

Review

Activated Carbon, Biochar and Charcoal: Linkages and Synergies across Pyrogenic Carbon's ABCs

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Abstract: Biochar and activated carbon, both carbonaceous pyrogenic materials, are important products for environmental technology and intensively studied for a multitude of purposes. A strict distinction between these materials is not always possible, and also a generally accepted terminology is lacking. However, research on both materials is increasingly overlapping: sorption and remediation are the domain of activated carbon, which nowadays is also addressed by studies on biochar. Thus, awareness of both fields of research and knowledge about the distinction of biochar and activated carbon is necessary for designing novel research on pyrogenic carbonaceous materials. Here, we describe the dividing ranges and common grounds of biochar, activated carbon and other pyrogenic carbonaceous materials such as charcoal based on their history, definition and production technologies. This review also summarizes thermochemical conversions and non-thermal pre- and post-treatments that are used to produce biochar and activated carbon. Our overview shows that biochar research should take advantage of the numerous techniques of activation and modification to tailor biochars for their intended applications.

Keywords: activated charcoal; pyrolysis; activation; modification; pyrogenic organic matter; adsorbent; negative-emission technology

1. Introduction

Both biochar and activated carbon are pyrogenic carbonaceous materials (PCM). They are produced by thermochemical conversion of carbonaceous feedstock (pyrolysis or/and activation). Biochar is produced from sustainably sourced biomass and is used for non-oxidative applications in agriculture (e.g., in soil) and is also discussed as a raw material for industrial processes. By definition, it is used for carbon sequestration [1,2]. Hence, if “biochar” is used as a fuel, i.e., it is burned and the carbon is transformed (oxidized) into CO₂, it is actually classified as charcoal. Activated carbon is produced from any carbon source (fossil, waste or renewable) and engineered to be used as sorbent to remove contaminants from both gases and liquids [3,4]. Thus, it is defined as a material for contaminant sorption without exigencies in regard to the sustainability of its production nor to the fate of the carbon after its use. Both materials have their distinct history, widely separated scientific communities and

separated bodies of literature. Unfortunately, a generally accepted terminology and definition is lacking [1,4].

However, as the proposed applications of biochar and activated carbon increasingly overlap, awareness of the “other” domain in each case can be beneficial. As an example, nowadays both biochar and activated carbon are used for soil remediation, which before has been solely an application of activated carbon [5,6]. When the activated carbon is not removed after the application and if this activated carbon was produced from renewable feedstock and is complying to further specifications [2,7], it can be considered as biochar. Moreover, there is an increasing need for specialized sorbents in environmental technology including waste-water treatment and soil remediation, resulting in numerous studies on biochar-based materials that may replace conventional activated carbon [8,9]. Thus, the aim of this review is to provide an overview on definitions, uses and production of biochar and activated carbon and related pyrogenic carbonaceous materials to highlight their similarities and differences.

2. Pyrogenic Carbonaceous Materials (PCM): Brief History and Definitions

Pyrogenic carbonaceous material is defined by Lehmann and Joseph (2015) [1] to describe “all materials that were produced by thermochemical conversion and contain some organic C”. For this chapter, we follow broadly both their definition of PCM as the umbrella term as well as their definitions of the different classifications of PCMs.

All carbonaceous materials ultimately originate from biomass. Coal results from coalification, i.e., a geological process after biomass is covered with water and sediment. Peat and lignite are intermediate stages of this process. Charcoal, biochar and activated carbon are products of thermochemical processes and defined thus as PCM. Thus, the latter three materials are similar with respect to elemental composition and prevailing chemical bonds, but each has its own history, distinct properties and, especially, specific applications (Figure 1). In addition to the above materials, natural pyrogenic matter and other solid products obtained by pyrolysis classify as PCM. This review, however, does not cover carbonaceous matter produced in liquid phase, such as the products of hydrothermal carbonization (hydrochar) or liquid crystals; or in gas phase, such as soot, carbon black and carbon nanotubes [3]. Still, charcoal, biochar and activated carbon contain particles (e.g., condensates) that can be classified as soot [1]. There is increasing research interest in hydrochar that is suggested as a biofuel, as an adsorbent in soil and water, as well as a catalyst or for energy storage [10]. Thus, there is a considerable overlap of potential applications of hydrochar with those of biochar, activated carbon and charcoal. However, due to fundamental differences in history, production process and technology as well as both physical and chemical structure, hydrochar is not discussed in this review [10,11].

