

Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis

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The carbonization of biomass residuals to char has strong potential to become an environmentally sound conversion process for the production of a wide variety of products. In addition to its traditional use for the production of charcoal and other energy vectors, pyrolysis can produce products for environmental, catalytic, electronic and agricultural applications. As an alternative to dry pyrolysis, the wet pyrolysis process, also known as hydrothermal carbonization, opens up the field of potential feedstocks for char production to a range of nontraditional renewable and plentiful wet agricultural residues and municipal wastes. Its chemistry offers huge potential to influence product characteristics on demand, and produce designer carbon materials. Future uses of these hydrochars may range from innovative materials to soil amelioration, nutrient conservation via intelligent waste stream management and the increase of carbon stock in degraded soils.

Biomass has been assigned many roles to play in strategies for sustainable consumption. In addition to being a food source and renewable raw material [1], it can be used for energy production [2,3], **carbon sequestration** [4–6] and, finally, as an essential element to increase soil fertility [7]. Estimates of how much biomass is available for the various applications vary widely, depending on the focus of the investigators and how issues of soil management and biodiversity, among others, are addressed; for example, the energy and raw material substitution potential of biomass in the USA has been estimated to comprise more than a third of the current US petroleum consumption for power, transportation and chemicals by 2030 [1], while the worldwide potential for a competing use in sequestering photosynthetically bound carbon as

biochar to increase soil fertility has been estimated to be 1 GtC yr⁻¹ [8] – approximately one eighth of the global CO₂ emissions from fossil fuels in 2006 [301].

A major disadvantage for almost all applications is the high degree of heterogeneity in the form, composition and water content of biomass. Therefore, drying and/or conversion processes are usually required to improve material properties for easier handling, transport and storage of such materials. A variety of thermochemical or biological processes can be used to convert biomass in the absence of oxygen to products with higher degrees of carbon content than the original biomass. Gas or liquid products (biogas or alcohol) predominate in biochemical transformations, while solids (charcoal) are the major commercial products of the thermochemical conversion

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Key terms
Soil carbon sequestration: Addition of degradation-resistant carbonaceous substrates to soil.
Biochar: Distinguished from charcoal and similar materials by the fact that biochar is produced with the intent to be applied to soil as a means to improve soil health, to filter and retain nutrients from percolating soil water, and to provide carbon storage [301].
Pyrolysis: Thermal decomposition of biomass under anaerobic conditions.
Hydrothermal carbonization: Carbonization of biomass in water under autogenous pressure and temperatures at the lower region of liquefaction process [32], also called wet pyrolysis.
Char: A solid decomposition product of a natural or synthetic organic material [10,11].
Hydrochar: Char produced from hydrothermal carbonization.

process **pyrolysis**. Several million tons of charcoal are produced every year [9].

During pyrolysis, the organic matter in the biomass is thermochemically decomposed by heating in the absence of oxygen. If it is carried out in the presence of subcritical, liquid water, it is often called hydrous pyrolysis or **hydrothermal carbonization** (HTC). Dry or wet pyrolysis is used here to carbonize the biomass, making products with higher carbon contents. The product characteristics, their relative proportions in the gas/liquid/solid phases and the process energy requirements depend upon the input material and the process conditions. The advantage of HTC is that it can convert wet input material into carbonaceous solids at relatively high yields without the need for an energy-intensive

drying before or during the process. This opens up the field of potential feedstocks to a variety of nontraditional sources: wet animal manures, human waste, sewage sludges, municipal solid waste (MSW), as well as aquaculture and algal residues. These feedstocks represent large, continuously generated, renewable residual streams that require some degree of management, treatment and/or processing to ensure protection to the environment, and are discussed in more detail in this review.

Currently, researchers in many disciplines are participating in the search to find environmentally sound conversion processes and applications for biomass. This has resulted in a variety of terms to describe the solid product from dry or wet pyrolysis. Chemically, the solid is a **char** – “a solid decomposition product of a natural or synthetic organic material” [10,11]. Traditionally, such solids are called charcoal if obtained from wood, peat, coal or some related natural organic materials. In the fields of soil and agricultural sciences, the term ‘biochar’ has been propagated to mean charred organic matter, which “is applied to soil in a deliberate manner, with the intent to improve soil properties”, distinguishing it from charcoal, which is usually used for cooking purposes [12]. A more restrictive concept of biochar, requiring that the solid fulfil positive environmental criteria, has also been suggested [13]. In this review, we adopt this naming convention, using biochar only for the product of the dry pyrolysis process when it is used for soil applications, and charcoal for other purposes [302]. The wet pyrolysis process is referred to as HTC with the solid product consistently called ‘**hydrochar**’, regardless of its application,

in order to distinguish it from biochar produced from dry pyrolysis. Char will be used to include solids from both processes.

Extensive reviews and books have been published in recent years on charcoal [9], biochar [7,8,13–15], hydrochar [16,17] and their production processes. The renaissance of research on conversion processes and their products has been initiated by current strategies to reduce global warming using CO₂-neutral energy technologies and carbon sequestration in organic matter [18]. The growth in the number of publications on biochar has been almost exponential [13], stimulated by the discovery of its role in sustained fertility in Amazonian soils known as ‘Terra preta’ and its stability [19–21]. HTC had fallen into relative obscurity after the initial discovery, and the research activity in the early 20th Century to understand natural coal formation [16], until recent studies on hydrochar chemistry and applications in innovative materials [16,17, 22,23] and in soil-quality improvement [24,25] revived interest. Therefore, literature on the wet process and its product hydrochar is limited in comparison to that on char from dry pyrolysis.

This review focuses on contrasting the information available for the two types of char in regards to the use of biomass residues and waste materials as feedstocks, the conversion processes and chemistry involved in their production, as well as current and potential applications (**Figure 1**), with the intent to highlight the areas requiring more research. The applications in focus are those that exploit the material properties of the chars (e.g., biochar, adsorbents and catalysts), rather than those based on the thermal properties such as carbon-neutral fuels. The open questions, especially on hydrochar’s suitability as a soil amendment, are discussed in the following sections and summarized in a section focusing on research needs.

