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Techno-economic analysis reveals the untapped potential of wood biochar

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GRAPHICAL ABSTRACT



ABSTRACT

The United Nations estimates the rate of deforestation over 10 million hectares per year, with additional infested wood available due to drought, bark beetle calamity and other damage vectors. Processing the hard-to-reach infested wood into biochar via mobile pyrolysis units seems to be a good option for fire prevention. However, since most biochar is currently produced mainly from biological waste, there is not enough experience with wood biochar on a large scale. Review of current knowledge, followed by techno-economic assessment reveals that following the chemical composition of the feedstock, wood biochar outperforms other types of biochar in terms of high porosity. Therefore, wood biochar shows excellent results in increasing the amount of plant-available water content in soil and appears to be an excellent tool for recycling nutrients (especially into plant-available forms of phosphorus and nitrogen). The overall positive effects of biochar application change from abiotic to biotic over time because as it decays, many of its physical properties disappear, but it can boost soil microbial communities on which soil fertility depends. As global climate change creates a wide range of factors that damage forest cover, wood biochar consequently represents untapped potential in the field of soil, nutrient, and energy management.

Keywords: Wood biochar, circular economy, nutrient recovery, bioeconomy, soil water retention, bark beetle

1. Introduction

Biochar refers to the powdery carbonaceous pyrolytic products of biomass origin, where "bio" suggests the intended use in agriculture, forestry, orcharding, pastoralism and other types of environmental engineering. Although, historically, the main source of char used to be exclusively wood, today the vast majority of both char and biochar is produced from various biological wastes such as food production wastes, sewage sludge, postharvest residues, etc., in order to minimize production costs (Xiong et al., **2021**). The lowest production costs (lower than $30 \notin t^{-1}$, all prices as of 24 August 2021) and highest profitability are reported for biochar production from fermentation residues originating at biogas plants (Stehel et al., 2020). This is because biogas plants are (1) a reliable source of feedstock of stable parameters, (2) waste heat from biogas combustion is constantly available, and (3) there is onsite use for the product. As far as biochar from wood is concerned, given the steeply rising price of wood as a building material, this product has so far been produced mainly from waste wood such as branches, bark, shingles or wood waste from the demolition of buildings (Bai et al., 2015). Many research studies have independently indicated that the unique physical and chemical characteristics of biochar makes it a promising material for soil improvement (Strunecky et al., 2021), wastewater treatment (Cheng et al., 2021), carbon sequestration (Hašková, 2017), energy storage (Brynda et al., 2020), fertilization (Stávková and Maroušek, 2021) and many others (Shen et al., 2020). As a result of the above, journals are receiving a plethora of manuscripts covering the same old topics: pyrolysis of municipal biowaste, analysis of sewage sludge biochar, material and energy flows following biochar production from kitchen waste etc., but not (many) regarding long-term and commercial-scale application of biochar made from wood (Streimikiene et al., 2016). And if any such studies are available (Wan et al., 2020), these tend to focus on theoretical aspects of sustainability (Doskocil et al., 2016), various activation techniques (Chen et al., 2020) or they usually deal with research conducted under laboratory conditions (Dzhalladova et al., 2019) rather knowledge easily applicable in commercial practice (Muo and Azeez, 2019). Although data change rapidly during the ongoing pandemic (Sekar et al., 2021), on a long-term average, forests cover about a third of the world's surface and absorb about a quarter of anthropogenic CO_2 . Over the past decades, the intensity and frequency of droughts have increased, leading to increased forest loss (Bencsik et al., 2018). Curtis et al. (2018) reports that 27% of global forest loss is attributable to deforestation due to permanent land-use change for commodity production (mainly agriculture), with the remaining loss largely attributed to dying of trees. Drought and heat waves often interact with other forest-related events such as wildfires, erosion and windstorms and can significantly amplify the occurrence and severity of reckless human activities and other biological vectors such as insect and disease pests (Blazkova and Dvoulety, 2018). Tree mortality is a global phenomenon, and the main causes include drought; lack of available nutrients including carbon; biotic attack, and most often the interaction of these factors (Kliestik et al., 2020a). Sites of significant tree mortality due to drought and heat worldwide were mapped by Hartmann et al. (2018). According to projections by d'Annunzio et al. (2015), the rate of global forest loss will continue until 2030 but from then on there is growing hope that the pace will begin to slow. Betts et al. (2017) argues that the forest loss is so severe that it could trigger new wave of global extinctions. Bark beetle infestations in the northern hemisphere have reached unprecedented proportions and are expected to increase due to climate change (Cepel, 2019). In western Canada and the USA, tree mortality caused by bark beetle exceeded 30 million ha, with almost 35 M m³ of wood being destroyed in Europe, not including Russia (Hlásny et al., 2021). In the light of climate change, trees damaged by drought, bark beetle and other disease vectors are increasingly being charred on site via portable kilns to reduce the risk of fires or the blockage of a river and subsequent flooding (Sahoo et al., 2021). This method of production is difficult to automate and requires a considerable amount of labour in difficult terrain and is therefore not expected to reduce biochar production costs below $800 \notin t^{-1}$. For such biochar to be competitive, its added value needs to be significantly increased (Kubickova et al., 2021). However, a review of methods that reflect this new economic reality is not available. Given the industry's desire to keep costs to a minimum there is a lack of a comprehensive techno-economic overview of use of biochar made from wood, as well as commercial-scale experience with this material.