2.1. Natural Pyrogenic Organic Matter, Black Carbon and Char

Natural pyrogenic organic matter (PyOM) [12] also termed “pyrogenic carbon in soils” [13] is a ubiquitous constituent of soil organic matter and originates from vegetation fires (e.g., forest or prairie fires). PyOM represents a relevant pool for the global carbon cycle and has similar effects as anthropogenic addition of PCM to soil, i.e., biochar [12–15].

Char is a material that results from incomplete combustion of natural or anthropogenic origin and is sometimes used synonymously for PyOM [1,15].

Black carbon is probably the most common term for PCM dispersed in the environment across the atmosphere, water bodies, soils and sediments. It may be of anthropogenic (combustion of fossil fuels—soot) or natural (vegetation fires) origin [1,16].

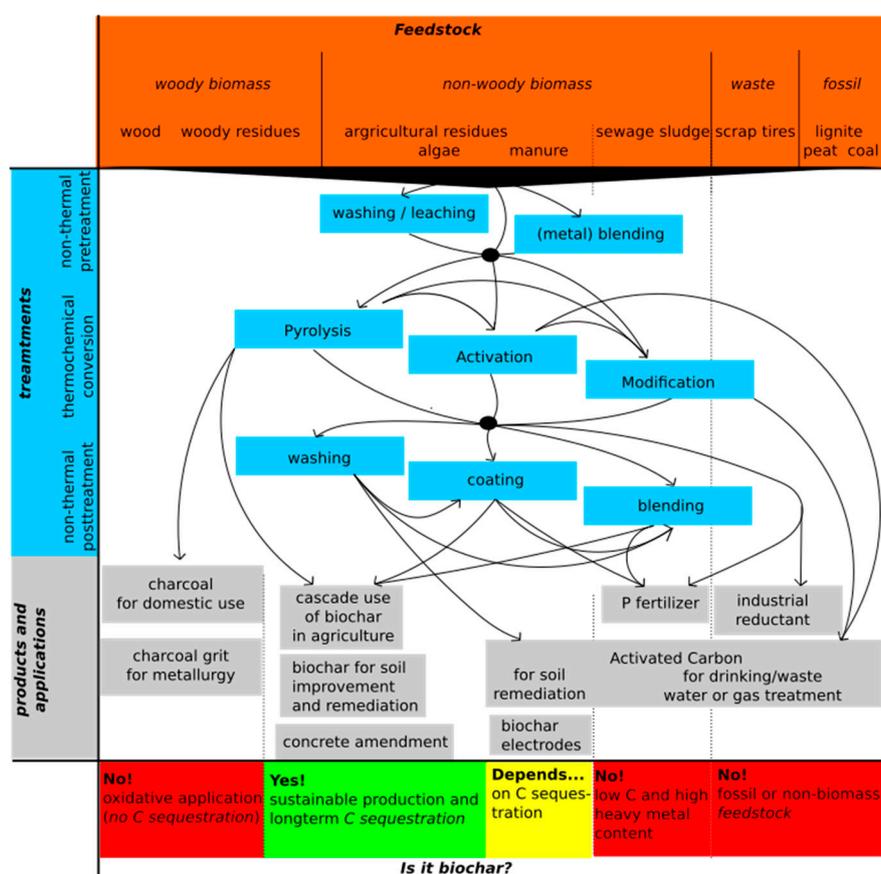


Figure 1. Overview on feedstock (orange), treatments for production (blue) and applications (grey) of pyrogenic carbonaceous materials (PCM). This figure intends (1) to highlight the numerous possibilities for combining thermochemical conversions both with each other as well as with non-thermal pre- and post-treatments; (2) to provide an overview on feedstock and applications; and (3) to answer the question if a PCM can be classified as a biochar [1,2], which depends on the intended application (non-oxidative for carbon sequestration), sustainable production (sustainably sourced biomass, no fossil feedstock) and chemical properties (carbon content e.g., >50% [2] or >10% [7], and a low content of pollutants as detailed in the guidelines of the European Biochar Certificate [2] or the International Biochar Initiative [7]). This figure does not aim to provide a full list of potential feedstock or applications.