Char production

▪ Conversion processes

The production of charred matter always involves a thermochemical conversion process. The decomposition of organic material under the influence of heat in a gaseous or liquid environment, without involvement of further reactants, is called pyrolysis from the Greek words ‘*pyr*’ for fire and ‘*lysis*’ for dissolution. It is an essential reaction step in any combustion or gasification process. The various pyrolysis processes differ in how fast heat is transferred to fresh feedstock particles, the maximum temperature that is reached (T_{max}), residence time of the input materials under these conditions, and the product distribution between the three phases. They are typically classified according to the reaction conditions and the product yields (mass ratio of product formed to initial feedstock based on dry weight). These are compared in **Table 1** and discussed later.

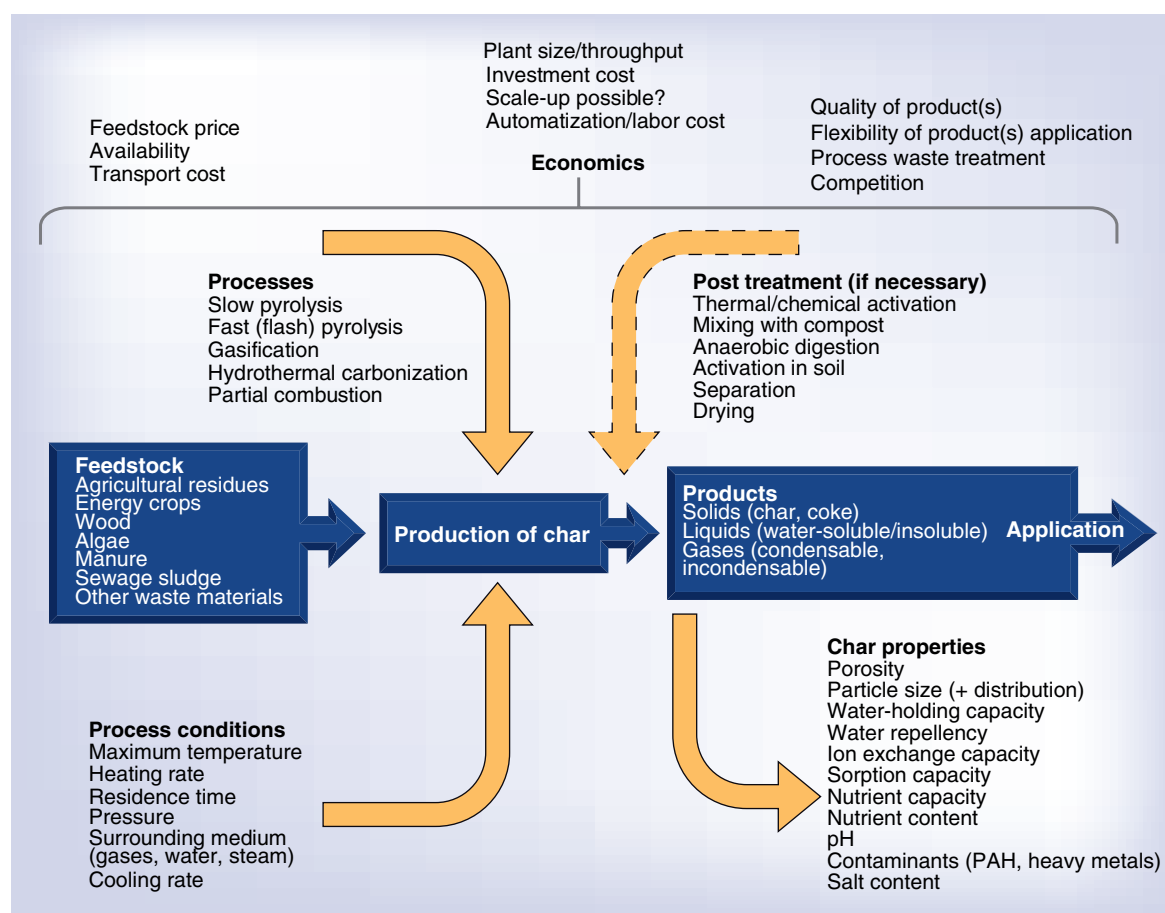


Figure 1. Factors influencing the production and applications of char.

Dry pyrolysis

The main process for char production with significant yields is the dry pyrolysis process. It has been used by mankind for millennia to produce charcoal and tar-like substances, although it can be operated to produce multiple products (e.g., oil and gas) besides char. The so called 'dry distillation' of wood [10,11,26,27] also yields methanol, acetic acid, acetone and many more base chemicals. Moderate heating rates with long residence times (slow or intermediate pyrolysis) yield high amounts of gases and vapors (30–35%) [28] and approximately 20–40% as char [9]. In industrial applications, these processes are operated in closed kilns where the non condensable gases are used to fire the reactors.

If the desired product is a liquid to be used as a primer for fuels, fast or flash-pyrolysis is used, which involves rapid heating of the feed and fast cooling of the generated vapors. The yield of liquid products increases from a few percent to up to 75%. Fast pyrolysis processes are operated in special reactors allowing for high heating rates and good mixing conditions [29].

Gasification

If an oxidizing atmosphere is applied by addition of air, oxygen, steam or carbon dioxide or mixtures thereof, such that only partial combustion takes place, the process is called gasification [30]. The product gases, a mixture of mainly H_2 , CO , CO_2 and CH_4 , can be used directly as a fuel or as a synthesis gas (syngas) in downstream catalytic conversion processes to generate synthetic natural gas (SNG), methanol, Fischer-Tropsch fuels and many more products. Gasification is generally operated in a continuous mode and maximized to produce gas, with yields of approximately 85% [28]; only a small amount of char is produced. However, since large gasifiers have a large throughput of biomass and are optimized for an economic operation (even with a small solid yield), large amounts of char could be recovered at acceptable costs. It should be noted that some tar is also produced in this process. As in all dry pyrolysis processes, condensation of this tar on the char should be avoided to prevent contamination with polycyclic aromatic hydrocarbons (PAHs). Depending on the feed, heavy metals in the char also could be an issue.

Table 1. Comparison of reaction conditions and typical product yields for thermochemical conversion processes with char as a product.

