Pyrolysis to Produce Hydrochar and Biochar Carbon Material for Carbon Removal and Sustainable Environmental Technology

Kim Yrjälä, Muthusamy Ramakrishnan, Huabao Zheng, and Eglantina Lopez-Echartea

Contents

K. Yrjälä (✉)
State Key Laboratory of Subtropical Silviculture, Zhejiang A&F University, Hangzhou, Zhejiang, China

Department of Forest Sciences, University of Helsinki, Helsinki, Finland
e-mail: kim.yrjala@helsinki.fi

M. Ramakrishnan
Co-Innovation Center for Sustainable Forestry in Southern China, Nanjing Forestry University, Nanjing, Jiangsu, China

Bamboo Research Institute, Nanjing Forestry University, Nanjing, Jiangsu, China
e-mail: ramky@njfu.edu.cn

H. Zheng
Zhejiang Province Key Laboratory of Soil Contamination Bioremediation, Zhejiang A&F University, Hangzhou, Zhejiang, China
e-mail: zhenghuabao@zafu.edu.cn

E. Lopez-Echartea
Department of Biochemistry and Microbiology, University of Chemistry and Technology, Prague, Czech Republic

Abstract Natural resources are continuously depleted globally, and accelerated climate change is a consequence of irresponsible human action. Planetary resources have to be better utilized not to threaten living ecosystems, the biodiversity and cause further land degradation. New nature-based and cost-effective materials are appearing for remediation purposes but need continued development since they require extra knowledge about structure-function relations. Within emerging circular economy new waste streams are detected which can serve as substrate for new valuable and smart materials and at the same time provide energy and even carbon removal. Biomass has been generated from both agriculture and forestry but lately also municipal solid waste has been recognized as resource in waste valorization. Waste can be converted to new products by hydrothermal processes that yield hydrochar and thermal pyrolysis processes to produce biochar; a multiuse carbon material. Ideal waste utilization processes have good energy yield at the same time as new materials are formed. Carbon removal can become a part of environmental societal solutions dealing with sustainable waste processing and application of new value-added products coming from development of new smart materials. Carbon removal efforts are currently supported through the voluntary market and the total value of global carbon markets grew by over 20% in 2020 – the fourth consecutive year of record growth. This chapter displays different waste streams and their suitability for thermal treatments to produce hydrochar or biochar for understanding of how the choice of feedstock together with optimization of thermal process parameters will give best smart products.

Keywords Carbon removal, Chemical and physical activation, Municipal solid waste (MSW), Remediation, Waste streams

1 Introduction

The rise of standard of living globally is virtuous but it's always connected to increased consumption and demand for consumer goods followed by increased generation of municipal solid waste (MSW) [1]. Several competing technologies

are available for treating this waste and their sustainability is becoming a prominent factor. In addition to ecological and societal sustainability technologies need to be economically feasible to be applied on larger scale. One important quality criterion for waste treatment is suitability for energy and fuel production. In Europe the main renewable energy source is wood, which represents over 60% of all non-conventional energy used in the EU-27 [2]. Lignocellulosic woody biomass constitutes arborous forestry residues and residues from the wood processing industry. The activated sludge process produces solids that have mostly been considered as a waste without any good reuse and sewage sludge from biogas reactors has created challenges for reuse [3]. Sludge is, however, a suitable biomass for fuel production. The advantage with the hydrothermal process (HGT) is that the biomass does not need drying pretreatment and requires less energy. The yield of solid product, hydrochar, is greater in lower temperature pyrolysis (200–300°C) [4].

From the prospect of climate change, there is a great demand for swift and efficient methods to capture and sequester carbon away from the atmosphere. It was very recently reported that production, use and storage of biochar are carbon negative, and if applied into practice an estimated sequestration of 0.3–2 Gt CO_2 $year^{-1}$ by 2050 could be achieved [5]. The most relevant technologies offering carbon removal from atmosphere are forestation, direct air carbon capture with utilization and storage, carbon sequestration into soil, and wooden building elements for biochar production. The carbon fees on the voluntary carbon markets range from 12 to 1,045 European euro per ton CO_2 [5]. These carbon removal services by means of biochar are currently offered through full-bodied marketplaces that require wide-ranging certification, verification, and monitoring to add credibility and authenticity. Simultaneously biochar production is hopefully improving with increasing knowledge on feedstock usability, pyrolysis and in future more tailored applications to show that the biochar system is realistic to be applied at large scale [6].

Just as there are new usable waste streams, so are their potential uses that require more studies to become effective in environmental remediation, which is an actual field application of biochars [7]. Biochar production from lightly contaminated waste timber (WT) has been coined as a promising waste handling option for valorization of such residues into biochar sorbents that can be used for contaminant stabilization [8]. A challenge with wood waste is the presence of trace environmental pollutants that threaten the sustainable recycling of this waste. Impurities comprise adhesives, paints, trace metals fire retardants, waxes and plastics. Very recent studies have proposed thermochemical treatment of wood waste like gasification and pyrolysis that can give different new products, but also energy. Polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and trace metals are formed and/or emitted during thermochemical conversion. Their formation depends on both the operating conditions and the type of feedstock used. These pollutants may also appear in the resulting biochar [9, 10].