2.2. Charcoal

Charcoal is defined as carbonized wood used mainly as fuel or as reductant in industry, e.g., to reduce oxidized iron ores in iron and steel production. The production of gunpowder containing 15% charcoal was the principal driver for research on charcoal [17]. This included trials on different types of wood as feedstock and on production technologies overall aiming at low ash contents to enable a clean combustion. Charcoal was and is mainly used as a smokeless fuel for cooking, heating and steel production [15]. It can be considered as the oldest chemical product, as already e.g., the Tyrolian ice man was tattooed, potentially for medical purposes, by using charcoal as a pigment more than 5000 years ago [18,19]. However, medical use of charcoal is nowadays included in discussions about biochar.

According to the United Nations Food and Agriculture Organization (FAO) [20], 50 million tons of wood charcoal were produced worldwide in 2015, which is three times more than in 1961. Approximately 25% of globally harvested wood is used for charcoal production; however, the FAO admits that there is large uncertainty in this data [21]. Two thirds of the production is located in Africa [20,22], where it is an important commodity that may even be subject to trade bans if controlled

by large criminal organizations to finance their illegal activities as e.g., in Somalia [23]. Across the African continent, charcoal is still an important domestic fuel, but it is also exported e.g., to Europe, where it is almost exclusively used for barbecues, because in industrial processes it was mostly replaced by fossil coal, which is cheaper [24]. In Brazil, however, charcoal is still used in metallurgy due to its low ash content [25] and lower local price compared to coal. Other uses include the production of sodium cyanide, carbon disulfide or silicon, as a filling compound for bottled gas, as lining of molds in metal foundries and for steel hardening, as a cementation granulate, and for pyrotechnics and explosives as well as electrodes and batteries [26].

Charcoal can be produced in industrial retorts that allow the use of side products (wood vinegar, acetic acid, smoke flavors) and state-of-the-art treatment of exhausts [26]. However, often it is still produced using very basic technologies like earth mounds that do not treat exhaust and thus are a concern to health and the environment due to emissions of carbon monoxide, methane, fine particulate matter and volatile organic compounds [15,21,25].

2.3. Activated Carbon

Activated charcoal was initially defined as “any form of carbon capable of adsorption” [27]. Historically, it began with the use of charcoal as a sorbent being traced back to both the Roman and Chinese Empire, and potentially even further. The Romans realized that charcoal can purify water; a property we still utilize. However, despite this long history of charcoal’s use for purification, it took humans over 3000 years to optimize charcoal for the removal of specific contaminants. In 1863, Smit [28] observed that charcoal removes oxygen from air for an extended period of over a month. However, not all charcoals had the same capacity, with animal bone-based charcoal having a higher capacity than wood-based charcoals. This was the starting point for a quickly growing field of research about differences and characteristics of charcoals that result in different sorption properties.

It was noticed early in the 19th century that charcoal also contained a variety of sorbed organic compounds [29]. Thereby, the first “activation” strategies were aimed at reducing absorbed chemical species after production. Chaney (1919) [30] considered thermal activation to be the only technique capable of removing the adsorbed organic compounds from the surface of the charcoal. The charcoal skeleton remains and new surface area (pores) are exposed. Thus, chemical groups become “active”, i.e., available for sorption. With this, the science of charcoal activation and activated carbon began.

The first patents for charcoal activation were granted in the 1920s [31–33]. However, there was little theoretical grounding explaining the observations of increased sorption capacities. Several of the pioneering works were largely empirical and focused on different activation temperatures as well as different chemicals, but were lacking a focused hypothesis or a mechanism. It was generally assumed that the increased sorption was due to the increased surface area (and maybe even new pores) [34]. Activation in the 1950s was further defined as “any process which selectively removes the hydrogen or hydrogen-rich fractions from a carbonaceous raw material in such a manner as to produce an open, porous residue” [35]. Chemical and structural alterations leading to increased surface areas and tailored modifications of chemical moieties are still the key elements of activation today. However, also important are the secondary traits of mechanical strength, total porosity, surface charge, and diffusivity [36].