Process	Reaction conditions (temperature [°C]; vapor residence time)	Product distribution (weight%)		
		Char	Liquid	Gas
Pyrolysis: slow	~400; h-week	35	30	35
Pyrolysis: intermediate	~500; ~10–20 s	20	50	30
Pyrolysis: fast	~500; ~1 s	12	75	13
Gasification	~800; ~10–20 s	10	5	85
HTC	~180–250; no vapor residence time, ~1–12 h processing time	50–80	5–20% (dissolved in process water, TOC)	2–5

HTC: Hydrothermal carbonization; TOC: Total organic carbon.
Adapted from [16,28].

Hydrothermal processes

In hydrothermal processes, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in (high)-pressure reactors. As in dry pyrolysis, reaction temperature (and pressure) determines the product distribution. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, very little gas (1–5%) is generated, and most organics remain as or are transformed into solids. At higher temperatures, up to approximately 400°C, and with the use of catalysts, more liquid hydrocarbons are formed and more gas is produced. This so called ‘hydrothermal liquefaction’ has drawn some interest, although most liquefaction work is performed using organic solvents instead of water [31].

If the temperature and pressure are increased further, the supercritical state for water is reached and the primary product is gaseous (hydrothermal gasification) [32]. Depending on the process conditions, either more methane or more hydrogen is generated; char is not yielded in noticeable amounts [33].

▪ Feedstocks

Conversion to char via dry pyrolysis has been traditionally restricted to biomass with low water content, such as wood and crop residues, because of the high energy requirements associated with the inevitable drying prior and/or during the reaction by the evaporation

of water. Potential feedstocks for wet hydrolysis span a variety of non-traditional, continuously generated and renewable biomass streams: wet animal manures, human waste (i.e., excrements and faecal sludges), sewage sludges, MSW, as well as aquaculture residues and algae.

These feedstocks usually require some degree of management, treatment and/or processing to ensure protection of the environment. Many of these streams (e.g., human waste and MSW) already have substantial collection and treatment costs associated with them. For some applications, it may be beneficial to have a mobile **carbonization** facility.

Carbonization of biomass has a number of advantages when compared with common biological treatment. It generally takes only hours, instead of the days or months required for biological processes, permitting more compact reactor design. In addition, some feedstocks are toxic and cannot be converted biochemically. The high process temperatures can destroy pathogens and potentially organic contaminants such as pharmaceutically active compounds [34,35]. Furthermore, useful liquid, gaseous and solid end-products can be produced [36], and at the same time contribute to GHG mitigation, odor reduction [9] and additional socio-economic benefits. In addition, use as biochar may contribute to climate change mitigation and **soil amelioration** [37].

Biomass in general is defined in this review in terms of source: “*the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste*” [38]. Using a similar definition, the US Departments of Energy and Agriculture estimated the total sustainable biomass feedstock that can be harvested from US forest and agricultural land to be 1.18 billion dry tons [1]. Estimates for the more densely populated Germany show a potential of only 0.24 billion tons [2,39]. How much biomass is actually available for various applications is a matter for discussion and research [39,40].

Feedstock characteristics such as chemical composition, volatile and noncombustible fraction, moisture content, particle size and energy content significantly affect conversion efficiencies and char characteristics in both processes. Typical values for these parameters for the feedstocks targeted in this review, as well as for other typical biomasses (e.g., woods and grass) are presented in **Table 2** [41–49,303,304]. Further research on quantifying their effect on process energetics, product distribution between phases and product quality is needed, especially for HTC.

Agricultural residual feedstocks

The current total sustainable biomass feedstock that can be harvested from US agricultural land is approximately 176 million dry tons annually [1]. It includes crop residues, grains for ethanol production, corn fiber, MSW and animal manures. Although animal manures make up a large portion of this biomass (18%), they have not

Key terms

Carbonization: a process by which solid residues with increasing content of the element carbon are formed from organic material usually by pyrolysis in an inert atmosphere [10].

Soil amelioration: soil quality build up or improvement of soil fertility.

Table 2. Feedstock properties relevant to thermal conversion processes.

Feedstock		Woods [†]	Grasses [‡]	Manures	Sewage sludges			Municipal solid waste	
					Primary	Activated	Digested	Total ^{##}	Organic [§]
Elemental analysis (% daf)	Carbon	50–55	46–51	52–60 [¶]	53.3 [¶]	-	54.4 [¶]	27–55	47–52
	Hydrogen	5–6	6–7	6–8 [¶]	7.2 [¶]	-	7.7 [¶]	3–9	0.63
	Oxygen	39–44	41–46	26–36 [¶]	32.0 [¶]	-	29.9 [¶]	22–44	40–42
	Nitrogen	0.1–0.2	0.4–1.0	3–6 [¶]	5.3 [¶]	-	5.6 [¶]	0.4–1.8	0.16–0.25
	Sulfur	0–0.1	<0.02–0.08	0.7–1.2 [¶]	2.1 [¶]	-	3.2 [¶]	0.04–0.18	0.002–0.003
Volatile fraction (% db)		70–90	75–83	57–70 [¶]	60–80 ^{††}	59–88 ^{††}	30–60 ^{††}	47–71	
Ash (% db)		0.1–8	1.4–6.7	19–31 [¶]	25 [¶]	-	37.5 [¶]	12–50	0.02–0.2
Moisture content (% fresh weight)		5–20 (dried wood for fuel) 35–60 (green wood)	NR	21–99.7 ^{††}	90–95 ^{††}	97–99 ^{††}	88 ^{††}	15–40	45–70
Particle size (mm)		NA	NA	NA	<5 (82% wt. <0.1 mm) ^{§§}	<1 (66% wt. <0.1 mm) ^{§§}	<1 (61% wt. <0.1 mm) ^{§§}	Average ^{**} : 180–200 Range ^{**} : 0.2–600	Average ^{**} : 180–200 Range ^{**} : 0.2–600
Energy content (MJ/kg _{db})		19–22	18.3–20.6	13–20 [¶]	23–29 ^{††}	19–23 ^{††}	9–14 ^{††}	2–14	8.9–11.5

[†]Data from soft and hard woods (22 samples) [41].
[‡]Biocrop grasses including energy grass pellets, poplar pannonia and tree of heaven [42].
[¶]Values estimated based on % composition values provided by [303] and elemental composition, moisture content and energy content values provided by [43].
[§]Data from [45,46].
[¶]Exemplary values [47].
^{††}Moisture contents after thickening [48].
^{##}Data from [304].
^{§§}Exemplary values for weight percent of solids with particle size less than 0.1 mm [49].
^{**}Neglecting bulky items.
^{**}Data from [43,44].
daf: Dry ash-free weight; db: Dry weight; NA: Not applicable; NR: Not reported.

been as extensively studied as other plant-based feedstocks. The change in animal agriculture toward concentrated animal feeding operations (CAFOs) over the last decade makes the discussion of feedstock from animal manures timely and well justified. Manure production from CAFOs is often greater than local crop and proximal pastureland nutrient demands. Over-application of the animal manure can spread pathogens, emit ammonia, GHGs and odorous compounds, and enrich surface and ground waters with nitrogen and phosphorous compounds, leading to eutrophication [50,51].