2. Production

Biochar is a dust made of solid but brittle aromatic polycyclic structures obtained by pyrolysis, which means heating the carbonaceous biomass in an atmosphere with limited oxygen (O_2) . Older batch technologies are better suited for mobile use in the forest because these are technically less demanding and do not require an external power source (Rosales et al., 2017). They also have the advantage that infested wood does not need to be disintegrated before the process, but only after pyrolysis has been completed (He et al., 2021). This makes production more competitive and less energy intensive because the char is more brittle than wood (Skapa, 2012a,b). Although the production technology has undergone significant changes throughout history (from primitive earth pits and mound kilns, through batch retorts and continuous screw reactors, to modern catalyzed bubbling fluid bed reactors, which are part of biorefining complexes, Liu et al., 2021), the basic principles remain unchanged (Meile et al., 2021). Nevertheless, understanding the production process is a key to environmentally as well as financially sustainable biochar management, which covers a wide range of fields from waste management to engineering, forestry, environmental engineering, chemistry, and agriculture to name a few (Marakova et al., 2021). Das et al. (2021) reminds that the pyrolytic process can be understood to mean dry distillation or, in other words, removal of volatile organic compounds (VOC) from the fixed structures of aromatic carbon (C) in the biomass. Collard and Blin (2014) argue that the development of aromatic rings (benzene rings in particular) is a crucial step of the pyrolysis process. On one hand, because benzene rings are the key component, which constitutes the mass of the biochar and the rate at which they are formed and associate together significantly influences biochar yields (Nguyen, 2020). On the other hand, for the reason that whatever the considered application (production of substrate, wastewater management, improvement of compost quality indicators, production of special fertilizers, regeneration of nutrients, improvement of water and air management in soil, etc.) the composition of the substituents of the benzene rings will impact the usability of the following steps of biochar commercialization. Laird et al. (2017) indicates that rapid heating contributes to increased tar formation, while a gradual process increases the proportion of biochar produced. Throughout the pyrolysis process, a jungle of decomposition reactions occurs in multiple directions and also repeatedly (dehydration, depolymerization, isomerization, aromatization and decarboxylation to name the most important ones, Wang et al., 2020). It is mainly the (1) dynamics of operating parameters (such as maximum reaction temperature, retention time, heating rate, pressure, vapour residence time, reaction atmosphere, etc.), (2) reactor design, and (3) fragmentation, the ratios and characteristics of major feedstock compounds (lignin, cellulose and hemicel-lulose) that define the resulting biochar characteristics (Akhil et al., 2021). Given the complexity of biomass pyrolysis, the vast majority of authors find it more convenient to study the conversion of each compound separately. However, evidence from commercial practice indicates that the knowledge gained in this way has only theoretical significance (Skare and Cvek, 2020). For instance, the interaction between hemicellulose and lignin results in formation of lignin-derived phenols (Wang et al., 2021), therefore hampering hydrocarbon (HC) synthesis. This is because lignin is a complex polymer of phenylpropane units comprised of different aromatic ring substitution patterns, all of which are randomly linked together through various ether linkages and condensed bonds. The amorphous structures of hemicellulose linking decrease the likelihood of cross-linking reactions, therefore, the intramolecular dehydration reaction is responsible for most of the weight loss at the beginning of the pyrolysis process (Collard and Blin, 2014). This is why lignin tends to interact with cellulose, which can hinder the development of L-glucose polymer (which tends to transform subsequently into tar) from cellulose and thereby limit biochar production). In contrast, Wang et al. (2020) argues that interaction between cellulose and hemicellulose has a negligible effect on the formation and distribution of pyrolytic products. Pyrolysis of feedstock like coconut shells and hardwoods can result in biochar consisting of over 90% C but it can also be much less than 15% when using mineral-rich feedstock such as sludge from sewage treatment plants or animal manure (Li et al., 2018). It is the different thermal stabilities and interactions between these major compounds during pyrolysis, which defines the majority of the properties of the biochar. Cellulose pyrolysis starts at temperatures as low as 200 °C, producing organics with conjugated π -bond structures (**Zhang et al., 2021**). The weakest inner linkages between phenyl-propane units, such as ether linkages, are rapidly broken even at slightly increased temperatures (Marousek et al., 2015). Pyrolysis of each compound is accompanied by a group of reactions during which these compounds interact with each other, their fragments and resulting derivatives, which creates a complex web of multiphase reactions (Zhang et al., 2021). Although cellulose is a polymer of a simple crystal structure composed solely of $\beta(1 \rightarrow 4)$ linked D-glucoses, its thermal degradation might result in an overabundance of breakdown reactions including dehydration, dehydrogenation, retro-aldol condensation and many others. The resulting monomer units consequently undergo intramolecular rearrangement to form levoglucosan and L-glucose derivatives (Xing et al., 2021). Levoglucosan is assumed to be the key intermediate influencing the formation of anhydro-monosaccharides through isomerization and dehydration reactions, which sooner or later form solid biochar via polymerization, dehydration and fragmentation. Long et al. (2020) identified that the major pyrolysis products of L-glucose derivatives are glucose, anhydro-disaccharides and disaccharides of various linkages. The glycosidic linkages between monomer units subsequently become very active and begin to split via a series of joint reactions, including enol-keto tautomerization and dehydration. These reactions lead to the formation of anhydro sugars. These intermediate products subsequently undergo dehydration, decarboxylation, aromatization and intramolecular condensation to form solid residues. Hemicellulose (commonly represented as xylan, the most easily degradable polymer) breakup occurs between 228 °C (due to breakdown of the side chains of glucuronic acid and arabinose, Khaire et al., 2021) and 275 °C (due to breakdown of the xylan backbone). At temperatures above 300 °C, the internal structures of almost all the polymeric chains in the biomass begin failing and fragmentation to form smaller molecules begins. These detached fragments are released as VOC and tend to react with the remaining polymers to create new complex structures (Kwapinski, 2019). Cellulose breakdown occurs between 315 and 400 °C. Up to 350 °C the primary products are dehydrated sugars, which subsequently form different types of furans (Mardoyan and Braun, 2015). The aromatization of VOC could take place at temperatures as low as 350 °C, producing phenols, substituted benzene and branched phenolics, which are transformed into aromatic hydrocarbons at slightly higher temperatures. If there is enough energy in the process (e.g. from an external source, Jandacka et al., 2017), even the C-C bonds could break down and form gaseous products, which could condense to form aliphatic compounds with long chains or undergo aromatization to form phenolics or aromatic hydrocarbons and eventually biochar. Once temperatures of around 400 °C are reached, significant amounts of VOC and gases (mostly H₂ and O₂) are released. From 450 to 650 °C the substantial elimination of O-containing functionalities dominates the process