2 Biowaste Streams for Thermal Treatment

2.1 Composition of Agroforestry Waste (AFWs)

Timber logging generates large amounts of forestry waste residue. The global forests cover 4 billion ha, which is almost 30% of total land area, and on average 0.62 ha/capita [11]. Around 50% of this forest area is in developing countries [12]. The forest residue is typically stumps, branches, and leaves, and wood processing waste in form of logs and sawdust. The recovery of different residues depends on geography and related conditions, like type of tree species. For every cubic meter of logged material removed from the forest it has been estimated that a cubic meter of waste remains in the forest. The types of processing waste are bark removal and branch trimming (about 12% of this material arrives at mill facilities, slabs/blocks/further trimmings (about 34%) and sawdust constitutes about 12%. Waste comes also from kiln drying, shavings (about 6%), and sawdust/trimming (about 2%). On the scale woody biomass contributes around 4.6 Gt annually, from which 60% is used for energy, 20% is used as industrial "round wood," and the remaining 20% is in the primary production pool remaining in the forest where it decays. A surprisingly large part, ~80% of forest tree mass is then lost as waste, and from that wood about 20% ends up in kiln-dried sawn product [13].

Agricultural biomass wastes and residues are mainly crop stalks, leaves, roots, fruit peels, and seed/nut shells. These residues are mainly discarded or burned although they are valuable supplies of feedstock material [13]. It imposes challenges to estimate the degree of produced crop biomass in relation to what is the "loss" in production, including harvesting and processing, and also in relation to what is considered as "waste" that again entails retail or consumer loss. The production of "food" seems to be measured as the edible parts of a crop (harvest index), which again is not taking into account non-edible biomass parts, that are crops or not. One example to stress this point is sugarcane that requires processing generating waste streams in addition to the primary biomass waste in harvesting.

Based on Food and Agricultural Organization [14] estimations, Russia, Indonesia, USA, Brazil, and China produce most AFWs and industrial wood wastes. The potential production of residues could be more than 700 Mt./p.a. This large loss is a resource that could be used as fuel source. Typically, in the developing countries they are main household fuel and major energy source as part of industrial energy consumption [15]. The composition of AFW greatly influences the performance of AFW conversion system. In developing countries, most of the biomass residues are left in the field to decompose or alternatively burned on the spot, resulting in major environmental impacts. In the urbanization process the demand for products increase and alternative sustainable energy sources and raw material supplies are in need. So far, the biomass wastes are not efficiently taken into reuse as material and source of energy. Even less activity has been devoted to develop "low-carbon" solutions for valorization.

Forest residue amounts are defined as 46% of total forest stock [16]. Globally Russian Federation, Indonesia, USA, and Brazil produce most the forest residue, 5,718, 2,221, 2078 and 1,613 million tons (Mt), respectively. China, Sweden, France, and Finland are the next largest producers of forest residues of which Sweden and Finland represent Nordic countries with large proportion of forests land cover.

2.2 Municipal Solid Waste

Municipal solid wood waste (MSWW) constitutes a quite low share of total MSW, but the relatively high volume and inadequate prospects for reuse are causing cities difficulties in treatment, selection, and transport of the waste with the goal to mitigate MSWW environmental impacts [17, 18]. The common solution has often been the incineration of MSWW to produce energy [18]. In the time of circular economy worldwide [19], alternative policies have become the norm to reduce the environmental impact of incineration and instead promote the reuse of this waste category and prolong its life cycle [17]. In the present situation incineration should only be used as last of options since wood waste entails great reuse potential, and by recycling MSWW many opportunities arise still including efficient energy recovery.

3 Hydrothermal Carbonization (HGT)

Biochar has long been a known way of carbonization of different types of biomasses and in recent years hydrothermal carbonization (HTC) has in parallel been developed as an alternative method of processing biomass for value-added products [20, 21]. The solid char product formed during HTC is called hydrochar to be distinguished from biochar which is formed in pyrolysis process in temperatures from 300–650°C [22]. During the HTC process, biomass is heated in an oxygen free environment in presence of subcritical water under autogenous 2–10 MPa pressure [23]. The HTC process has several benefits compared to pyrolysis, including a lower energy consumption and the generation of less emissions. It is especially suited for high moisture feedstocks with a high moisture content that produces lower amounts of solid material after drying, and that makes them inadequate sources for pyrolysis [23]. This gives possibilities for a variety of feedstocks to be used for the production of hydrochar when drying the feedstock is not necessary [24]. Another gain compared to biochar is that by HTC the char yield is larger and produced with lower amounts of energy. Since the feedstock does not need to be dried, and operating temperatures for HTC (200–300°C) are lower, the yield is greater with less energy compared to biochar pyrolysis [25]. The char biomass is activated in the presence of liquid heating up the process, which enables lower process temperature compared to biochar production. The heating of the biomass initiates hydrolysis, dehydration,
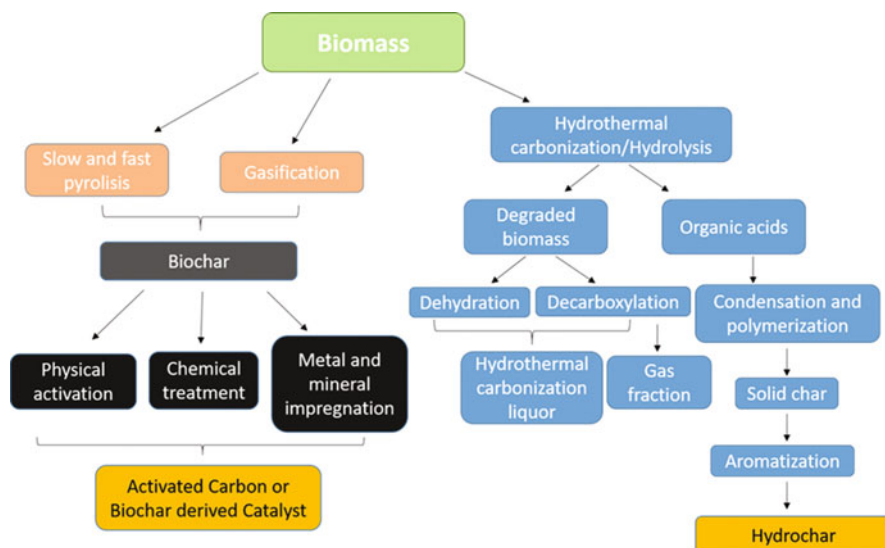
Fig. 1 Processes involved in the production biochar and hydrochar from biomass

decarboxylation, and aromatization that changes the physical structure of the biomass (Fig. 1) [26]. The hydrolysis is the primary reaction in HTC, and it has lower activation energy than the other reactions.