Carbonizing surplus animal manures from CAFOs is a viable manure management alternative, which not only provides environmentally acceptable manure treatment, but may also bring potential income revenue to farmers from producing value-added biochar. The process can also use a variety of blended on-farm seasonal crop residues with animal manures, and concentrate the animal and plant nutrients (e.g., P, K and possibly N) into a nutrient-dense char. This is not only potentially useful for nutrient recovery and soil fertilization, it may also offer a sound route to sustainable nutrient cycling.

Animal manure feedstock characteristics (Table 2) can vary widely. Poultry and feedlot operations collect a mixture containing manure, bedding, waste feed, and, in some instances, underlying soil. These mixtures

generally have low moisture contents (typically <50%), making them good candidates for dry pyrolysis. By contrast, dairy and swine feeding operations produce wet waste streams (typical water content >90%) comprised primarily of discharged wash water, but also manure, urine and undigested feed.

Human waste & sewage sludge

The amount of human waste (untreated excrement and faecal sludges) and sewage sludges (primary and secondary sludges from wastewater treatment processes) is continuously increasing, not only through the installation of new sanitation facilities in developing countries, but also through intensified wastewater treatment in developed countries [52]. Currently, it is estimated that at least 10 million tons on a dry weight basis of sewage sludge per year will accrue in the EU [53,54]. In 2005, the annual US biosolids production was estimated to be approximately 8 million tons [305].

The direct conversion of human waste and sludges via pyrolysis meshes well with the holistic approach of ecological sanitation [55]. It can be used to support a more systematic closure of material flow cycles and resource conservation, since secondary wastewater treatment by biological processes and the generation of stabilized sewage sludges is accompanied by the removal of

valuable organic carbon, nitrogen and energy (Table 2). New sanitation concepts with separated waste streams and reduced water use can produce concentrated, relatively homogeneous waste streams requiring only minor pretreatment before pyrolysis. This can be combined with nutrient-recovery processes.

The present pyrolysis-based reuse concepts for sewage sludge apply to the energy recovery from feedstocks [56–59] and the material reuse of the solid conversion products as technical adsorbents [60–63] or soil ameliorants [64–66]. By contrast, no experimental work has been published to date on the HTC of sewage sludge or on the conversion of human waste by either wet or dry pyrolysis.

Municipal solid waste

Municipal waste-generation rates vary with location and have been shown to correlate with average income, ranging from 0.1 tons/person-yr (low income countries) to over 0.8 tons/person-yr (high income countries) [67]. MSW is broadly defined as wastes originating from residential (i.e., product packaging, newspapers, magazines, food waste, grass clippings, yard waste and recyclables), institutional (i.e., schools and prisons), and commercial sources (i.e., restaurants). Construction and demolition debris and combustion ash are not generally characterized as MSW. For the purposes of this review, industrial and municipal wastewaters are not classified as MSW.

Thermochemical processing of MSW has the potential to reduce GHG emissions associated with current waste management techniques (i.e., landfilling and composting), while producing value-added products, such as activated carbon. The heterogeneous nature of MSW (in terms of composition, chemical properties, and particle size, see Table 2) complicates its use as a feedstock for pyrolysis, potentially requiring the waste to be processed (i.e., shredded and sorted) prior to introduction, in order to minimize operation and maintenance issues [43,44,68–71].

Chemistry

Many similar reaction pathways occur during both dry pyrolysis and HTC of biomass. Biomacromolecules degrade to form liquid and gaseous (by-)products, while solid–solid interactions led to a rearrangement of the original structure [72,73]. However, the difference in the reaction media plays a defining role in the chemistry and characteristics of the products justifying separate consideration.

Reactions

Dry pyrolysis of biomass at temperatures between 200 and 500°C in a largely inert atmosphere leads to the thermal degradation of biomacromolecules with no

oxidation except by the oxygen contained in the biomass feed. Despite centuries of research, reaction mechanisms are only partly understood due to the high degree of feedstock complexity and number of possible reaction mechanisms. Bond cleavage, manifold intramolecular reactions, decarboxylation, decarbonylation, dehydration, demethoxylation, condensation and aromatization are some of the characteristic mechanisms [73]. The reaction temperature largely governs which reaction dominates. However, owing to the nonuniform temperature profiles within pyrolysis reactors, it is common for many of the aforementioned reaction mechanisms to occur in parallel. The highest (peak) temperature reached during the process has a critical influence on the pyrolytic reactions and the properties of the char product [72]. Decomposition of specific compounds can also be characterized by temperature. Hemicelluloses mainly decompose between 200 and 400°C, while cellulose decomposes at higher temperatures (300–400°C). By contrast, lignin is the most stable component, gradually decomposing between 180 and 600°C [74].

In comparison, during HTC the biomass is heated in subcritical water to between 150 and 250°C at autogenic pressures for time frames typically greater than 1 h. Feedstock decomposition is dominated by reaction mechanisms similar to those in dry pyrolysis, which include hydrolysis, dehydration, decarboxylation, aromatization and recondensation [16,32]. However, the hydrothermal degradation of biomass is initiated by hydrolysis, which exhibits a lower activation energy than most of the pyrolytic decomposition reactions. This has been shown by calorimetric measurements [75]. Therefore, the principle biomass components are less stable under hydrothermal conditions, which leads to lower decomposition temperatures. Hemicelluloses decompose between 180 and 200°C, most of the lignins between 180 and 220°C, and cellulose above approximately 220°C [76]. Although it has been observed that both time and temperature influence product characteristics [77], temperature remains the decisive process parameter [16,78]. It should be noted that a manipulation of the water pH has a significant impact on the reaction mechanism of cellulose in water [76]. Alkaline conditions are often used for the liquefaction of biomass (i.e., a shift to products with a high H/C ratio) [79].