Theoretical studies were initiated by Wright [37] studying bromine sorption on charcoal and activated charcoal. A comparable bromine sorption capacity was observed before and after activation. The mechanism of bromine sorption had changed; from anion substitution prior to activation to chemical addition reactions to carbon after thermal activation. It was hypothesized that the activation increased the presence of unsaturated C-bonds. Focusing on this mechanism, Lowry [38] observed in 1930 that the sorption capacity of activated charcoal was correlated to the total hydrogen content (presence of unsaturated/non-aromatic C-bonds). With the advent of new instrumentation to investigate crystalline structures, Ruff and colleagues [39] provided evidence that, in addition to changes of the surface chemistry, distinct alterations in the physical structure occur. They observed

small, isolated fragments of graphite and the activated charcoal lacked the semi-continuous graphite sheet character that was present prior to activation.

There are several complicating factors that hamper the identification of the sorption mechanisms. A first factor is that charcoal is being altered, even at ambient conditions. Shelton [40] noted in 1920 a three-fold change in the sorption capacity for N₂, following storage at laboratory conditions. A second factor is that even the inorganic precipitated salts on the charcoal (ash content) contributed to sorption processes [41].

Aside from sorption, activated carbon also can act as a catalyst, e.g., in anaerobic reduction of azo dyes, and supports the formation of radicals to oxidize dyes or pollutants in an (electrochemical) oxidative treatment of industrial effluents [42,43] and is further used for electrodes in microbial fuel cells [43,44].

Today, there are several markets that are increasing the global demand for activated carbon. These include drinking-water conditioning, energy-storage technology as well as environmental technology driven by new legislation (e.g., imposing clean-up requirements for mercury emissions from power plants) [45]. The annual net value of the activated carbon market is estimated at \$3.0 billion (USD) [45]. Powdered activated carbon accounts for approximately 50% of the total activated charcoal market in 2015 [45]. Granular activated carbon (GAC) was approximately 30% of the total market (removal of volatile organic compounds (VOCs) and chlorine), with polymer-coated, extruded, impregnated-activated carbons accounting for the remaining 20% [45].

2.4. Biochar

The discussion on biochar originates mainly in the research about the highly fertile anthropogenic soils rich in pyrogenic organic matter such as the Amazonian dark earth (also called “Terra Preta do Indio”). Here, charred biomass is considered as a key agent transforming poor soil into highly productive agroecosystems [46,47]. Thus, biochar was originally defined as carbonized biomass (in early publications, also still called “charcoal” [48]) used for agricultural purposes. While the initial debate focused on the direct application of biochar to soil, nowadays the so-called cascade use of biochar describes it as a multifunctional material that can be used to address several challenges within a life cycle (Figure 1) [49,50]. For example, biochar can be used as a feed supplement to improve the health and productivity of e.g., ruminants or poultry [51]. When the fed biochar is excreted again with the animal feces, it reduces odors and nutrient losses from the manure, both in fresh form, as well as during its composting. Eventually, when the biochar containing manure or compost is applied to soil, biochar serves as a slow-release fertilizer [52]. Also, biochar is used in biodegradable packaging materials to extend the shelf-life of fruits and vegetables, eventually improving soil quality after co-composting the packaging boxes [50].

Recently, the application of biochar as an amendment in concrete has been suggested to reduce the amount of cement [53] or sand [54] needed. Furthermore, recent studies investigate the use of biochar as a raw material for electrodes in microbial fuel cells [55] or for new types of supercapacitors, which requires post-pyrolysis treatment (modification) of the initial biochar [56].

Carbon sequestration is either a direct goal or indirect positive outcome of all biochar applications. Applied to soil or to concrete, biochar is stable for decades to centuries [57,58] and thus stores carbon that was previously removed from the atmospheric carbon pool by photosynthesis. Biochar amendment to soil is, therefore, discussed as one of the most promising negative emission technologies [59,60].

Werner et al. (2017) [61] suggested pyrogenic carbon capture and storage (PyCCS) as a more sustainable and carbon-efficient method than conventional biomass-energy carbon capture and storage (BECCS—capturing and geological storage of CO₂ derived from burning of biomass). They calculated that the 1.5 °C goal as specified in the Paris Agreement [62] can be achieved through plantation-based PyCCS, but would require the conversion of natural vegetation to biomass plantations in the order of 146–3328 Mha globally.