(Lenhard et al., 2019). Production of aliphatic aldehydes, ketones and carboxylic acids reaches its maximum at around 650 °C (Buchalcevova and Gala, 2012). Cracking of (almost finished) biochar and gasification of VOC commences above 650 °C, producing CO, CO_2 , CH_4 and H_2 as the main products. The remaining aromatic structures can adsorb these VOC via π - π interactions. Nevertheless, lignin breakdown occurs continuously from 150 °C to 900 °C (above these temperatures the condensed bonds become active and begin to break, promoting the production of lignin monomers; Bilan et al., **2020**). Within this temperature range, lignin is being depoly-merized via breakup of β -O-4 and β -5 linkages into its phenolic monomers (Lancefield et al., 2015). Fewer β -O-4 and β -5 linkages in the remaining clusters subsequently begin causing the substantial breakdown of glycosidic ether or C-C bonds. In general, biochar depolymerization can be described as the breaking of bonds between individual monomer units of the carbonaceous polymer, which results in decline of the rate of polymerization (Collard and Blin, 2014). After each rupture, the new chain ends are stabilized and the released molecules become volatile. When the released VOC are not stable under the process parameters, they tend to undergo reactions such as cracking or recombination until they reach an energetically stable state. The pyrolysis products can undergo repolymerization reactions via the condensed linkages and are finally converted to solid char products. As a result, biochar is widely considered a heterogeneous mixture with different C fractions, including stabilized C pool, labile C pool, ash fraction, and even inorganic and organic constituents (Xing et al., 2021). The biggest advantages of biochar made from wood include high surface area and lower ash content. This is due to the higher proportions of lignin and cellulose of a high degree of crystallinity in wood (Shaheen et al., 2019).

3. Water retention

The property of soil to retain water during long-term drought or heavy rain is crucial to sustainable land use (Postula and Raczkowski, 2020). The addition of biochar has repeatedly and independently proven to be an effective tool for improving soil water management and reducing erosion (Cai et al., 2020). As reviewed by Razzaghi et al. (2020), the field capacity, wilting point, and plant available water content are among the 3 most common soil water management criteria in terms of considering soil as a medium for growing plants. Nevertheless, the application of biochar (in particular the anomalies associated with its multilevel porosity; Marikina, 2018) highlighted some minor weaknesses of these traditional criteria, making any quantitative comparisons of biochar application across international literature inaccurate (Dedina and Sanova, 2013). Provided that biochar porosity is represented by a wide range of particle size distribution, diverse internal pore volumes and variable surface areas (Vaheddoost et al., 2020), environmentalists investigating various phenomena beyond the soil - water -nutrient - plant continuum traditionally advocate application of biochar as a method for reducing water evaporation, decreasing soil bulk density, mitigating water erosion and improving soil water retention (Venclova et al., 2013). This ability of biochar to improve soil properties has been repeatedly and independently confirmed and its mechanism is being attributed to the physical properties of biochar, such as capillary forces, pore structure and the swelling effect (Jacka et al., 2018). Accordingly, Sun and Lu (2014) reported a significant increase in soil aggregate steadiness and a decreasing risk of topsoil sealing. Extensive efforts have been made to predict water management following interactions between biochar and soil, by measuring the total volume of biochar intrapores (pores in the interior of biochar fragments attached to peripheral pores), and interpores (pores on the biochar skeleton). Yi et al. (2020) pointed out that changes in water retention occur mainly due to (1) sorption in biochar intrapores, (2) capillary water penetrating into intrapores and (3) modification of interpores. However, conflicting factors have also been reported under certain conditions. Garg et al. (2017) demonstrated that many studies did not consider the particle size and age of the biochar. Yi et al. (2020) reminds that aging reduces the physical water-binding capacity of the biochar because (1) as intrapores are broken down, the volume of water retained decreases, (2) as narrow tubes are broken down, the capillary forces decline, (3) as interpores break off, the surface charge lowers and the porosity of the biochar is reduced. Small biochar pores (resulting from its disintegration) are able to retain more water against gravity than soil aggregates. Due to its high porosity (inner chambers with a wide range of radii), the black carbonaceous structure of biochar captures a wide spectrum of electromagnetic solar radiation and thus heats up the soil surface. Worse still, some types of biochar exhibit strong and longlasting hydrophobicity (controlled by the surface functional groups (carboxyl; hydroxyl and phenolic; Hussain et al., 2020), which prevents rainwater or dew from penetrating into the soil and it consequently remains on the soil surface until it evaporates. Over time, the soil biota fills biochar pores and decreases its specific surface. Water therefore ceases to be physically trapped and becomes part of soil organic matter (habitat for microbes and fungi; Sun and Lu, 2014). Wood biochar usually holds more water (mechanically, as water enters the mesopores) than biochar from various biowaste, and this water is then more readily available to plants (Twarakavi et al., 2009). There are indications that, in some cases, improved water management accompanying the development of soil biota associated with biochar decomposition could even overcome the hydrodynamic effects associated with the physical forces that characterize freshly produced biochar (Kovacova et al., 2019). The biochar's newly opened porous structures provide an attractive habitat for microorganisms, thereby accelerating its population and metabolism processes making more nutrients readily available to plants. It has been reported that the finest structures of biochar (capable of filling interpores between coarse soil particles), traces of ash and new hydraulic properties (sometimes even hydrophilic surfaces are reported) boosted the diversity of soil microbiota and composition of nitrifying (also interacts with mycorrhizal fungi and rhizobial bacteria) and P mineralizing bacteria. It is especially recognised that living soil biota incorporates large amounts of bodily fluids into its bodies and enhances plant growth by accelerating nutrient streams and by coping with abiotic (including drought and excessive moisture) as well as biotic (diseases) stresses (Pathy et al., 2020). Additionally, there are indications that some molecules (aromatic HC; heterocyclic compounds, polycyclic, and benzofurans) from decaying fragments of biochar could (1) work like catalysts and simplify interactions between enzymes and substrates, (2) act as allosteric regulators, (3) lessen the activation energy of an enzyme catalyzed reaction, (4) inhibit certain enzymes and (5) trap some signalling molecules with potential to change cell-to-cell communication.

