochar materials to agronomic soils reduces N_2O emissions (Bruun et al., 2011), reduces nitrogen fertilizer leaching (Liu, Q. et al., 2019), improves nitrogen fertilizer availability to the soil, thus can help to raise crop productivity (Hussain et al., 2017), and promotes the activity and diversity of soil microbes (Hardy et al., 2019).

The soil nitrogen dynamics of biochar fertilizer (Clough et al., 2013) and sustainable remediation practices in the soil environment are of substantial interest (Wan et al., 2020); including in terms of influence on nitrogen fixation (Olszyk et al., 2020), nitrogen leaching (Xu et al., 2016), nitrification, denitrification, and emission of greenhouse gas N_2O (Liu et al., 2021). Several studies indicated that biochar materials demonstrate higher bonding affinity during the adsorption of ammonium ($NH4_+$) (Fidel et al., 2018), an acid-aged biochar reported for ammonium adsorption (Wang, Z. et al., 2020), nitrogen removal through mechanism of cation-exchange (Liang et al., 2016), sequential carbon dioxide and ammonia adsorption (Krounbi et al., 2020), however, biochar showed negligible efficiency for nitrate (Feng et al., 2020). Ammonia fertilizer absorbed within biochar materials is recently reported for their ready bioavailability (Taghizadeh-Toosi et al., 2012); thus, modified biochar materials can be regarded as a nutrient-bank or retention agent in achieving sustainable nitrogen fertilizers into the agronomic soils (Ding et al., 2010; Spokas et al., 2012). The application of biochar-amendment to the nurseries substrates and for seed coating has been suggested to produce healthy seedlings.

Another report also explored the physicochemical properties of biochar-amendment, especially water availability and movement, resulting in improved seedlings growth (Radin et al., 2018).

Mulabagal et al. categorically stated that biochar acts as a “soil conditioner” owing to improved tilth the physical condition, water holding capacity, and nutrient holding capacity of the soil (Mulabagal et al., 2014). Furthermore, biochar involves stabilizing both the greenhouse gases, nitrogen, and carbon, thus decreasing the environmental emissions of N_2O and CO_2 reported for soil amended with anaerobic digesters (Martin et al., 2015). Biochar samples were also described for their critical role in microbial-based nitrogen fixation by leguminous crop *Phaseolus vulgaris* by increasing from 50% without biochar to approximately up to 72% when biochar added 90 g kg^{-1} (Rondon et al., 2007) and, another study on acidic soil planted with Rapeseed crop *Brassica napus* revealed that biochar also implicates in stimulating in both the denitrification and nitrification process by the effect of decreasing emissions of N_2O (Xu, H.-J. et al., 2014).

The N_2O emissions reduction efficiency reported for biochar derived from giant reed (*Arundo donax*) at increasing pyrolysis temperature as an additive to the soil, temperature conditions comprising 200, 300, 350, 400, 500, and 600 °C (Wang, Z. et al., 2013). Cayuela et al. gave a detailed account of the potential of biochar for reducing N_2O emissions. They proposed the functioning of biochar materials as an “electron shuttle” owing to the facilitation of electron transfers in the microbial denitrifying process in addition to its “liming effect”, which can encourage the decrease in the conversion of N_2O into N_2 gas, likely achieving from 10 to 90% reduction in N_2O emissions liable to the type of agricultural soil (Cayuela et al., 2013). The nitrogen and carbon cycles get influenced by three different ways for biochar. First, carbon layers develop more recalcitrant during biochar processing in correspondence nitrogen turns into less available, owing to improved stability of the biochar products (Soong and Cotrufo, 2015). The second route is the adsorption of NH_4^+ within the carbon layers of biochar also promotes the retention of nitrogen fertilizer in the soil. Third, plant and microbial growth in soils amended with biochar get limitation due to lower nitrogen content, and fewer microbial activities together may also reduce and stabilize mineralization of fixed carbon within the soil (Prayogo et al., 2014).