2.5. Other Solid Products Obtained from Pyrolysis

Pyrogenic carbonaceous materials can be produced from all kind of feedstock beyond biomass or fossil carbon sources. Here, we briefly introduce products obtained from thermal treatment of bones, sewage sludge and scrap tires. Due to low carbon content, products obtained from bones and sewage sludge cannot be classified as activated carbon or biochar by strict definition [2,4], but these materials may be used as sorbents and/or soil amendments. However, for sewage sludge and especially for scrap tires there are also considerable sustainability concerns, especially the high content of heavy metals that would not allow them to be classified as biochars [2].

Bone char, also called spodium [4] or bone black or animal char [63], is a blackish material obtained from the thermal treatment of bones, that only contains approximately 11% carbon, but up to 78% calcium phosphate [4]. It was first mentioned in the United Kingdom in 1815 [63] and its primary use was in the sugar industry for refining the sugar during its production process. For this purpose oxidative activation was not necessary, as the calcium phosphate of the bone turns into a highly porous structure already during carbonization [4]. Still, bone char can also be activated or modified by various techniques [64]. Today, lab-based studies investigate amongst other things the suitability of bone char for the removal of arsenic [65] and cadmium [66] from water. Other studies suggest its use as a soil amendment, especially as a source of phosphorous [67].

Sewage sludge is a relevant resource. In Germany, for example, 2 million metric tons of dry matter sewage sludge are produced annually [68], which equals approximately 20–25 kg per capita and contains 3.5% nitrogen and 5.5% phosphorous (P_2O_5). Due to hygienic concerns and its considerable content of both organic and inorganic contaminants, its direct application in agriculture is increasingly restricted by legislation. Pyrolysis of sewage sludge and biochar-like application e.g., to paddy soil is suggested as a promising management practice, which eliminates the organic contaminants in the sewage sludge by thermochemical conversion, reduces the availability of selected heavy metals and promotes plant growth. However, these findings are based on a greenhouse study, and long-term effects need further investigation [69]. Also, sewage sludge can be used as a feedstock for the production of activated carbon [70–72].

Scrap tires are a considerable environmental issue, with the European Union (EU), United States and Japan together producing about 6 Gt of this complex, non-recyclable waste [73]. There is intensive research on scrap-tire pyrolysis that mainly aims at high yield of liquids and gases for fuel and energy generation [74,75]. The solid residue can be used as a precursor for activated carbon. Despite its high carbon content, it cannot be defined as a biochar, as it is not produced from biomass and contains e.g., up to 2% of Zn.

3. Producing Pyrogenic Carbonaceous Materials: Thermal Conversions and Additional Treatments

Pyrogenic carbonaceous materials are produced by thermo-chemical conversion of carbon-containing precursors. Thermo-chemical conversions are defined based on temperature, duration and the presence or absence of oxidants and classified as either pyrolysis, gasification or activation. These classifications may be further distinguished in sub-classifications [25].

In a nutshell, pyrolysis and gasification result in a solid residue as the desired main product (pyrolysis) or as a desired or often undesired side product (gasification) that is enriched in carbon by removing hydrogen, oxygen and other elements. Activation is the optimization of sorption capacity by increasing the specific surface area, which can be achieved either by direct activation (one step) or by an activation after pyrolysis (two steps) [3,4]. Modification is the introduction of non-carbon moieties to the surface of carbonaceous materials to improve their sorption capacity for specific sorbates [76]. Modification can be done after or instead of activation.

3.1. Pyrolysis and Gasification

In the literature, the term pyrolysis is used to describe the production of charcoal, biochar and precursors for activated carbon. Carbonization is used alternatively and exchangeable.

By definition, pyrolysis is the thermo-chemical treatment of a feedstock in the strict absence of oxygen or any other additional oxidant [25]. Still, partial oxidation might happen e.g., due to the inherent content of oxygen in biomass or lack of air-tightness e.g., in traditional kilns or mounds.

So-called fast pyrolysis (sometimes called “flash pyrolysis”) and intermediate pyrolysis aim at the production of a mainly liquid product within less than 30 s. This is also often carried at lab scale for mechanistic studies and in combination with analytical chemistry (e.g., mass spectrometry) to investigate the pyrolytic behavior of different feedstock during thermochemical conversion [77].

Slow pyrolysis takes minutes to days and aims mainly at a solid product, e.g., biochar or charcoal. If slow pyrolysis is performed at low temperatures (<300 °C), the process can also be called torrefaction, which is so far mainly used to increase the caloric value before combustion for energy production or as a preparatory step for downstream chemical treatment of biomass. At higher temperature (300–900 °C), slow pyrolysis can also be called carbonization [25].