3.1 Feedstock Nature

The classification of feedstocks into wet and dry biomass can be done based on initial moisture content. Newly harvested biomass like sewage sludge, vegetable residues, algae, animal wastes, etc. often has high moisture content (>400%) and is then called "wet biomass." Agricultural residues and some wood species have low moisture content (<30%) when they are harvested and are thus called "dry biomass" [24]. The wet biomass can be dried to become low moisture content feedstock with complementing drying techniques, but their downside is the high-energy requirement that will be economically costly.

Biomass is an excellent source for bioenergy [27], that basically is clean energy and HTC can be applied to large varieties of feedstock like lignocellulosic residues [28], animal wastes [29], agricultural residues, food wastes [30], municipal wastes [31], and wastewater treatment plants' (WWTPs) activated sludge [32] that have detrimental effects on the quality of hydrochar. Overall, both hydrochar and biochar have their advantages and disadvantages. In future research biomass treatment can be combined with the hydrothermal carbonization process and pyrolysis process. The catalytic performance of the product materials needs to be further investigated [33].
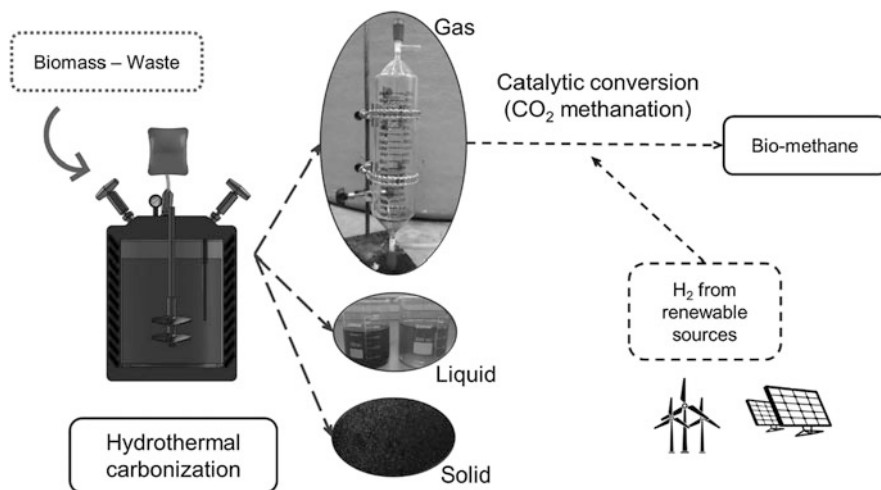
Fig. 2 Integration of HTC with methanation of gas phase [34]

Alternative fuels are sought to achieve required process temperatures in industrial processes as electricity becomes more expensive [34]. The gas phase obtained in hydrothermal carbonization can be subjected to a methanation stage, when the resulting methane could be used to fuel the process. Such process idea is depicted in Fig. 2. Such solution could be a step forward for integrated process according to circular economy principles. Moreover, the needed hydrogen for methanation should come from renewable sources.

Biomass has so far been utilized in many ways, but pyrolysis is a new way of dealing with biomass sustainably. The biological conversion has been applied with biogas reactors in fermentation and anaerobic digestion where the crucial step is what to do with the sludge to avoid it becoming a waste. Densified biomass like pelletization of forest residue has the challenge that it has mainly been used for heat production instead of channeling it into the biochar system (FAO) according to the principles of circular economy. The forms of biomass utilization are compared with pyrolysis and hydrothermal processes in Table 1.

4 Pyrolysis for Biochar Production

Biochar is a solid, carbon-rich product acquired from the pyrolysis process under an oxygen-limited atmosphere and high temperature [22]. The handling of all kinds of agriculture and forestry has become a priority. In the EU, about 23 Mt/p.a. of biomass (dry) is available as residual straw from cereals [16] whereas from example emerging economies like India, ca. 368 Mt/p.a. straw residue is available [35].

Table 1 Evaluations of waste biomass use

Biomass processing	Advantages	Disadvantages	Technology and objective
Pyrolysis	High efficiency and flexibility with sustainability prospects	Requires pretreatment of especially wet biomass waste	Slow or fast pyrolysis to receive biochar, bio-oil, and gases
Hydrothermal process	Direct application for wet biomass	The products not easily separated and demanding equipment	Carbonization, liquefaction, and gasification to receive hydrochar, bio-oil and gas
Anaerobic digestion	Low energy needs and large capacity	Requires large investments and is time consuming	Anaerobic digestion in biogas plant (bioreactor)
Solid fuel	Densified fuel into smaller space	High hydrophilicity catching moisture	Pelletization and briquette production

Biochar can be produced in different types of units and reactors to achieve the desired yield and quality. Reactors are similar, but the oxygen use, heating rate, and final temperature affect the quality and distribution of final products [36]. The thermal process for optimizing biochar yield is slow pyrolysis, which is conducted in 300–700°C in the absence of air producing bio-oil and biogas as by-products. Torrefaction is another process optimizing biochar yield, carried out at 200–300°C in the absence of air and it does not produce by-products. By prolonging the biochar residence time at ~400°C for more hours a higher yield and quality could be obtained [36].