4. Nutrient recovery

The greatest opportunities for nutrient recovery are currently seen in connection with farming, food production and wastewater treatment plants, where waste nutrients are found in high concentrations. A way to reduce eutrophication of water by capturing P and N more cheaply is being intensively sought (**Strunecky and Koblizek, 2021**). Countries that are dependent on nutrient recovery are turning to nutrient recovery in particular in the hope of importing them. Given that biochar is often used as a substrate, soil or compost enhancer, its competitive advantage can be increased if it also contains nutrients or other plant promoting agents (see **Fig. 1**). As a side effect, biochar increases the metabolic activity of the microbial community and thus indirectly facilitates nutrient mineralization (**Xu et al., 2021**). According to **Gul and Whalen (2016)** many soils, as well as substrates and composts, are limited in their ability to provide sufficient nutrients to plants because the plant accessible ionic forms of N and P are easily lost through leaching (NO₃⁻ and the ortho-P ions H₂PO₄⁻ and HPO₄²⁻), transition to gases (NH₃, NO, N₂O and N₂), and precipitation or fixation (NH4 fixation in clays, precipitation of ortho-P ions

with CaCO₃ in alkaline soils and with Al and Fe oxides in acidic soils). The most valuable nutrients are phosphorus (P) and nitrogen (N), whereas the most valuable is currently P (Liu et al., 2021). This is due to 2 factors, firstly P is unevenly distributed over the planet, making most countries fully dependent on its import (Prokopchuk et al., 2018). Secondly, P is completely irreplaceable in many biological processes (Rowland et al., 2019). Much research has been devoted to technologies capable of enriching biochar by custom-mixed fertilizers, which have the ability to stimulate the production of chosen bioactive substances (Vochozka et al., 2020). Nevertheless, the latest trend is to engineer the properties of biochar, so it efficiently recovers P from wastewater. This business opportunity might futile because P is already being captured in most wastewater treatment plants. However, this is still mostly performed using out-dated precipitation technologies, which were originally developed more than a century ago to prevent pipes being clogged with struvite (a sparingly soluble phosphate mineral) in sewage pumps and pipes (Fattah and Chowdhury, 2015). Nowadays, these technologies are considered tools to prevent eutrophication (minimizing P leakage into waterways, Komarek et al., **2020**), required by regulations and subsidized in the form of increased water bills. However, the legacy of precipitation technologies persists, because when they were designed it was not believed that the P captured in this way would be used for plant production (Bradford-Hartke et al., 2021).

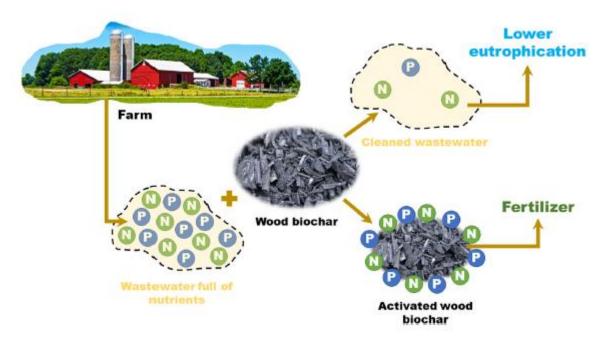


Fig. 1. The high porosity of biochar from wood is one of the main factors that enables the production of biofilters whose performance exceeds that of conventional biofilters made from conventional biological waste. This increases the amount of nutrients captured from waste waters and reduces eutrophication of surface water bodies.

P was relatively cheap at the time and new deposits were still being found. As a result, the captured P is now most often precipitated in the form of minerals with complex nucleation, such as struvite, hydroxyl-apatites or vivianite. Although plants need calcium and aluminium phosphates for their nutrition, these crystallized forms of P are known for their sturdy crystal morphology, making only a tiny part of P captured in this way available for plant intake (**Kulhánek et al., 2019**). Even worse, release of P into soil is influenced by soil properties, in particular by (1) the type of clay minerals present, (2) the characteristics of soil organic matter, (3) the levels of Fe and Al, and (4) pH (**Kolář et al., 2011**). As the price of P has risen significantly over the past 2 decades, some suppliers of precipitation technologies have already started to claim that capturing P in this way is becoming profitable.