Gasification is defined as thermo-chemical treatment optimized for the yield of gaseous fuels that are mainly used for the generation of heat and electricity [25]. This is achieved by the presence of oxygen during the high-temperature (>800 °C) process at stoichiometric rates of 0.15 to 0.28 of supplied oxygen to carbon present in the feedstock [78].

In practice, it is often difficult to categorize actual technologies according to these definitions (Table 1). The conditions of pyrolysis of e.g., biochar widely define their resulting properties and allow the design of biochars to address specific challenges such as soil quality [79].

Table 1. Parameters of thermal conversion processes of biomass. Not all parameters are strictly in line with the definitions stated in the text. Note that these are only examples that do not aim to provide an extensive overview.

Process	Temperature Range [°C]	Heating Rate [°C s ⁻¹]	Vapor Residence Time	Primary Product
Slow pyrolysis	550–950 [80]	0.1–1 [80] “low” [81] 1–100 [85]	5–30 min [81,82] “long” [83] Hours–days [84] Hours [85]	35% Char [82–84] 15–40% Solid, 20–55% Liquid, 20–60% Gas [85]
	600 [81]			
	500 [82]			
	“low-moderate” [83] 400 [84] 350–700 [85]			
Fast and intermediate pyrolysis	850–1250 [80]	10–200 [80] “very high” [81] >1000 [85]	0.5–5 s [81] 1 s [82] <2 s [83] <1 min [85]	bio-oil [81] 75% liquid [82–84] 50–70% liquid [85]
	650 [81]			
	500 [82–84]			
	450–550 [85]			
Gasification	>750 [82]	Variable [85]	10–20 s [82] “long” [83] Seconds–minutes [85]	85% Gas [82–84] 90–100% Gas [85]
	>800 [83]			
	750–900 [84]			
	>800 [85]			

3.2. Chemical Activation

To yield a chemically activated PCM, feedstock material (coal, lignite, peat or biomass) is mixed (impregnated) with concentrated aqueous solutions of an activation agent (Table 2), of which ZnCl₂, KOH and H₃PO₄ are the most common ones on industrial scale [3]. Feedstock-to-agent ratios (degree or coefficient of impregnation) are typically in the range of 1:0.5 to 1:3 based on dry matter. The effect of the activation agent increases with increasing dose. Thus, the degree of impregnation can be seen as an analog to the magnitude of burn-off in physical activation as discussed below [4,76,86]. However, the extent of activation is also defined by the selection of the chemical itself, the intensity of the

mixing, and the temperature and the duration of the subsequent activation [3]. At high chemical concentration or excess reaction time, the pore volume decreases due to the physical collapse of the carbon structure [86]. Mixtures often are kneaded thoroughly to initiate the degradation of the feedstock. $ZnCl_2$ applied to wood sawdust results e.g., in a brown plastic paste [4]. This mass is then activated, i.e., it is heated in the absence of oxygen (pyrolysis). Temperatures can be lower than for physical activation (600–700 °C for $ZnCl_2$ [4]) but KOH for example still requires temperatures above 850 °C [3]. Finally, the product must be washed to remove the activation agent, which often can be reused or recycled, although the activation agent can partially volatilize during the activation process [4]. Thus, chemical activation at industrial level demands considerable effort in the treatment of exhaust and washing effluent to minimize its environmental impact, which in turn increases the costs of this process.

Although the mechanisms of activation vary between activation agents, there are common principles [3]: already during the intensive mixing, the original structure of the feedstock starts to degrade. In plant biomass, bonds between cellulose molecules loosen and ions of the activation agent occupy the resulting voids and thus define the microporosity created during the following activation that becomes available after washing of the activated carbon. Furthermore, the activation agents avoid the formation of tar and thus prevent the clogging of pores.

Table 2. Typical agents used for chemical activation of biomass or carbonaceous materials.