4.1 Slow Pyrolysis, Temperature Regulation

In slow pyrolysis the temperature range is 300–600°C, with a long residence time (several hours to several days) and requires only low heating rate. It is generally believed that slow pyrolysis is the best pyrolysis method optimizing the biochar yield and structure [36, 37]. Zhang et al. [38] prepared three types of cow dung biochar under slow pyrolysis which revealed differences in morphology, surface area, pore structure, surface charge, and oxygen-containing functional groups where the biochar yield was 30–60% and the specific surface area <400 m^2/g.

The temperature is an important parameter in the design of biochar that governs physicochemical properties of the pyrolyzed product. It affects the aromatic condensation and aromaticity of biochar. With increased pyrolysis temperature the liquefied aromatic ring structure in biochar increases, at the same time as the unstable nonaromatic ring structure decreases [39]. Along with aromaticity hemicellulose, cellulose, lignin, protein, polysaccharide, and other macromolecules decrease in the resulting biochar. This leads to lower polarity of the solid product, but also lower hydrophilicity of the surface, forming separated aromatic rings. Zhang et al. [39] found that the pyrolysis temperature played a significant role in the properties of

biochar. The temperature correlated positively with the carbon content, ash content, pH, surface roughness, and conductivity. The (O + N)/C, O/C, and H/C ratios, however, correlated negatively with temperature [39]. The higher temperatures favor formation of crystal structures. Biochar produced in lower temperatures becomes acidic, polar with low aromaticity and hydrophobicity. With the increasing temperature functional acidic groups like –OH and –COOH decrease along with biochar yield. This leads to appearance of more alkaline functional groups, higher pH and ash when the biochar surface area increases as volatiles evaporate from the biomass.

4.2 Pyrolysis Atmosphere

In recent years the biochar synthesis has been refined and a number of different functional structures of biochar are better controlled through adjustment of synthesis parameters, not only pyrolysis time and pyrolysis temperature, but also by choice of biomass, and different pretreatment process. It is the gap between functional structures and mechanisms that needs to be bridged for achieving better results with biochar applications [40].

It is possible to optimize the pyrolysis process by changing the atmosphere in-situ activation for production of more potent biochars. This has been reported in several studies where the conventional N_2 atmosphere has been changed, for instance, to CO_2 as carrier gas [41, 42]. The activation with CO_2 improved the aromatic surface properties of biochar in temperatures of 500, 600, and 700°C [43].

Using spent coffee ground (SCG) the authors Cho, Chang [44] found two key roles of CO_2: the thermal cracking of VOCs appearing from the thermal degradation and the reaction of CO_2 with VOCs. They concluded that the morphological modification was initiated after depleting VOCs by the thermal degradation of the SCG sample in CO_2 atmosphere.

4.3 Co-Pyrolysis of Biomass with Activator/Dopant

When biochar is going to be used as a catalyst or adsorbent sufficient surface functionality is wanted providing more active sites for catalysis and adsorption of pollutants. High porosity and large surface areas are also advantageous for biochar utilized for storage of energy since they enable higher fluxes of mass transfer and active loading [45]. For biochar use, porosity and surface area of biochar and surface are critical and need to be properly assessed, or else desirable biochar features must be stimulated through suitable activation strategies (Table 2). Directly after the production process the biochar has low tendency to absorb or adsorb compounds. The surface area, pore size, pore volume, and the amount of pores present contribute to the reaction characteristics [56]. The produced biochars without proper activation

Table 2 The surface area, pore volume, and pore size of different biochars [46]

Surface area, pore size, and pore volume of various biochar-derived catalysts

Catalyst support	Catalyst support	Surface area (m²/g)	Pore size (nm)	Pore volume (cm³/g)	References
Glucose solid acid catalyst	Unsulfonated glucose solid acid catalyst	3.65 ± 0.26	–	–	[47]
	Sulfonated glucose solid acid catalyst	10.67 ± 0.90	–	–	
Douglas fir wood chip biochar	Biochar catalyst	3.51	–	–	[48]
Polyethylene terephthalate waste	Activated carbon	1,105	–	–	[49]
	Carbon acid catalyst	624.20	–	–	
Palm kernel shell biochar	Biochar	0.02	–	–	[50]
	Biochar-based catalyst	290.44	–	–	
Peat biochar	Peat biochar	83.78	89.26	106.90	[51]
	30 K/PB-600	20.04	42.02	31.55	
	30 K/PB-600 (fresh)	20.04	–	31.55	
	30 K/PB-600 (recovered)	17.81	–	26.62	
Chicken manure biochar	Silica (commercial)	451.1	5.98	0.88	[52]
	Biochar (350°C)	0.043	31.47	0.043	
	Biochar (450°C)	0.072	19.595	0.072	
	Biochar (550°C)	0.067	22.198	0.067	
Oat hull-derived biochar	B600	49.32	1.04	0.008	[53]
	BS100	30.59	2.30	0.055	
	BS140	5.43	1.03	0.008	
Waste pig meat and bone meal biochar	Meat and bone meal biochar	142.6	45.3	190.6	[54]
	AMB	430.5	128.6	586.5	
	30 K/AMB-550, fresh	80.0	59.4	61.4	
	30 K/AMB-550, recovered	91.6	66.4	74.5	
Wood char	Wood char	354	3.8	0.34	[55]
	Wood char-derived acid catalyst	337	2.7	0.24	

contain (1) abundant intermolecular spaces as a result of bond breakage between the organic components (2) clogged pores that cause generation of tar (3) inadequate pore size reducing the distribution of surface area (4) condensate contaminants like, ashes, etc. that decrease the pore size and volume.