However, this is only true if the quantity of P is considered, not its use for plant nutrition. Since char has traditionally been used for water purification due to its sorption properties and filtration of farm liquids due to its porosity, an increasing number of research hypotheses concern its use in modern wastewater management (Shaddel et al., 2019). Capturing organic forms of P is easy, whereas unmodified biochar serves as a filter and any charge does not play a role. Inorganic forms of P are represented mainly by anions (mainly H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻, depending on the pH) and are therefore repelled by negatively charged biochar surfaces (Zhang et al., 2020). However, many studies have shown that activation of biochar with a strong divalent cation, such as magnesium (MgCl₂), is sufficient to overcome this difficulty. Other activators such as cationic polymers, Al or La have also been reported to enhance P capture, however, none of these technologies indicates financial sustainability. There is increasing demand for a technology to be set up in such a way that biochar is produced from waste feedstock using waste heat, so that its actual production is profitable on its own. This has already been achieved (revenues from waste liquidation and waste heat treatment) in biogas plants, for example, where waste heat from cogeneration units is used to pyrolyze fermentation residues (Mardoyan and Braun, 2015). At the same time, he cost of the nutrients used needs to be kept as low as possible, ideally so that a profit can be made even during this step. Initial calculations by Stavkova and Marousek et al. (2021) from semi-operational validation suggest that capturing P from sludge water via biochar allows significant savings on reactants required for conventional struvite precipitation-based solutions. However, it is recommended that the biochar be modified to make its phosphorus sorption capabilities techno-economically viable (Nättorp et al., 2017). The overuse and low efficiency of nitrogen (N) fertilization generates not only economic losses, but also many ecological dilemmas such as water eutrophication, contamination of shallow aquifers by nitrates (due to the release of unutilised and nitrified N from mineral fertilisers, especially in soils where the natural retention capacity is reduced and N fertilisers are applied in large quantities so that the soil produces at least some crops), emissions of nitrous oxide (N₂O, greenhouse gas) and soil acidification (Clough and Condron, 2010). Loss of N from soils is caused by (1) leaching of ammonium (NH4+) and nitrate (NO₃⁻), and (2) gaseous emission (N₂, N₂O, NO, NH₃). N is a crucial nutrient for plant growth and many reports independently indicate that biochar should exhibit many of the properties essential to improve the N cycles in soil, in particular by prompting nitrification mechanisms by (1) ammonia (NH₃) adsorption and (2) increasing ammonium (NH₄⁺) storage by enhancing cation exchange capacity in soils (**Clough and Condron, 2010**). The unique properties of biochar made from waste wood should theoretically exhibit additional effects in terms of reducing gaseous N losses, such as from leaching of nitrous oxide (N_2O) and nitrate (NO_3^{-1}). Similar assumptions are consistent with Bai et al. (2015) who predict that wood biochar should alter N cycles via various mechanisms which involve sorption of Norg, NO₃⁻, NH₃, NH₄⁺, and also through interactions with various soil organisms and microbial processes. Given that oxygen containing acid functional groups (mostly carboxyl and hydroxyl) are developed on biochar surfaces that are being aged or activated, such biochar can hypothetically absorb even more NH_4^+ (Kolář et al., 2012). As summarized by Clough and Condron (2010), based on indirect evidence biochar is expected to (1) increase nitrification rate, (2) stimulate N immobilization, (3) reduce N₂O emissions, (4) decrease NH₃ volatilization, (5) enhance NH₄⁺oxidizing microbiota and (6) alter N availability to plants in general. However, hundreds of different case studies report contradictory results (Gul and Whalen, 2016). According to Zhang et al. (2020) capturing ammonium (NH4⁺) using unmodified biochar has been repeatedly demonstrated as possible, but not reasonable due to low efficiency. This is in agreement with Liu et al. (2021), who claims that wood biochar did not exhibit much adsorption capacity for NH4+, NO₃⁻ and H₂PO₄⁻. According to Nguyen et al. (2017) oxidized biochar should adsorb NH₄⁺ well by electrostatic attraction, whereas NO3~ adsorption should be weak because two equally charged subjects repel each other. Nevertheless, many researchers report poor results even with intentionally strongly oxidized biochar, which should theoretically solve the problem. The activation of biochar by mixing with organic N-fertilizers (typically manure for example) causes N to be gradually released into the soil, thus reducing leaching of N not utilised by plants in the form of N_2O and especially NO_3^- (into groundwater). Since wood has a high porosity, it will attract large amounts of N-rich water (in the form of NO₃⁻ and NH₄⁺). Chen et al. (2017) argues that biochar capability for capturing CH₄⁺ can be improved by the addition of materials with high cation exchange capacity, such as montmorillonite or by activation via Mg²⁺. However, even these findings do not seem commercially viable. Consistently with theoretical assumptions, the consensus across literature is that unmodified biochar shows almost zero adsorption capacity for NO₃⁻ (Gai et al., 2014). To make matters worse, biochar made from wood frequently increases soil pH, which causes NH3 volatilization (Gul and Whalen, 2016). Nevertheless, Sika and Hardie (2014) report that pine wood biochar has shown potential to reduce inorganic nitrogen (N) losses by leaching and strongly reduced not only the amount of ammonium and nitrate leached from sandy soils, but also the amount of recoverable, exchangeable ammonium and nitrate after leaching. Leng et al. (2020) notes that once N containing functional groups of biochar are achieved, they have a wide scale of applications, such as catalysis, energy storage and adsorption of various reactants (including pollutants). According to Gul and Whalen (2016) wood biochar in particular demonstrates a direct effect on the activity of ammonia oxidizers and nitrifiers by altering NH4⁺ accessibility. Although biochar generates changes in soil water management, pH and other abiotic properties could affect the functions of ammonia oxidizers and nitrifiers on a microbial level. In other words, the chemical and physical differences can change the competitive ability and some metabolic processes of soil bacteria, archaea and fungi that catalyze NH4+ oxidation and nitrification reactions. Although knowledge regarding chemical and physical (abiotic) fixation of N is quite contradictory and largely depends on the properties of the biochar (porosity and degree of oxidation in particular), the consensus across literature is that biochar increases mineralization of organic N to inorganic N (Nguyen et al., 2017). When there is a surplus of NH_4^+ in well-aerated soils and pH is simultaneously in the neutral to alkaline range, NH4+ goes through oxidation (nitrification) into NO₃ (Gul and Whalen, 2016). In relation to the capability of adsorbing NH₄⁺, biochar tends to reduce NH₄⁺ levels in soil that is accessible to NH_3 oxidizers. As a result, the decline in soluble NH_4^+ levels accompanying a higher dosage of wood-based biochar were evidently accountable for the lower nitrification rates. Given that the vast majority of reactions in the soil N cycle are driven by soil biota, it is not surprising that a greater influence on N cycles can be attributed to biotic interactions (free-living soil microorganisms responsible for organic N mineralization are significantly stimulated by biochar application; Placier, **2011**). The microbial reduction of NO_3 to N_2 (denitrification) is the main biological reaction producing N₂O in wetter soils, with additional N₂O emitted from the nitrifier-denitrification pathway in aerobic soils. There is a wide belief that the increase in soil porosity (caused by biochar application) results in an increase in the population of microorganisms (for example, bacteria possessing the nitrogenase enzyme), which seems to be linked to acceleration of the mineralization of organic matter in soil. According to **Gul and Whalen (2016)**, this is because highly porous biochar structures can result in (1) a safe niche for adaptable soil microorganisms, (2) unstable fragments from fresh biochar, (3) an increase in soil moisture and pH, (4) a contribution of macro- and micro-nutrients (P in particular), (5) immobilized inorganic N, (6) intensified nodulation, (7) disruption of soil chemical signalling and (8) an increase in temperature.