Activation Agent	References
ZnCl	[87–90]
FeCl ₃	[91,92]
H ₂ SO ₄	[71,87,93–95]
H ₃ PO ₄	[96–106]
HCl	[107]
HNO ₃	[108]
NaOH/KOH	[107,109–124]
Na ₂ CO ₃ /K ₂ CO ₃	[102,119,125,126]
Urea	[111]

3.3. Physical Activation

Physical or thermal activation is the partial oxidation of a carbonaceous precursor or intermediate material to increase its porosity. Physical activation is the oldest method of preparing activated carbon, where the term “physical” stems from the early misconception that steam would only physically volatilize and remove condensates from charcoal. However, at high temperatures (>750 °C), H₂O becomes an oxidant for carbonaceous materials (Table 3). Thus, “physical” activation is also based on oxidative reactions i.e., chemical processes.

Looking at physical activation performed as a second step after carbonization, some authors distinguish two stages of activation: during the first stage of activation, disorganized (amorphous) carbon-like tar is burnt (oxidized) with the effect that clogged pores open. During the second stage, parts of the carbon crystallites are also oxidized [4]. The first stage primarily increases the specific surface area; the second stage both further increases the specific surface area by creating new (micro) pore space or creating new interconnections between pores, but also changes the surface chemistry [127,128]. Oxidized functional groups including phenolic, ketonic and carboxylic groups are created on the aromatic surfaces of the carbonaceous material [3,4].

Table 3. Activation of carbonaceous materials by oxidative gases (“physical activation” or “thermal activation”).

Oxidant	Idealized Reaction [3,4]	Energy Balance [3]	References
Steam/H ₂ O	$C + H_2O \rightarrow CO + H_2$ $2C + H_2 \rightarrow 2C(H)^1$	endothermic	[72,95–97,112,118,120,124,125,129–158]
CO ₂	$C + CO_2 \rightarrow C(O) + CO^1$ $C(O) \rightarrow CO$ sum: $C + CO_2 \rightarrow 2CO$	endothermic	[106,129,133,139,140,145,153,159]
Air/O ₂	$C + O_2 \rightarrow CO_2$	exothermic	[104,105,114,119,139,158,160–165]

Note: ¹ C(H) and C(O) refer to surface hydrogen and oxygen complexes (chemisorbed hydrogen/oxygen) [3].

The degree of physical activation can be characterized by the burn-off, i.e., the mass loss during activation [4,76,86]. In general, higher burn-off correlates with higher porosity of the product. However, burn-off above 40–50% may result in a net destruction of porosity as the external burning of the carbonaceous materials may outweigh the formation of porosity [128].

Oxidation by limited amounts of air was used, for example, to modify the properties of biochar by Suliman and colleagues [164]. They used low-temperature physical activation by oxygen (“post-pyrolysis oxidation” at 250 °C) to optimize biochars for their application to increase soil water retention. Xiao and Pignatello used a similar technique at 400 °C [165]. However, the use of oxygen or air results in rapid reactions, which may hinder a controlled production process. Thus, for the production of activated carbon with a higher burn-off, often steam (H₂O) or CO₂ are preferred. Here, chemisorbed oxygen and hydrogen (C(O) and C(H); chemical equations in Table 3) on the carbonaceous surface inhibit the oxidation and thus slow down the activation process [3]. C(O) is an intermediate of the activation using CO₂, and C(H) is a byproduct due to the formation of hydrogen during steam activation.

The porosity of activated carbon depends on a multitude of factors including feedstock, temperature, duration of the activation process, and the choice of the oxidant. Oxidation with CO₂ first results in the opening of new pores. Steam activation, however, widens existing microporosity quite quickly. Thus, CO₂ predominantly supports the creation of microporous materials and steam-derived activate carbons rather show a wider pore-size distribution [128].

Aside from H₂O, CO₂ and O₂, also chlorine, ammonia, sulphur and sulphur dioxide can be used as agents for physical activation, although they are rarely used [4]. The use of ammonia or sulphur dioxide can be also considered as a modification, as discussed below.

3.4. Modification

Aside from the porous morphology, the chemistry of the surface defines the sorption characteristics of an activated carbon [127]. Modifications aims at the optimization of the surface chemistry toward the sorption of specific sorbates. Rivera-Utrilla [76] defines the categories of oxidation, sulfuration, nitrogenation and coordinated ligand functionalization treatments.

Oxidative modification of carbonaceous materials is not the same as activation, as the oxidation is carried out by hydrogen peroxide (H₂O₂) [108,160] or nitric acid (HNO₃) at low temperatures (ambient to 100 °C) and mainly aims at the creation of oxidized functional groups and not at an increase in surface area. In fact, HNO₃ is especially known to decrease the specific surface area and the pore volume due to the destruction of the porous structure [76]. Oxidation of activated carbon was reviewed in depth by Daud and Houshamnd [127]. Oxidative modification with ozone can also be considered as physical/thermal activation.