5.4. Phosphorus

Phosphorus is an essential and key plant nutrient for good growth and higher yield of crops, whereas phosphorus requirement in plants naturally is lower than that of potassium, calcium, and nitrogen. Unlike oxygen, hydrogen, carbon, and nitrogen element, which may lose depending on the pyrolysis temperature, but, the phosphorus not does vaporize into an environment below temperature 700 °C (Atkinson et al., 2010), allows filling phosphorus content under the typical pyrolysis process. Ngo et al. described prodigious domination by inorganic phosphorus content as compared to the organic phosphorus specifically for biochar-derived from bamboo biomass at pyrolysis temperature 500–600 °C (Ngo et al., 2013). Considering these facts, Uchimiya and Hiradate (Cantrell et al., 2012), studied the transformation of phosphorus species during pyrolysis and it was revealed that the phosphorus in most of the biomass is generally in an organic form such as phosphate di-esters and monophosphate. In another study applied 31-P NMR, suggested that the phytate groups get transformed into an inorganic phase of phosphorus particularly within manure biomass and also from some plant-derived biochar at pyrolysis temperature 350 °C (Uchimiya and Hiradate, 2014). The pyrophosphate ($P_2O_7^{4-}$) in plant origin biomass materials were found to be persistent in biochar prepared at temperatures 650 °C owing to the inorganic form of phosphorus, and the orthophosphate ($PO4^{3-}$) turns into sole phosphorus -species within biochar derived from manure biomass materials during pyrolysis at a temperature higher than 500 °C (Uchimiya and Hiradate, 2014).

Solid-state 31-P NMR, XRD, and XANES techniques are also can be used to characterize phosphorus phases lingering onto the solid phase biochar after consecutive extraction process (Hunger et al., 2008). For instance, poultry chicken litter mainly contains inorganic phosphorus in the alkali extraction method by NaOH and organic phosphorus in the solid phase extraction (Seiter et al., 2008). Their report further reveals that the alum-modified poultry chicken litter was rich in organic phosphorus in an aqueous phase, and in the solid phase was in form of calcium phosphate. The phosphorus geochemical cycle is unidirectional; it starts from land reach to sea owing to there is no emission of above-described species of phosphorus, and it is almost not possible to transport phosphorus species from the ocean back to the soil ecology except through a slow process of movement of diminution at crustal plate environment (Elser and Bennett, 2011). Estimation of a main soil nutrient phosphorus for their fluxes, such as the dispersal of phosphorus fertilizer from agricultural soil, ranges from three to fivefold, and some other factors, such as the global return of phosphorus fertilizers from harvested produce, are unclear (Pinitpaitoon et al., 2011).

The solutions to save more phosphorus lie in recycling and recapturing from food waste, human waste, and some other phosphorus-rich residues as well transferring from rich sources to where there is a need and also developing ways to utilize it more effectively (Smol, 2019). Some strategies are simple and readily accessible, even poor farmers from developing countries can involve in implementation. Therefore, making slow-releasing biochar based phosphorus-additive was suggested to sustain more phosphorus fertilizers in soil settings (Yao et al., 2013). The influence of the cations, anions, and pH on the release of phosphorus fertilizer from soil have to be further investigated (Silber et al., 2010). That study also reported that the high pH values significantly hinder the loss of phosphorus, however, some of the anions can enhance the release of the orthophosphate (PO_4^{3-}) owing to opposite ion-exchange reactions, and in other case competing for cations also involves decreasing the release of phosphorus, if there is the formation of precipitated materials (Qian et al., 2013). In short, phosphorus present in biomass can be transformed from their intrinsic organic phase of phosphorus to inorganic phase phosphorus by carbonization/pyrolysis process and thus aid as inorganic nutrient bank for the soil fertility as well as acting as adsorbent for metal ions. Similar to the phosphorus element, silicon element is also a key inorganic nutrient for certain crop plants, rice fields and enhance microbial growth.

5.5. Silicon

Though not all types of biomass samples or organic residual wastes are useful for pyrolysis into biochar consist of silicon (Gan et al., 2021); phytolith-rich biomass includes rice husk (Shen, 2017), rice straw (Marxen et al., 2016), and corn straw (Yang, X. et al., 2020), and those are essential crops for food production and also key biomass feedstocks can be used for large-scale biochar production (Xiao et al., 2014). Certainly, silicon nutrient is essential in silicophilic crop plants (such as barley, rice, maize, and wheat) (DalCorso et al., 2014) and is also involved in plant protection to these crops from insects, diseases, metals, excess sunlight, and drought conditions (Zargar et al., 2019). It involves several factors in influencing soil availability of silicon to crop plants, including choice of materials, soil type, organic matter, soil pH, temperature, and soil texture (Miles et al., 2014). Moreover, previous studies suggested that the biochar-amended silicon and microbes together can contribute to the adsorption and protection of crop plants from toxic metals cadmium (Roh et al., 2015), aluminum (Qian and Chen, 2014), lead (Han et al., 2017), and some others in aqueous media (Harindintwali et al., 2020). It revealed the release of silicon nutrients from biochar materials in the form of monosilicic acid in aqueous media as effective in performing biochar mediated adsorption of several heavy metals (Chen et al., 2015).