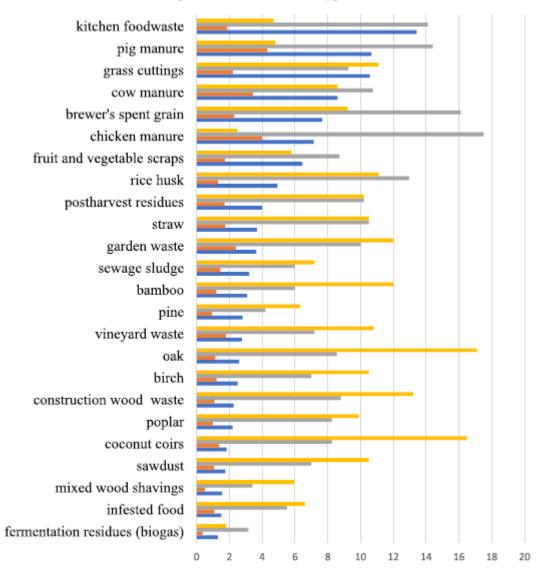
5. Sorption and ion exchange on biochar

For several decades biochar was understood to be chemically and biologically inert (**Cheng et al., 2008**), which was considered the main reason for recommending it as a carbon negative tool capable to sequester some 12% of anthropogenic CO₂ (**Glaser et al., 2009**). It has only recently been discovered

that biochar might show relatively high chemical and physical activity. The sorption and ion-exchange properties of char are among the most underestimated (Zhao et al., 2015). However, it appears that they may be among the most decisive properties. The understanding of these properties is difficult to grasp and it is all the more challenging because it changes over time. Char from forest fires is routinely found to be more than 10 k years old (Preston and Schmidt, 2006) and char captured in speleothems may even be much older (Kaal et al., 2021). The sorption and ion exchange characteristics of this char are in complete contrast to freshly produced biochar. The aging processes are driven by oxidation, which results in increased oxygen and hydrogen and decreased C (Cheng et al., 2008). The first oxygen groups (-COOH) begin to appear on the greatest protrusions from the surface of the biochar. Phenolic groups (-OH) are subsequently formed. The surface of the biochar therefore gradually acquires a negative charge, which can be regarded the genesis of ion exchange (Kolář et al., 2011). Similar to other organic matter in soil, biochar generally does not contain appreciable amounts of anion exchange capacity (Cheng et al., 2008). Char with a large specific surface has a larger number of sites with adhesive surface forces that allow any particles from the surrounding dispersive environment to be trapped and more or less firmly bound. These forces can be supported by (1) the electric charge of the sorbable particles; (2) the dipole character of the sorbable particle, but also by (3) chemisorption, where the sorbable particle reacts with the active site of the sorbent surface to form either a completely insoluble or even a slightly dissociated substance (Trakal et al., 2014). A typical example is the sorption of a phosphate anion by the calcium cation of the sorbent to form insoluble $Ca_3(PO_4)_2$, but also more or less dissociated CaHPO₄ or Ca(H_2PO_4)₂. As emphasised by Kolar et al. (2012) sorption processes can therefore involve ions, molecules and hydrated colloids - i.e. virtually all particles (electrically charged or uncharged) present in the dispersion medium. On the other hand, ion exchange is very specific, involving mainly ions, less so molecules (only if they have a significant electrical charge). As the name suggests, ion exchange is always an exchange. This means that there must be a group capable of dissociating its hydrogen ion and replacing it with the ion of the same or different valence from the dispersion medium present on the surface of the sorbent (which in this situation is called the "ionex"). Nevertheless, this active group (which initially operated with the hydrogen ion) can then also exchange the newly bonded ion, e.g. calcium for two hydrogen ions, or three calcium ions for two aluminium ions, etc. If an ion (which is bonded by active surface groups) significantly exceeds the other exchange cations (bonded to that ionex) in charge, we call that ion "in cycle". It may be "in a cycle" of hydrogen; potassium, calcium, etc., and since the active surface groups do not necessarily exchange hydrogen but also OH ions, a situation, whereas ionexes with a hydrogen charge capable of exchange acquire a negative charge because of the absence of positively charged hydrogen, can be created. Such ions are called catexes and exchange only positively charged ions - cations. Ionexes capable of dissociating the OH-group acquire an excess positive charge and are called "annexes", and are able to exchange negatively charged ions (anions). In general terms, it can be stated that ion exchange has certain rules and is therefore a rather orderly process. In contrast, sorption processes are poorly understood and many authors describe them as somewhat chaotic and random (Borthakur et al., 2021). For this reason, it is strongly recommended that sorption should always be experimentally verified under the specific conditions (Nefzi, 2018). On the other hand, ion exchange has its own fixed rules: the ion that has (1) a higher charge, (2) a higher concentration, (3) a smaller hydration envelope and (4) a higher ability to form a weakly dissociated compound, is bound as a matter of priority. If a component is to be removed from the system, such as a dye or some larger molecules (anything that is not wanted in the system), the solution is a sorbent. If an unwanted ion is removed from the system and replaced with another ion, the solution is an ionex (Hadzima et al., 2007). A typical industrial example of sorption is the removal of excess chlorine from water by activated carbon sorption, or the removal of dyes from diffusion juice in a sugar mill. A typical commercial example of ion exchange is softening water for steam boilers by replacing calcium and magnesium with sodium. Most of the biochar samples reported in literature are effective sorbents, similar to charcoal, activated carbon, clay and all materials with a large specific surface area (Marousek et al., 2020). The sorption activity of biochar, like other sorbents, is highly variable. In general, it is strongly dependent on: (1) the material to be pyrolyzed (biochar from coniferous or deciduous wood chips are different, with major differences between biochar from wood and biochar from rotten sewage sludge), (2) the pyrolysis temperature (generally the sorption capacity decreases with increasing pyrolysis temperature), (3) the pyrolysis technology used, and (4) the type of activation (superheated steam, ZnCl₂, acids, magnetism, etc.). It is typical for biochar that its sorption equilibrium can be established very quickly. Nevertheless, significant amounts of material can only be sorbed from highly concentrated solutions. Biochar (or any other sorbent) is not suitable for capturing reactants from highly dilute solutions. However, it must be highlighted that the low ion exchange capacity is typical mainly for freshly produced biochar. Prolonged contact with airborne oxygen, especially in alkaline environments, results in gradual surface oxidation of biochar particles, which may produce functional groups capable of hydrogen dissociation. These are mostly carboxylic (COOH) and phenolic (OH) groups. It depends on the raw material and the technology. It should be remembered, however, that the ion exchange on biochar is never high and that biochar cannot therefore replace humic substances in the soil, especially humic acids, whose ion exchange capacity can reach thousands of mmol chemical equivalents H⁺ kg⁻¹. Therefore, until the surface of biochar is properly oxidized, only sorption, not ion exchange, should be considered.