The similarity of some of the reaction pathways during dry and wet pyrolysis processes are illustrated in Figure 2 [9,16,32,80]; for example, a substantial amount of liquid oil and water is produced from flash pyrolysis of biomass [81], so that hydrolytic reactions are likely to take place during conventional pyrolysis, especially at elevated pressures [9]. In addition, (dry) pyrolytic degradation pathways are likely to occur, to some extent, during hydrothermal conditions [82,83]. However, owing

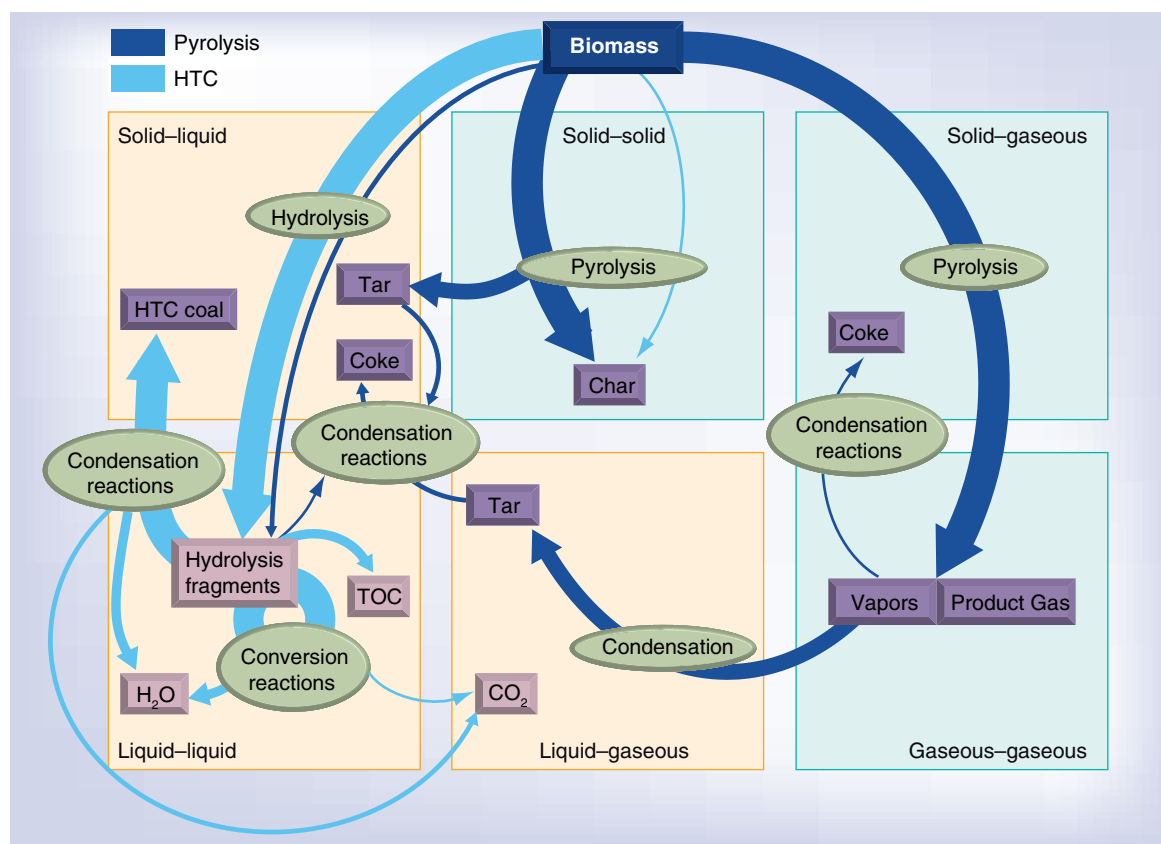


Figure 2. Comparison of simplified reaction schemes of hydrothermal carbonization and dry pyrolysis with regard to the reaction phases governing the processes and typical product classes.

TOC: Total organic carbon in the liquid phase of hydrothermal carbonization (organic acids, furfurals and phenols among others).

Based on work from [9,16,32,80].

to the different reaction media, a shift in the reaction network takes place, which leads to distinct products in quality and quantity; this will be discussed in the following sections [16].

Products

Products from pyrolysis are solids, liquids and gases (Table 1). Compared with dry pyrolysis, HTC produces higher solid yields, more water soluble organic compounds and fewer gases, comprised mainly of CO_2 [84]. In addition, the composition and structure of the solid product (hydrochar) from HTC differs substantially from dry pyrolysis chars [85]. The chemical structure of hydrochar more closely resembles natural coal than charcoal, with respect to the type of chemical bonds and their relative quantity, as well as its elemental composition [86,87]. Both chars exhibit lower H/C and O/C ratios than the initial product, owing to the evolution of H_2O and CO_2 in the dehydration and decarboxylation reactions. However, hydrochar generally has higher H/C and O/C ratios similar to natural coal [88] than

the solids resulting from dry pyrolysis (Figure 3) [9,86, 89,90, AND RO, UNPUBLISHED DATA]. This implies that the ratio of the reaction rates of decarboxylation to dehydration is higher in HTC than in dry pyrolysis [78,91].

It can be observed that the elemental ratios for the hydrochar from animal-derived biomass are comparable to those from plant material, although their feed compositions may differ substantially (see Figure 3). Naturally, this results in different product characteristics.

Although chars from both processes contain extensive aromatic structures, they are arranged differently. The structure of char from dry pyrolysis consists of turbostratically arranged sheets of conjugated aromatic carbon that grow above 400°C [72]. By contrast, carbon spheres with a distinctive size distribution have been observed for the case of HTC of glucose [22,92–95]. These spheres were hypothesized to exhibit an aromatic core of cross-linked furanic rings with mainly aldehydic and carboxy functional end groups [96]. Recent publications have revealed that other carbonaceous structures of

Key term

Coke: a solid high in content of the element carbon and structurally in the nongraphitic state. It is produced by pyrolysis of organic material that has passed, at least in part, through a liquid or liquid-crystalline state during the carbonization process [10].

high technical importance can be systematically created using hydrothermal conditions (see the 'Other applications' section).