Sulfurization by treatment with SO₂ or H₂S also may have a destructive effect on porosity but may, for example, considerably increase the sorption capacity for mercury [76,166].

Nitrogenation or nitrogen modification of activated carbon is mainly achieved by treatment with ammonia (NH₃) in a gaseous or dissolved state to increase polarity and basicity in order to optimize sorption, but also the catalytic properties of the activated carbon [76,167]. For biochars, for example, Yang and Jiang used nitration with subsequent reduction to improve the sorption of copper [168].

Functionalization with coordinated ligands mainly aims at the optimization of metal sorption on activated carbon, although it seems that it could easily be adapted to optimize, for example, nutrient carrier behavior of biochar for soil amendment. For this purpose, activated carbons are treated with complex organic liquids. These treatments can be performed with a multitude of agents and conditions as reviewed by Rivera-Utrilla [76].

3.5. Non-Thermal Pre- and Post-Treatments

Aside from thermal treatments, there are numerous other steps that may be part of the production process of biochar or activated carbon (Figure 1). Prior to thermal treatments, feedstock can be blended to optimize the conditions for downstream pyrolysis and/or to optimize the resulting pyrogenic carbonaceous material. Moist and dry feedstock can be blended to optimize moisture content and energy density to avoid the necessity for a drying process, for example by blending manures with straw [169]. Also, biomass can be treated with metal salts to create biochars optimized, for example for the sorption of arsenic [170]. In contrast to chemical activation, the dosage of salts to the biomass feedstock are considerably lower and the metal salt is applied not as a catalyst, but to provide specific sorption sites in the final product. However, potential interactions of the intended functions should still be considered when planning such experiments.

After thermal treatments, the resulting pyrogenic carbonaceous material can be impregnated, for example with metals, to create additional sorption sites, e.g., by precipitating iron(oxy)hydroxides on a biochar (inorganic impregnation) to optimize its specific sorption e.g., of arsenic [171]. The results may be similar to metal-blended biochars, although the production process differs considerably (addition of metal before or after thermal treatment). Recently, the formation of an organic coating was described on biochar as the result of the interaction of natural organic matter with biochar, which allows the optimization of nutrient retention by biochar after production and prior to their use in soil [172–174]. The oldest post-thermal treatment is washing, for example of activated carbon, to remove residual condensates and ashes in order to further optimize sorption [142] or to simply remove the agents of chemical activation [4].

In essence, there are numerous potential combinations of pre- and post-thermal treatments with pyrolysis, activation and/or modification. However, they should be selected with care: a lower number of different production steps ease the repetition of a specific protocol, both for further scientific purposes or potential large-scale application.

4. Conclusions and Future Research

This review provides an overview of definitions of biochar and activated carbon. We highlighted that the strict distinction of biochar and activated carbon is mainly based on the final use of these materials. We revealed that research on activated carbon and charcoal is much older than biochar science and provides an immense source of information beneficial for the biochar community. For example, partial activation with adapted protocols might help to “tailor” biochars for specific applications. This may enable preparation of an organic coating on biochar, which was recently identified as the key to explaining the capture and slow release of nutrients by co-composted biochar. Sorption of organic molecules to form the organic coating is likely to be facilitated after a surface oxidation during the early stages of composting [172], which could potentially also be achieved by physical activation.

Looking at steam activation, we showed that the moisture of the feedstock is an important parameter when producing biochar via slow pyrolysis. Feedstock moisture is not just a question of the energy balance of biochar production, but has also the potential to define biochar properties. Although

moisture can increase biochar yield at low temperatures [175], the formation of steam and subsequent steam activation might result in lower yield and partially activated biochar in high temperature production scenarios (>800 °C).

For comparative studies of biochar and activated carbon, both materials could be produced from the same feedstock using different impregnation ratios and burn-off rates, respectively, producing comparative series from non-activated to fully activated biochar/activated carbon. Such studies will allow an overall economic evaluation, as there will be a trade-off of, for example, contaminant sorption capacity (increases with increasing degree of activation) and yield (decreases with increasing degree of activation).

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