6. Economic implications

Char seems to be the first ever synthetic material produced by mankind (Urbancova, 2013). If the process is carried out in batches, pyrolysis is an undemanding technology, which has been known to humans for about as long as fire (Salkova et al., 2019). Mobile pyrolysis units that: (1) demonstrated good throughput through the terrain; (2) do not require any external power source and (3) do not have any electronics or other structurally demanding elements; are the most suitable for deployment in forests (Popescu et al., 2020). Boateng et al. (2019) presented a mobile fast pyrolysis unit whose economy is being improved by production of pyrolytic oil that is subsequently processed in stationary refineries (Škapa and Vochozka, 2019). Chen et al. (2018) argues that units of similar design show a payback period of less than 6 years. Nevertheless, transferability of such findings is always limited by location and time (Medina-Martos et al., 2020). However, the economic aspects are complicated by the fact that the higher added value in the commercialization of pyrolysis oil is only achieved by refining it (Tousek et al., 2021), which is relatively investment intensive (Chen et al., 2021). Another risk is the volatile demand for refinery products, which is highly linked to fossil fuel prices and related policies (Gavurova et al., 2021). If only units designed to produce biochar are considered, Thengane et al. (2020) claims that the breakeven comes at 310 €t⁻¹ of biochar. However, Keske et al. (2020) estimated the lowest possible cost of biochar production in mobile units at 423 €t⁻¹. The large differences aren't a big surprise as Kim et al. (2015) notes that biochar production in mobile units is highly sensitive to labor costs and there are countries in Europe alone where the average wage is below 0.2 k€ per month (Ukraine; Kovacova et al., 2020) as well as over 5.2 k€ monthly (Monaco; Novak et al., 2021). The differences are even greater if we consider the issue from a global perspective while in East Asia it is possible to find wholesale biochar prices in the vicinity of $170 \notin t^{-1}$ (Durana et al., 2021a) and in the United Kingdom for more than 550 \notin t⁻¹ (**Riley et al., 2021**). The situation is changing recently as simple mobile biochar production concepts such as "Kon Tiki" are entering the market (Pandit et al., 2017). These technologies can be produced for less than 100 € and it takes under 5 min of work to produce a 200 L batch (Cornelissen et al., 2016). Thus, the price of the feedstock (and production cost in general) and logistics becomes an important factor in the price competitiveness of different types of biochar which is indirectly confirmed by survey of the European market (for estimation of current production cost prices see Fig. 2). Producing and later burning char for the first time, made it possible to achieve stable flame temperatures well over 1 k °C (previously unattainable with wood mainly due to the great water content). High C density linked with high calorific values initially allowed the smelting of tin followed by production of bronze tools and subsequently other alloys and metals (Kwapinski, 2019). From an economic point of view (Peters et al., 2020), understanding the balance of material and energy flows is crucial (Kliestik et al., 2020b). Although the technology can generally be seen as an exothermic process, any opportunity to dry the feedstock better or to supply an external energy source allows increasing biochar yields or increases the quality (Valaskova et al., 2020). To manage the cost efficiency of the process, it is a good idea to reflect that at temperatures lower than 500 °C, the pyrolysis of hemi-cellulose and lignin is driven predominantly by exothermic reactions, while the pyrolysis of cellulose is endothermic. However, at temperatures higher than 500 °C, the situation changes inversely (Kwapinski, 2019). There is a general consensus that when biochar is made from biomass it represents a net withdrawal of CO_2 from the atmosphere (previously captured by photosynthesis; Skapa, 2012a,b). Belmonte (2021) extends this construction by arguing that biochar producers should therefore be rewarded for sequestered C. Although many countries have accepted the emission allowance policy, biochar producers cannot yet see it as the mainstay of their business (Ungerman et al., 2018). Nevertheless, the understanding across literature is that biochar application is among the most cost-effective method of CO₂ sequestration (Buss et al., 2019) and, in some cases, it even financially outperforms forestry production (Luz et al., 2018). Nevertheless, there is little consensus across literature on how to quantify the CO₂ sequestration potential of biochar (Jandacka and Holubcik, 2020). Sceptical authors prefer to exclusively convert the C present to CO₂ using molar calculations, noting that some fractions of C tend to oxidize, and additional CO₂ is released during the production stage (Gupta and Kua, 2017). Life cycle assessment according to ISO 140401 and ISO 14044 performed by Kafkova and Weinzettel (2021) revealed that 1 ton of biochar sequesters some 2.72 t of CO₂. The prevailing view, however, is that the issue is more complex since the application of biochar to soil has a large spectrum of positive impacts that ultimately lead to increased photosynthesis at the application site (Jung et al., 2019). Mašek et al. (2019) demonstrated that addition of K into biochar can further increase its CO_2 sequestration potential; by up to 45%. The agronomic benefits of biochar directly quantified by calculating cash-flow changes regarding (1) fertilizers, (2) agrochemicals, (3) tillage, (4) crops yields and (5) other factors, indicate that application of biochar alone has a long profit return period (Vochozka et al., 2016). It cannot be claimed that the application of any biochar to any soil will improve the yield of any crop (Kliestik et al., 2020c). Nevertheless, in almost all circumstances, revenues are slowly generated from lightning the soil and improving its ability to manage water (both to resist drought and to retain heavy rainfall), rather than by providing supplementary nutrients (Strunecky et al., 2021). According to Fibirova and Petera (2013), the most profitable segments of the biochar business concern (1) wastewater treatment, (2) revenues from waste treatment and (3) production of special fertilizers (ordered by most profitable). The highest synergies therefore occur when (A) waste is used to produce biochar and revenues are realized to process it (the average fee for biowaste landfilling in the EU is currently just under 25 € t⁻¹), (B) waste is pyrolyzed using waste heat and revenues are realized to process it (in some countries as a condition for obtaining subsidies for example), (C) the resulting biochar is enriched with nutrients (preferably from waste) and revenues are generated to process it, and (D) biochar is used for targeted fertilization of special crops (Maroušek and Maroušková, 2021). Most reports agree that significant financial benefits can be realized through savings on liming because biochar contains concentrations of Ca and Mg that are capable of significantly raising pH (Sheng and Zhu, 2018). Further profits are associated with savings on herbicides, given that the black colour of the biochar allows the soil to warm up more quickly and engage the cultivated crop (Bamminger et al., 2016). The same mechanism causes extension of the growing season and increases the metabolic activity of the soil biota, which increases the potential for higher yields overall.