The distinctive differences in the solid product composition and structure result from a shift in the reaction mechanisms governing the processes. Radical mechanism pathways, which take place especially at low temperature dry pyrolysis [97], are suppressed in subcritical hot water in favor of ionic reactions [98,99]. However, the major difference is that HTC primarily starts with the hydrolysis of biomacromolecules, yielding oligosaccharides, hexoses, pentoses and fragments of the lignin [76]. The resulting fragments in the aqueous phase may allow initiation of completely different chemical pathways and possible products (Figure 2) [100,101,32]. For example, during the dry decomposition of cellulose, one principle intermediate of dry pyrolysis is proposed to be anhydroglucose [9,97]. In HTC its formation is comparably low [101]. Instead, 5-hydroxymethylfurfural (HMF) is proposed as a crucial intermediate [102]. HMF is an interesting platform chemical between carbohydrate and hydrocarbon chemistry because it can be used to derive an 'impressive array of highly useful organic intermediate chemicals and marketable products' [100]. Research interest in the production of HMF has a long history [103,104].

Hydrolysis can lead to a complete disintegration of the physical structure, which is not the case during dry pyrolysis. However, the fraction of biomass that can be hydrolyzed significantly depends on the temperature profile and process design [83,105]. Increasing reaction severity usually results in an increasing amount of colloidal carbon particles, while less structural features of the original feedstock remain [106].

Many (thermal and hydrolytic) decomposition fragments of biomass are highly reactive, especially those associated with lignin [83,107]. In dry pyrolysis, these intermediate products recombine to form a solid product, so-called 'coke' [9,108]. Containment of the gases can be used to increase the chance of these recondensation reactions, therefore increasing solid yield and coke content [109,110]. As a consequence, the composition of the product changes [88]. Under hydrothermal conditions, nearly all fragments remain in the liquid phase where they have low mobility; thus, a similar effect to containment is achieved (Figure 2). The formation of solids is predominated by recondensation reactions, (i.e., hydrochar is composed of a significant fraction of the above mentioned 'coke') [94–96].

Results from HTC experiments highlight these effects. For biomass without a structural crystalline cellulose scaffold, carbonaceous nanoparticles were obtained, with particle size depending mainly on the carbonization time and concentration [95,106]. For biomass with a structural crystalline cellulose scaffold, an 'inverted'

structure was found, with the carbon being the continuous phase, penetrated by a sponge-like continuous system of nanopores (representing the majority of the volume). These products exhibit highly functionalized surfaces with the potential for a variety of applications (see the 'Other applications' section).

In conclusion, HTC differs from dry pyrolysis in that hydrolysis is the determining first step. The solid product hydrochar is largely formed by recondensation reactions and exhibits distinct characteristics from dry pyrolysis char. The availability of the fragments from hydrolysis in the liquid phase offers a huge potential to influence product characteristics on demand.

▪ Energetics

A crucial element in determining the feasibility of a biomass conversion process is the energy balance. This is

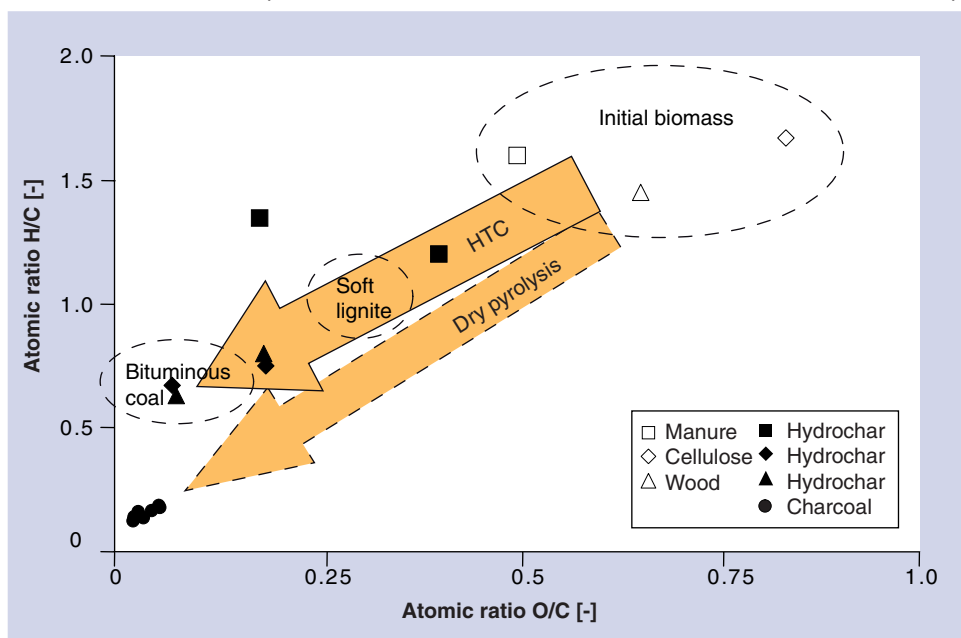
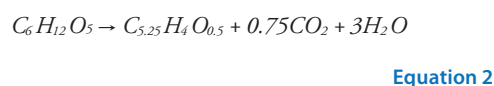
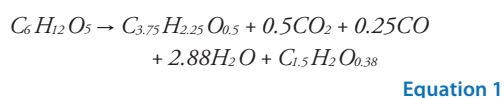


Figure 3. Development of the elemental composition (molar ratios) of cellulose, wood [86] and manure [Ro, UNPUBLISHED DATA]. Regions for typical compositions of biomass [89], lignite and bituminous coal [90] as well as charcoal [9] are illustrated for comparison. HTC: Hydrothermal carbonization.

the case especially if the char is to be used as a fuel, but is also required for determining energy requirements to judge ecological and economical feasibility when using such processes for other purposes (i.e., soil amendment and value-added products). Preliminary results have been published for biochar from dry pyrolysis [111,112]. However, owing to the fact that research on the technical development of hydrothermal production systems is still in its embryonic stage, a detailed energetic analysis for this technology cannot be given here. Instead, a comparison of the energetics of dry pyrolysis and HTC will be discussed on the basis of reaction enthalpy, followed by a qualitative comparison of the decisive energetic differences in their production processes.