Xiao et al. examined silicon transformation in biochar derived from rice straw at different pyrolysis temperature conditions (Xiao et al., 2014). In another report, it was reported that silicon in biomass existed mostly as a phytoliths in its form of polymeric silicon and water-soluble silicic acid, which was revealed as for easy availability to roots (Ma and Takahashi, 2002). This report further describes that the silicon turns to dehydrate and is polymerized during pyrolysis; however, the polymeric silicon is partly crystallized after further pyrolysis process. Rice straw derived biochar at high-temperature pyrolysis showed higher silicon dissolution property than that of biochar prepared at low pyrolysis temperature conditions (Southavong et al., 2018). Furthermore, silicon-rich biochar materials showed much higher tendencies of silicon dissolution than that of ash or soil sources, which consist of higher levels of silicon content in silicate form (Wang et al., 2001). Most of the arable soil types globally are suffering from the depletion of silicon (Haynes, 2014); thus, silicon-rich biochar materials with better dissolution capacities for silicon can provide alternative silicon-fertilizer for slow-release in soil (Li and Delvaux, 2019).

The inorganic phase of silicon represents a major fraction present in silicon-rich biochar (about~35–38% of the dry mass content in ash derived from rice straw) and it can be separated from organic matter that presents within biochar (Xiao et al., 2014). In accordance with the results of SEM-EDS, this report further reveals a mutual relationship exists between silicon and carbon during the increasing pyrolysis temperatures. In particular, the silicon gets protection from dissolution owing to the carbon layer under the pyrolysis process; then, carbon gets protection from the silicon layer thus can avoid carbon loss under the high pyrolysis process (Xiao et al., 2014). Another comprehensive report on the recalcitrance of biochar, molecular mechanisms, and the role of silicon and carbon components indicated that the silicon can directly back stability and recalcitrance of biochar materials (Guo and Chen, 2014). That report further illustrated coupling cycles for silicon and carbon present within biochar and in the topsoil ecosystem.

The silicon-rich biomass materials have the ability to respire CO_2 from the air and soluble silicic acid through the roots system in the soil. A wide range from 0.1% to 10% of silicon distribution in the dry weight of biomass normally allows for silicon to get accumulated in biochar materials during pyrolysis processes (Rizwan et al., 2018). The plant-derived silica is abundant and useful to prepare silica nanoparticles and their composites (Prabha et al., 2020), hot-water-treatment allows to separate silica from rice husk residues (Mochidzuki et al., 2001), ash morphology of the silicon can be transformed from amorphous to crystalline silica nanoparticles by increasing pyrolysis temperature (Zhang et al., 2012) and there is possibility of causing a strong interactions between carbon and silicon (Wu, J. et al., 2019). However, the interlaced carbon-silicon content begins to become discrete at increased pyrolysis temperature and forms composite crystals that are stable for a long period (Dutta et al., 2014). Such a kind of carbon-silicon coupling demonstrates the key role of biochar materials in the geochemical cycle of silicon an essential inorganic nutrient (Wang, Yoo et al., 2018). The silicate and carbon minerals cause emission of CO_2 owing to its slow release over several years, thus silicic acid becomes accessible to roots of crop plants, makes possible in completing silicon and carbons geochemical cycle (Hughes et al., 2020). Wang, Y. et al. reported a comprehensive study on the structural features of silica-containing biochar and its application in pollution remediation and soil improvement (Wang et al., 2019b). Some of the recent reports also indicated that there is a need for more research activities with the direction of revealing the significance of biochar materials better in global silicon and carbon balance (Wang et al., 2019b), and also their essential agronomic functions of silicon in biochar materials (Li and Delvaux, 2019) and potential applications in ferrosilicon production (Riva et al., 2019).