Cost competitiveness of different types of biochar

Fig. 2. Analysis on production costs in current European economy in relation to: (A) porosity [blue, €/(m²g⁻¹)]; (B) sorption capacity (orange, €/100 g phosphates captured from 20 g/kg phosphate solution); (C) water retention (grey, €/10 m³ of topsoil with improved water retention by 5%); and (D) metabolic activity of soil biota (yellow, €/10 m³ of topsoil with basal respiration capacity improved by 5%) shows that biochar from fermentation residues performs best, followed by biochar from infested wood. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

7. Concluding remarks

Urban parks, commercial plantations, and even protected areas such as national parks are all subject to natural ecosystem dynamics as well as climate change. More than 39% of protected areas in Europe are covered by conifer-dominated forests, which are naturally susceptible to spruce beetle, which is also the main biotic cause of its death. **Dobor et al. (2020)** reminds that damages from bark beetles

have increased sevenfold in Europe since 1970s. **Hicke et al. (2020)** estimated via aerial surveys that bark beetles destroyed 4.7% of forest area (4.3 Mha-3.8 109 killed trees) in the western USA. **Andrei and Ifrim (2021)** mapped and summarized global damage over last decades and report that insects destroy 30 Mha of forest annually. It can be argued that across the literature there is a broad consensus that bark beetles are globally the most destructive forest pests, and its impacts are likely to increase further in the future (Judit et al., 2017). Wayman and Safford (2021) showed evidence that raised frequency of droughts increases the incidence of interactions between bark beetle epidemics and wildfires. Biochar made from various biowaste has repeatedly and independently demonstrated the ability to resist drought (Thengane and Bandyo-padhyay, 2020). However, it is intuitively counterproductive to transport biochar into the difficult forest terrain where there are many damaged trees readily available, notwithstanding the fact that the price of biochar from biowaste is 40-70% lower than that of biochar from wood (Vochozka et al., 2016). Mobile biochar kilns such as "Kon-Tiki" are technically suitable because they are virtually fail-safe, have excellent ground clearance and do not require qualified personnel (Pandit et al., 2017). The crucial criterion of the whole concept becomes the price of human labour which is necessary due to working with open flames (**Durane et al., 2021b**).

8. Conclusions

It was reviewed that:

- the techno-economic advantage of the production of highly porous biochar from wood is that, unlike various biological wastes, it does not require an external energy source to initiate or maintain the pyrolysis process because it takes place at temperatures above 500 °C (lignin decomposition is a fully exothermic process);
- wood biochar represents a product with a high surface area and porosity caused mainly by the elevated process temperatures that are associated with high proportions of lignin and cellulose of a high degree of crystallinity in wood;
- wood biochar is a very suitable soil amendment for improving its retention capacity (even from the long-term point of view);
- wood biochar is a promising agent for P and N recovery;
- this char represents an appropriate biofilter for (waste)water purification (during which time its various modifications, such as surface activation, are often required);
- this material presently represents a cheap feedstock as a consequence of the bark beetle disaster;
- on-site pyrolysis of wood that is infested with bark beetle is a suitable tool to control its spread.

Following the above, it is concluded that production of biochar from bark beetle calamity (and its subsequent and its possible improvement with nutrients or biota) is a reasonable method to reduce wildfire outbreaks occurrence and severity while combating the drought that triggers the cycle.

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