Reaction enthalpy

Both dry pyrolysis and HTC of biomass can be exothermic reactions. The amount of heat released is dependent on the feedstock used and the reaction parameters, mainly temperature and residence time. A rough estimate of the heat of reaction for each process can be made from the approximate stoichiometric equations (**Equation 1**: dry pyrolysis [113]; **Equation 2**: HTC [85]), which were deduced from experimental results using cellulose ($C_6H_{10}O_5$) as a model substance:



The higher heating values from **Equations 1 & 2** are summarized in **Table 3**. These approximations should be treated with care, since the chemistry of neither process is fully understood. **Equation 2** does not consider any liquid organic reaction by-products that represent an important fraction [91,114,115]. In addition, biomass

cannot be regarded as a well-defined reactant because of its high degree of chemical complexity and heterogeneity. Nevertheless, these theoretical considerations offer insight to what can be expected.

Experimental results from calorimetric measurements with cellulose support these theoretical estimations. Values between 0.4 and 0.7 MJ/kg_{Cellulose} have been reported for the (slow) pyrolysis of cellulose [75], while similar measurements for HTC produced values of approximately 1 MJ/kg_{Cellulose} [FUNKE, UNPUBLISHED DATA]. Thus, the calorific nature of dry pyrolysis and HTC reactions is comparable. However, it is important to keep in mind that complex reaction mechanisms are involved in the processes and highly dependent on reaction conditions; for example, although the overall reaction is exothermic, the initial phases of both dry pyrolysis and HTC are endothermic. As a consequence, a mild pyrolysis (torrefaction) is slightly endothermic [116,117], and the same can be expected for mild HTC, owing to the endothermic nature of the hydrolysis of cellulose [118].

Process comparison

These theoretical energetic considerations can be used to provide some guidance in the choice between wet and dry processes. From a thermodynamic point of view, there is a certain water content that makes the use of dry processes uneconomical and/or senseless. A threshold exists where wet processes become energetically more efficient than dry processes. This has been illustrated by a theoretical comparison of wood combustion with and without HTC as a pretreatment process. Pretreatment with HTC is more efficient for feedstocks with a water content of more than 50% [119].

Comparison of the heat demand for the evaporation of water to the heat of cellulose pyrolysis reaction (**Equation 1**) shows that above a water content of 30%, more energy is required to evaporate the water than is supplied by the heat released during pyrolysis. In some process designs, product gas is burned to preheat the feed [112,120]. A process using this design could convert

Table 3. Comparison of the calorific nature of slow pyrolysis and hydrothermal carbonization of cellulose.

	Slow pyrolysis [†] (Equation 1)	Hydrothermal carbonization [‡] (Equation 2) [§]
Temperature range (°C)	300–500	180–250
HHV of feed (MJ/kg)	-17.6	-17.6
Heat of reaction (MJ/kg cellulose)	-0.8	-1.6
HHV of solid product (MJ/kg cellulose)	-11.3	-16.0
HHV of gaseous by-products (MJ/kg cellulose)	-0.4	0 [¶]
HHV of liquid by-products (MJ/kg cellulose)	-5.1	0 [¶]

[†]Data from [113].
[‡]Data from [85].
[§]This equation is not complete because liquid products, which represent an important product group, have not been considered.
[¶]Values are according to Equation 2. Published experimental results from carbonization of different feed range from 1–2 MJ/kg_{feed} for gaseous and 0.5–4.1 MJ/kg_{feed} for liquid by-products [FUNKE, UNPUBLISHED DATA].
 HHV: Higher heating value.

cellulose with a water content of up to 70% without external energy supply. To pyrolyze cellulose with an even higher water content, part of the char has to be burned, reducing the yield. At a water content of approximately 90%, all of the char would need to be burned (i.e. the break-even point for a complete combustion without the release of usable heat is approached). For biomass, these values will be lower because less energy is released during carbonization. Ro *et al.* reported that the moisture content of swine solids mixed with rye grass needs to be less than 56% in order to be carbonized without requiring external energy [46].

For the case of HTC, heat for water evaporation is avoided, but the reaction water has to be heated. Additional energetic aspects related to the transportation of water-rich feedstocks and post-processing of the hydrochar, such as dewatering, also have to be considered. An energetic advantage of hydrothermal processes can be expected when the conversion products can either be used without predrying, or when their dewaterability is improved compared with that of the feedstock. Carbonization reactions and disruption of colloidal structures have been shown to improve dewaterability [121].

To conclude, it appears unlikely that a dry pyrolysis process can be driven economically for the conversion of feed with a water content above approximately 50–70%. Such a process would only be capable of producing charred material and an insignificant amount of additional energy and/or product gas. The lower the water content of the feed, the more heat can be produced and used for other purposes [112]. By contrast, HTC typically runs at a 'water content' of 75–90% or even higher. The amount of external heat necessary for HTC depends on the process design, but it is expected to be substantially lower than for the dry pyrolysis of such a slurry. Hydrothermal carbonization of dry organic matter (water content <40%) is unlikely to have any energetic advantages over dry pyrolysis.

▪ Technical implementation

Knowledge of the energetic nature of the underlying reaction is of course essential for the design and technical implementation of the process; however it does not allow conclusions to be drawn about the economics and environmental impact of the complete production system. None of the thermochemical processes described can stand alone; pre- and post-processing units are also required, which depend on feedstock and the desired product characteristics. All aspects from feed handling to reactor design, heat recovery, product separation and auxiliary processes for by-product treatment can make substantial differences in the economic viability of the production system [111,112,122], and in the environmental impacts along the life cycle.

Moreover, sustainable char production must be based on efficient feedstock conversion and safe processes. Owing to its long tradition, dry pyrolysis has many process variations. Traditional slow pyrolysis processes require little (or no) external energy supply except manual labor, and are still applied widely today. However, the hazards associated with traditional kilns outweigh their advantage of simplicity. Low efficiency contributes to deforestation [9] and escaping product gases pose hazards to health and the environment [123]. Improved processes currently available include product gas handling (usually combustion), heat recovery and automated handling of the solids.