4.4 Activation by Chemical Agents

Chemical activation methods are generally one-step processes where the agents are added to biochar and subjected to further pyrolysis. An activated biochar is usually washed for removing excess chemical, and after that the surface is ready for adsorptive reactions depending on target use. Typical chemical activation is oxidation, sulfonation, and amination and agents used are H_2O_2, SO_3H, $ZnCl_2$, acids like HNO_3, bases like KOH, NaOH. The activation agent is selected on the bases of the target use of biochar. Adsorbing negatively charged elements requires activation with bases imposing positive surface giving affinity to adsorbate. For adsorbing positively charged element, biochar is in turn activated with acid for improving adsorption of positively charged elements [57].

4.4.1 Activation by H_2O_2

H_2O_2 is a low-cost activation agent used at ambient temperature that splits into H_2O and O_2 and it is used as oxidizing agent because of the following reasons (1) low cost, (2) works at low temperature, (3) end products are H_2O and O_2. Biochar made from grape wood activated by H_2O_2 at 350°C has been shown to effectively adsorb the cyhalofop herbicide (35.4%) due to strong affinity of herbicide to biochar [58].

4.4.2 Activation by Metals

Metal ions are often applied as agents for catalysis [59]. Iron, cobalt, and other metallic biomass elements have been used in advanced oxidation systems [60]. Loading metal is thought as one of the operational ways for expanding the catalytic ability of biochar. When metal particles are dispersed in biochar, they can lower metal leaching. Biochar can prevent the aggregation of metal nanoparticles and thus offers many more accessible active sites. Compared to other catalysis supports, biochar has economical and efficiency advantages.

Zn-Co-layered double hydroxide (Zn-Co- LDH) nanostructures were incorporated with biochar through hydrothermal process [61]. After loading on biochar, the specific surface declined from 112.9 to 95.7 m^2/g. At the same time gemifloxacin degradation efficiency was raised from 60.4% to 92.7%.

There are several techniques to analyze biochar properties. The surface chemistry can best be studied by Fourier transformation infrared spectroscopy, X-ray diffraction analysis, and X-ray photoelectron spectroscopy. Structural analysis is done by scanning electron microscopy and Brunauer-Emmett-Teller analysis. The elements in biochar can be revealed by energy-dispersive-X-ray spectroscopy. The acidity and basicity can be determined by temperature-programmed desorption using ammonia [46].

Usually before co-pyrolysis biomass is premixed by impregnation or mechanical mixing with an activator/dopant, and then pyrolyzed. Co-pyrolysis of biomass with activators/dopants such as KOH, $Ca(OH)_2$, $ZnCl_2$, $MgCl_2$, $FeCl_3$, chlorapatite, Fe $(NO_3)_3$, $KMnO_4$, melamine, and urea has been explored. By using hazelnut shells as a raw material, Zhao et al. [62] undertook the chemical activation of $ZnCl_2$ for co-pyrolysis and found that hazelnut shells were an effective material for producing a microporous structure. Liu et al. [63] pretreated straw with a $Ca(OH)_2$ water solution, and then synthesized the calcium-rich biochar in-situ with black liquor as a precursor, whereby $Ca(OH)_2$ was found to be a mesoporous forming agent in the synthesis process. With corn stalk as raw material and urea as nitrogen source, Li et al. [64] prepared a nitrogen-doped fractional porous biochar by in-situ co-pyrolysis. The addition of urea promoted the formation of biochar pores, and nitrogen atoms successfully became a part of the biochar skeleton. Biochar attained through the co-pyrolysis of biomass with activators/dopants has a larger surface area and more surface oxygen-containing functional groups in comparison with original biochar.

4.5 The Quality and Safety of the Produced Biochars

Waste material is an important resource in Circular economy [65]. The recycling and upgrading of waste require detailed evaluation of possible waste contaminants. In pyrolysis there is the need to assess them in the biochar product. In the pyrolysis process enrichment of metals takes place since most of them are not released by emissions [66]. Pyrolysis can release metals as a volatile metal mixture together with aerosols from the gases. Organic compounds like polyaromatic hydrocarbons (PAHs) can leak during pyrolysis as aromatic rings condensation, fused into PAH-like sheet assemblies [67]. The quantity of toxic elements in biochars has been examined [68]. PAHs are especially produced during incomplete combustion of biomass, and thus are integrally generated during biochar production. Due to their well-known toxicity and carcinogenic traits, they constitute an environmental risk.

The quality of biochars is an important issue especially in the commercial market where the biochar is intended for a spectrum of different uses. The European Biochar Certificate highlights the specific contaminant threshold levels in biochar for agricultural soil improvement [69]. The threshold levels are given as total content in the solid phase. Concerning contaminants, the bioavailable concentrations are crucial in accurate risk assessment and need some attention [70]. The heavy metal contents are dependent on both feedstock and process parameters of the performed pyrolysis [71]. The rise in pH supports lower heavy metal solubility [72]. The pH increase in biochar may not last due to leaching where soil pH might in the long term be reduced. Biochar application in agriculture requires thorough assessment of biochar quality since toxic organic contaminants of biochar may end up in the environment. European Biochar Certificate (EBC) values of the molar ratio of H/Corg <0.7 and O/Corg <0.4 does not ensure that biochar will not cause phytotoxicity [10].

5 Biochar for the Remediation of Contaminated Soil and Water

Soil amendment is the most common application of biochar and several studies have demonstrated the benefits of such practice [73, 74]. Biochar as an amendment in soil has been shown to improve soil properties such as soil C content, increase water holding capacity, and increase aggregate formation, stability [75] and plant growth [76]. It could also improve soil quality and fertility [77, 78]. The high porosity of biochar has taken advantage to immobilize heavy metals in soils [79], and in consequence reduce their uptake by plants [80], and remediate organic pollutant-contaminated soils [81].