5.6. Inorganic phase

Biochar materials are a combination of interlaced organic-inorganic structure mainly contributed by carbon matrices and other minerals that exist in biomass. This diverse range of inorganic phases interacts within structures and impacts the organic phases (Farbod et al., 2013), and involves in tuning their properties and applications (Chacón et al., 2017), thus, understanding transformations of mineral phases during the pyrolysis process are of great significance (Xu and Bhattacharya, 2019). Xiao et al. (2018) illustrated plausible transformation in inorganic phases of several types of mineral components produce involving several chemical reactions occurs within the inorganic phase throughout the pyrolysis process include drying up, polymerization, decarboxylation, dechlorination, crystallization, and also reduction-like reactions. For instance, silicic acid available within the silicon-rich biomass like rice-, corn- and wheat-straw polymerizes and forms silicon polymer materials and crystallize phase silicon turns further into the quartz phase during increasing pyrolysis temperature (Xiao et al., 2014). That report further revealed that the inorganic phase initiates from chloridized, carbonated, or hydroxylated metals and then transforms into metallic oxides under limited oxygen condition, some of the elements are reduced into pure metals owing to the strong reducing atmosphere during increasing pyrolysis temperature. Researchers are now readily producing zero-valent Fe (Peng et al., 2017), magnetic biochar (Chen et al., 2011), porous biochar zinc nanocomposites (Gan et al., 2015), and zero-valent Cu covered biochar materials (Liu et al., 2012) by using these transformation reactions during the pyrolysis process.

However, in addition to biochar being rich in organic carbon, it also contains a reasonable share of inorganic elements such as alkali-earth metals (Mg, Ca) and other alkali metals (Na, K). An important agent involved in the production of several chemical products called calcium carbide (CaC_2) can be produced by integrating fine biochar materials with CaO precursors under higher pyrolysis temperature (Li et al., 2010). The structural functions and various applications of inorganic content present within biochar materials comprise but not restricted to the subsequent: magnetic biochar materials for environmental remediation (Yi et al., 2020); pore-forming agents (Azargohar and Dalai, 2008), remediation of organic pollutants (Yan et al., 2015) and performing oxide materials-involved catalytic reactions (Cheah et al., 2013; Lahijani et al., 2013) and serving for carbon sequestration purpose (Li, F. et al., 2014), providing slow-release nutrient fertilizers (Tsai et al., 2012), heavy-metal co-precipitator agents (Xu et al., 2013), and heavy-metal stabilizing agents (Debela et al., 2012). Magnetism originates from the capping of γ-Fe_2O_3 (Yang, J. et al., 2016), and the catalytic activity emanates from the active sites of zero-valent iron (Oh et al., 2017), or some other transition metals (Lyu et al., 2020). Moreover, pore-creating agents include $ZnCl_2$ (Xia et al., 2016), KOH (Azargohar and Dalai, 2008), and some others (Angın et al., 2013). The influence on carbon fixation greatly depends on the types of mineral loaded within biochar materials, for instance, in laboratory scale 5-year experiment showed variation from 0.5% to 9% of carbon mineralization within biochar, and biochar derived from manure biomass mineralize faster than that of biochar derived plant biomass (Singh et al., 2012). In another experiment, it was reported that the co-pyrolysis with kaolin, calcite ($CaCO_3$), or dihydrogen phosphate of calcium ($Ca(H_2PO_4)_2$) reduces in broad range from 0.3% to 38% loss of carbon from biochar materials during the test using oxidation by potassium dichromate (Li, F. et al., 2014). This report further reveals that the results indicated that out of these three types minerals, particularly $Ca(H_2PO_4)_2$, was much functioning to improve retention of carbon, thus promoting the stability of biochar, that can be expected to result in an excellent mineral additive to produce the precisely designed biochar materials with great capacity over carbon sequestration and long-term stability.

In conclusion, various inorganic elemental species are in the biomass samples or used in pretreatments can transform to an inorganic phase of biochar using appropriate pyrolysis temperature and recycle for multifunctional applications in various fields. It can be also achieved by transforming difficult to dissolve inorganic species into their easy to dissolve metal species, in addition to this the heavy metal content can be stabilized within biochar materials (Debela et al., 2012). However, deep understandings are required about the carbon stability, solubility behavior, nano-effects, potential catalytic activity, and toxicity that would emanate from the inorganic nanocomposites of biochar (Ramanayaka et al., 2020). Reports on the biochar materials inorganic phases are comparatively easier to explain than that of the organic phase of biochar owing to the greater atomic sensitivity while characterization of metal atoms using various independent instrumentations. To date, there are several other metallic elements, species, in singular and composite crystals are yet remain unknown and thus need additional research efforts. Reports published on the structure and behavior of nano-biochar are insufficient to achieve clarity, despite the growing interest. Thus, further research efforts should be focused on exploring new techniques to increase the yield of nanobiochar while reducing aggregation, upscale production to use as an electrode material for supercapacitor production (Li, Panyu et al., 2020) and understand biocompatibility aspects for soil bacteria's (Kappler et al., 2014), plants (Ramadan et al., 2020), domestic animals (Schmidt et al., 2019), and humans (Dong et al., 2019). Future studies should focus on the inorganic matter within biochar materials, particularly on the components are of agronomic interest includes silicon, cobalt, copper, zinc, magnesium, calcium, boron, and many other for their role in altering morphology during biochar formation and their availability to the soil root zone.

6. Conclusions and implications

An extensive research expected on the biochar production, owing to biomass availability, portability of pyrolysis reactors, advances in characterization techniques, low-cost biomass materials, and their potential applications. The possibility of producing biochar materials from multiple biomass resources, their multilevel structural features, and inorganic phases besides their diverse range of functionalities have potential to transform many prospects in sectors as well as renewable energy, agronomic applications, and environmental protection. In this report, we summarized numerous aspects of biomass feedstock choice, the effect of pyrolysis temperature, relationships of biomass components, dynamic structural features of biochar, and their potential agronomic applications. It presents the multilevel analysis of biochar materials besides the molecular structure of biochar, organic phase with a diverse range of molecular compounds, surface functionalities, and lastly, bulk elements and inorganic phase. So far diverse range of potential applications have been established using biochar materials includes electrochemical devices, remediation of soil and water, soil amendment, carbon sequestration, and novel biochar-based products as renewable additives as topsoil nutrient bank including sorbents, fertilizers, and bio-augmentation agents for improving microbial habitat. About biochar structural features, there is need of deep understanding to anticipate bioavailability, surface functions, concentration, organic molecules, mobility, surface radicals, toxicity, and environmental fates. Moreover, the recent advancements in standard analytical and characterization methods are advantageous for several reasons, comprising but not restricted to the following features: identification and quantification of different phases, species, surface functionalities, and organic phase by identifying molecules of a diverse range having molecular different weights, applying standard methods for extraction protocols, comparison methods, and post-harvest biochar treatments.

For applications, there is also need of more profound understanding of application—structure relationships, thus, we could design and select desired biochar-based materials for particular application. As described, the relationship between the application and structure of biochar material is now gradually developing from semi-quantitative to quantitative measurements and finally understanding their qualitative relationship mechanisms. Though few of such relationship mechanisms have been formerly discovered, many R&D activities are yet to be devoted to the application—structure relationships are involved, particularly for understanding molecular structural relationships. In this review, based on the current understandings of molecular structures of biochar materials, we suggest further studies on biochar materials and that should be combined at microscopic and the macroscopic levels while clarifying characteristic features of both cause and effects. For instance, while looking at the fate of biochar materials in soil settings, data should report the dissolution and release kinetics of all possible elements including core element carbon, and the influence on the nano-biochar, the soluble extractable molecules of organic biochar phase, and the skeletal inorganic phase of biochar structures. Prior to considering biocompatibility, most aspects related to heavy metals, free radicals, extractable organic species, and the main skeletal inorganic of biochar materials need to be investigated in an organized and comprehensive manner. We should place more emphasis on elucidating the relationship between molecular structures of biochar materials with their appropriate applications owing to the fundamental understandings of biomass components and their pyrolysis mechanisms. We need precise quantification and predictions concerning various types of biochar materials with their structure-specific applications with extensive reports. Finally, this report anticipates intelligent design systems and future directions are essential for producing desired biochar materials in achieving all possible benefits for agronomic and environmental sectors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors express appreciation to the Dongguk University-Seoul, South Korea for Research Support Fund (RF: 2020—2022). The authors extend their appreciation to the Deanship of Scientific Research, King Saud University for funding this work through research group No (RG-1440-056).

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