5.1 Heavy Metals

Soil pollution poses a threat to human and environmental health as contamination can migrate into groundwater, or drain into other water bodies. But it may also get into the food chain and eventually reach humans [79]. Just in the USA more than 100,000 contaminated sites have been identified [82] and in Europe the estimate for the total number of potentially contaminated sites is 2.5 million [83]. Due to their high toxicity and health risks the remediation of heavy metal (HM)-contaminated soil has become a priority in the environmental agenda [84]. The use of biochar for the remediation of HM-contaminated soil has become a sustainable solution (Fig. 3). Biochar as a porous material has the capacity to bind HMs from soil and that way reduce the uptake of HMs by plants [80, 85, 86]. The raw materials and feedstock for biochar production together with the pyrolysis temperatures are the most important
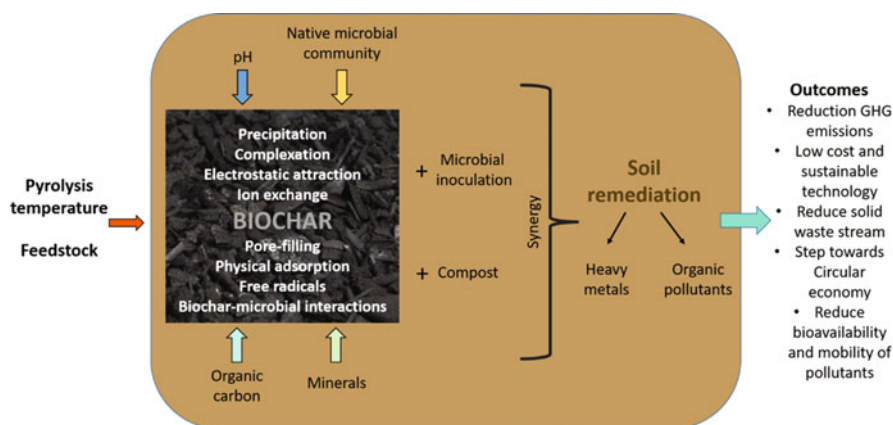

Fig. 3 Factors influencing the remediation of contaminated soil with biochar as an amendment and its advantages

criteria affecting the binding capacity of biochar. The interactions between biochar and HMs in soil can be direct in precipitation, complexation, or electrostatic attraction. The interactions can also be relatively indirect depending on soil pH, minerals, or organic carbon [87]. Biochar adsorbs the metal ions from contaminated soils due to its stronger sorption sites and high affinity to metal ions [88].

Choudhary et al. [89] used biochar from pine needle litter to serve for Pb adsorption from contaminated water. The study showed that Pb adsorption increased significantly as pH and temperatures increased and desorption results were promising with a lead recovery of 90–93%. They concluded that biochars possess the potential for aqueous removal of other metal cations [89].

5.2 Phytoremediation and Related Microbes

The most recent studies have been testing biochar as a carrier of HM-reducing strains or HM-tolerant bacteria and its effects upon its addition into contaminated soil [90]. Cr contaminated soil is of great concern due to the high toxicity of Cr(IV). A recent study successfully immobilized a Cr(IV)-reducing strain into biochar to treat Cr-polluted soil. Soil properties improved with aggregate formation, organic carbon content, and cation exchange increased. The Cr(IV) was transformed into less toxic Cr(III) and that Cr-residue fraction increased by 63.38% compared with control. The aggregates also reduced the Cr absorption of *Ryegrass* from the root and enhanced its growth [91]. Biochar inoculation with a HM-tolerant strain was reported to significantly increase residual fraction of Cd and Cu leading to the decreased bioavailability of the metals in soil. The inoculated biochar enhanced soil enzyme activity and the soil microbial community recovered at the end of the incubation, showing improved soil function after metal stabilization [92].

It has been demonstrated that solubility of Pb and Cd decreased significantly with biochar produced from agriculture residues providing evidence that biochar decreased HM toxicity [93]. Soil properties improved; pH increased together with organic matter and nutrient content. Maize planted on the treated soil with biochar performed better compared to the control demonstrated as an increase in biomass [93].

The interaction among biochar, plants, and microbes might alter the HMs behavior in the soil [94]. The beneficial roles of biochar on plant growth and on the enhancement of microbial activity were likely to improve the phytoremediation efficiency of the hyperaccumulators [95]. Biochar incorporation does not decrease the total heavy metal content of the soil but it reduces the bioavailability and phytotoxicity of heavy metals. Therefore, phytostabilization of metal-contaminated soils can be enhanced by combining metal immobilizing plants with biochar [96]. Biochar was used in Cd soil contamination for cell immobilization of two cadmium resistant bacteria (CRB), *Arthrobacter* sp. and *Micrococcus* sp. [97]. Biochar-immobilized (BC) CRB were able to survive in cadmium-contaminated soil (Fig. 4). The inoculation of BC-*Micrococcus* sp. increased the
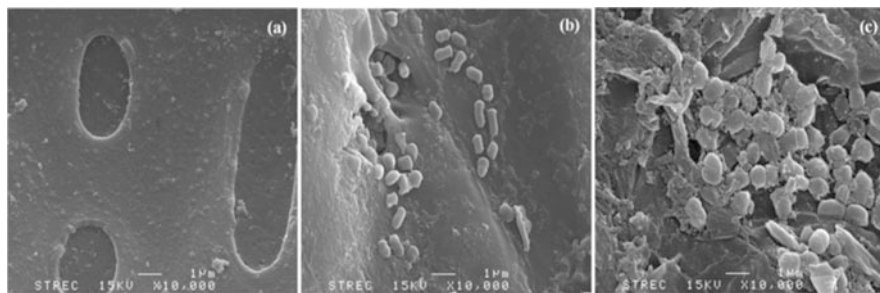
Fig. 4 Biochar of cassava stem (*Manihot esculenta L. Crantz*). HM Phytoremed with bacterial immobilization. Characteristics of (**a**) biochar, (**b**) BC-*Arthrobacter* sp., and (**c**) BC-*Micrococcus* sp. observed under SEM at ×10,000 magnification remove 5 [97]

root dry weight of *C. laxum* planted in cadmium-contaminated soil. Plants inoculated with either BC-*Arthrobacter* sp. or BC-*Micrococcus* sp. had the highest cadmium contents in the shoots and the roots. They concluded that *C. laxum* combined with BC-*Arthrobacter* sp. or BC-*Micrococcus* sp. inoculation achieved a high efficiency of cadmium phytoextraction in metal-contaminated soil.

5.3   Organic Pollutants

Biochar from biomass waste has successfully been used for remediation of organic pollutants [98]. Interactions of free radical-based chemical reactions and biochar-microbial communities are the most important mechanisms involved in the degradation of soil organic pollutants using biochar. Pollutants are preferentially adsorbed onto the surface and pores of the biochar in free radical-based chemical reactions. The radicals formed in advance oxidation process degrade the pollutants [73].

Colored contaminated water has been treated with different types of biochar with good results. An example is the recent study where engineered biochar was produced from food waste digestate to remove azo dye pollutant from water. Results were promising with a removal of >99% of the dye upon the addition of biochar (0.5 g/L) and peroxymonosulfate (1 mM) to wastewater. The removal efficiency was attributed to the catalytic sites in the biochar which could activate peroxymonosulfate to produce reactive oxygen species [99]. Biochar from wood apple fruit shell waste was used in the removal phenol and chlorophenols (4-CPh and 2,4-DCPh) from contaminated aqueous media [100]. The study revealed that this biochar was an effective adsorbent of these organic pollutants with pH and temperature being vital parameters to take into account for a rapid uptake and high sorption capacity: it could be used for the treatment of contaminant wastewater [100]. Efficient removal of Rhodamine B dye was achieved by a magnetic biochar produced from waste wood [101]. The adsorption process was governed by a chemical reaction and the adsorption process was a single-layer and heterogeneous surface adsorption. The equilibrium was

established within 1 min, indicating an excellent adsorption efficiency making this magnetic biochar a prospect in wastewater treatment [101].

Modified biochars with active oxidation agents, e.g. persulfate, peroxymonosulfate, chlorine, iodine, etc., have been utilized to generate free radicals and improve the degradation of organic pollutants [73]. Biochar from waste lychee branches was together with persulfate used for the removal of bisphenol A (BPA) in soils [102]. This type of biochar activates persulfate to generate sulfate and hydroxyl radicals for BPA degradation. Liu et al. 2020 [102] concluded that the combination of biochar and persulfate could be used for in in-situ remediation of organic contaminated sites.

Herbicides are organic chemicals that may undesirably impact human, wildlife, beneficial plants and soil organisms. In a multifaceted experiment by Wu, Liu [103] different types of biochar (peanuts (BCP), chestnuts (BCC), bamboo (BCB), maize straw (BCM), and rice hull (BCR) were applied to soil to study their sorption capacity, degradation, and effect on the bioavailability of the herbicide oxyfluorfen. The most important results showed that the biochars exhibited different sorption capacities for oxyfluorfen in the following order: BCR > BCB > BCM > BCC > BCP and that the addition of biochar to soil reduced the bioavailability of oxyfluorfen. Oxyfluorfen degraded faster in BCR-amended soil compared to unamended soil, i.e., degradation increased by ~1.2-fold with addition of just 2% BCR. Interestingly, the adsorption capacity of amended soil for oxyfluorfen decreased with increased aging time, however, it was still higher on the amended soil compared to the unamended soil after 6 months. In conclusion, the study indicates that the introduction of biochar is an effective method to modify soil contaminated with oxyfluorfen and to decrease the risk of contamination [103]. Sugarcane top-derived biochar was added to different types of soils to evaluate the sorption capacity toward atrazine herbicide [104]. The sorption coefficients had a positive correlation with the amount of biochar added into soil. The study indicated, however, that as a result of adsorption the degradation of atrazine decreased and that it could be a method to prevent atrazine leaching into groundwater [104].

The combination of biochar and compost has proven to be effective in the remediation of organic pollutants, when both amendments improve soil quality and fertility. The application of compost and biochar amendment decreased the concentration and bioavailability of PHCs [105]. The addition of compost enhanced biodegradation, while biochar contributed to lock the hydrocarbons in contaminated soils [105]. Hussain, Khan [106] observed that the combination of biochar, compost, and immobilized microorganisms resulted in the highest PHCs removal from soil compared to the control or the treatments alone.

6   Toward Circular Economy: Recycled Waste for Biochar Production

Pyrolysis and hydrothermal carbonization of biomass have attracted attention as expedient waste management methods [107]. Biochar has been produced from several organic waste material such as guayule bagasse, cotton gin waste [108], coconut shell [109], empty fruit bunches [110], and rice husk [111]. Biochar pyrolysis has been reported for food waste digestate and food waste [99], straw from crops (corn, wheat and bulrush) [112, 113], pig manure [107], and wood waste materials.

When waste wood is used as heating energy it will release CO_2 to the atmosphere, which is against current policies in Europe for reaching carbon neutrality. Furthermore, waste wood in landfills will create methane emission as product of the decomposition of lignocellulose compounds [114]. The construction and demolition industry produces waste wood that has become a viable source of biomass for the production of biochar. Countries including Taiwan have already implemented the reuse of waste wood as material and energy resource in carbon-negative policies, to reduce greenhouse gases (GHG) emissions [114]. Waste wood like wood shavings, waste timber, bark and pine needles litter has already successfully been produced [89, 109, 115]. The increase of the production of biochar from waste wood could become a global solution to reduce the landfills. It has been estimated that just in Finland wood waste accounts for 3,268,000 t from which 401,000 t comes from construction industry [116, 117].

Differently produced biochars have increasingly been used for soil amendment but also contributing to carbon sequestration. An interesting application is the introduction of biochar into building material like cement and concrete.

6.1   Novel Applications of Biochar

The use of biochar as soil amendment is the most common application of this material [78], however in recent years there has been several other useful and sustainable applications. Some of these examples are briefly mentioned in this chapter as in Fig. 5.

6.1.1   Carbon Sequestration for Carbon Neutrality

For achieving the goals of carbon (C) neutrality, municipalities need worldwide to apply negative emission technologies. The application of biochar as soil amendment represents a sustainable long-term carbon storage [118, 119] that has a mitigating influence on climate change and global warming. The conversion of waste wood into biochar has a positive effect on carbon sequestration. Around 50% of the carbon in waste wood is retained in biochar instead of being released into the atmosphere. In
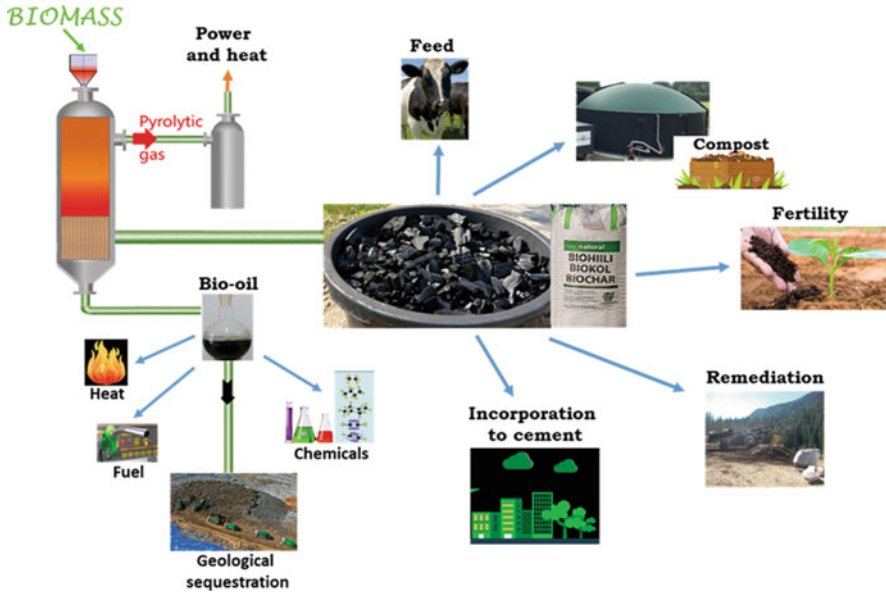
Fig. 5 Pyrolysis presenting the three main products, biochar, gas, and bio-oil. Potential applications for the carbon sequestered in biochar including soil fertility, feed in livestock farming, incorporation to building material, organic fertilizer, and environmental remediation. Bio-oil can be used for heating, but especially for upgrading to fuel, chemicals and even deposited as geological sequestration

this procedure the organic carbon is moved to a slower carbon cycle reservoir (biochar) that can remain in soil even for centuries [120]. Urban demonstration areas using trees and biochars for C sequestration have been implemented in Helsinki, Finland to show that urban C sinks in public parks need to be visible and scientifically sound for reliable cost-effective verification of carbon sequestration. Valuable synergies emerged from co-creation of urban C sink parks between stakeholders (scientists, city officials, companies, and citizens) for increasing impact of biochar application [121].

6.1.2   Composting

The addition of biochar into compost (Fig. 5) could increase the aeration process as biochar is a porous material with low density [122]. Moreover, due to its high sorption capacity it could reduce the loss of nitrogen and immobilize HMs and organic pollutants present in the compost materials [123]. It has also been demonstrated that it could reduce the emission of GHGs [124]. Moreover, research has demonstrated that the combined application of biochar and compost to soils could increase both; their agronomic value and reduce nutrients losses [125].

6.1.3 Livestock

Significant benefits of biochar in feed (Fig. 5) to improve animal health have been reported [126]. In an extensive survey (>100 scientific publications) on biochar in animal feeding, positive effects on digestion, feed efficiency, toxin adsorption, blood values, and meat quality were widely observed. GHG emissions were also reduced when biochar was added to feed [126]. In Europe it has recently been approved to add biochar to livestock feed at 1–2% for reducing vet and medical costs [127]. Biochar has further been effective in animal bedding for odor control [128].

6.1.4 Concrete

Other biochar applications include the incorporation of biochar into the concrete mixture for building (Fig. 5), with positive results and as carbon sequestration opportunity. Akhtar and Sarmah [129] tested three different waste sources of biochar to replace cement content up to 1%. The study concluded that biochar has the potential to improve the concrete properties, e.g. flexural strength while replacing minor fractions of cement [129]. Biochar from residual biomass of a bio-ethanol industry in mixture with concrete improved the sound absorption coefficient [130]. Biochar-concrete mixtures have also shown an improved water tightness, mechanical strength and minimal internal damage to concrete micro-structure [131].

7 Conclusion

The utilization of waste biomass for pyrolysis opens up great avenues for valorization of it to hydrochar and biochar. These higher value products may find a wide environmental range of applications ranging from fertilizers to remediation tools and use in building material to support the transition toward carbon neutral societies. The future success of these materials requires good separation of waste and channeling of waste streams into economic valorization. This will further depend on the ability to tailor various biomasses for specific purposes in an economically feasible way. The removal of carbon from atmosphere through biochar systems and the growth of the voluntary carbon market will speed up new applications for these very stable carbon products helping to reach carbon neutrality.

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