Hydrothermal carbonization production systems present different challenges in the technical implementation. One factor is the pressure: operation in a continuous-flow mode requires feeding against pressure, and material and safety aspects for the reactor increases capital costs [4]. Another important factor is heat recovery, which is essential for the process to be economical [84,115]. In HTC, heat must be recovered from the hot process water, while in dry pyrolysis, the product gas can be burnt to supply the necessary heat (either within the reactor or by heat exchangers). Furthermore, post-treatment is likely to be necessary in hydrothermal processes to separate solids from water, and to process the product water [124,125]. Thus, it is to be expected that the energetic requirements to run the process and its auxiliary equipment are higher for a hydrothermal system than for dry pyrolysis.

In addition, plans for technical implementation should include a comprehensive management concept, which should address the feedstock production and collection, treatment of by-products and recovery of nutrients. Any comparisons must consider the current substantial costs and environmental impacts of the alternative collection and treatment processes in use today, especially for wet biomass residuals.

Char characteristics

▪ Char yields

In both pyrolysis processes, the solid or char yields (mass ratio of char to feedstock on dry weight basis) usually decrease with increasing reaction temperature. More of the original feedstock is lost to gaseous (i.e., H₂, CO and CO₂) and liquid by-products. The H/C and O/C ratios in the chars also decrease. Typical changes in these parameters for the HTC process are shown in Table 4. Since significant amounts of liquid by-products are formed during the HTC reaction, the actual char yield measured can be significantly lower than the maximum theoretical yields, which are based on the assumption that only char is formed (Table 4). Several published results indicate that the actual and

Table 4. Comparison of experimental and theoretical solid yields from hydrothermal carbonization of cellulose and wood.

	Temperature (°C)	Time (h)	H/C [†]	O/C [†]	Solid yield (% db)	
					Experimental	Maximum theoretical [‡]
Cellulose	-	-	1.67	0.83	-	-
	275	3	0.75	0.19	47	56
	340	72	0.67	0.07	35	45
Wood	-	-	1.45	0.65	-	-
	225	504	0.8	0.19	62	63
	360	4	0.63	0.08	33	54

[†]Dimensionless atomic (or molar) ratios: H/C Hydrogen to carbon ratio, O/C Oxygen to carbon ratio.

[‡]Yield estimated from stoichiometry assuming only water and carbon dioxide as by-products.

db: Dry weight basis.

Data from [86].

maximum attainable yields approach one another as the residence time increases, probably a result of the continued reaction of intermediates to char.

However, these observations cannot be generalized yet, owing to the high variation in reported char yields from wet pyrolysis (Tables 4 & 5). Another influencing factor is the concentration of solids. In general, the more water added to the reaction, the higher the absolute carbon loss per unit mass of feedstock to the liquid phase. This carbon loss directly lowers the yield of hydrochar and produces a concentrated wastewater that requires further treatment (typically with several g/l chemical oxygen demand).

In dry pyrolysis, the theoretical solid yields for char-coal (e.g., 35% for cellulose from Equation 1) can be increased by condensation of the liquids (tars) to coke, achieving theoretical yields in the range of 50–71% [109], although these are normally not achieved. Experimental yields for hydrochar have been observed to be higher and thus closer to the theoretical yield.

For meaningful process comparisons, process conversion efficiencies for the various elements of interest should be reported and calculated from the solid yield and elemental composition. Carbon conversion efficiencies are of interest, especially for assessing carbon

storage strategies. Commonly in dry pyrolysis, 50% of the biomass carbon is converted to solids [111,126], while in HTC, 60–84% of the biomass carbon may remain in the hydrochar [RO, UNPUBLISHED DATA]. A further refinement is the fixed carbon yield [9], which describes the mass ratio of the fixed (nonvolatile) carbon in the char to the carbon in the initial biomass.

While it is important to increase the information measured and reported on chars, it must be kept in mind that any attempt to merge data generated via different methods must consider the different, operationally defined analytical windows detected by each technique, as well as the limitations and potential biases of each technique, as highlighted by Hammes *et al.* [127].

▪ Char composition

The nature of feedstock, process temperature and reaction time are the main factors influencing the char composition. A comparison of the elemental composition of chars from wet and dry pyrolysis (Tables 5 & 6) [9,46,68,86,128–130 AND RO, UNPUBLISHED DATA] demonstrates that chars from the dry pyrolysis of traditional feedstocks usually have a higher carbon and lower hydrogen content than those from HTC. However, as the temperature in HTC is increased, the carbon

Table 5. Product composition of hydrochar from different feedstock and process conditions.

Feedstock	Tmax (°C)	Time (h)	Solid yield (% db)	C (% daf)	H (% daf)	O (% daf)	N (% daf)	S (% daf)	Ash (% db)	Ref.
Cellulose	225	3	63	51.9	5.6	42.5	0	0	0	[86]
Cellulose	275	3	41	76.4	4.7	18.9	0	0	0	[86]
Cellulose	340	3	39	81.8	4.8	13.4	0	0	0	[86]
Wood	200	72	66.2	70.8	5.7	23.4	NR	NR	NR	[128]
Wood	250	72	50.7	77.1	5.3	17.6	NR	NR	NR	[128]
Wood	280	72	39.9	82.7	4.8	12.5	NR	NR	NR	[128]
Swine manure	250	20	60	70.2	7.9	16.8	3.6	1.5	27.6	[RO, UNPUBLISHED DATA]
Chicken litter	250	20	60	58	5.9	30.5	4.3	1.4	43.6	[RO, UNPUBLISHED DATA]

daf: Dry ash-free weight; db: Dry weight; NR: Not reported; Tmax: Maximum temperature.

Table 6. Product composition of char from dry pyrolysis for different feedstock and process conditions.

Feedstock	Tmax (°C)	Time (h)	Solid yield (% db)	C (% daf)	H (% daf)	O (% daf)	N (% daf)	S (% daf)	Ash (% db)	Ref.
Pine wood	NR	NR	NR	95.2	1.1	3.1	0.1	0.04	0.69	[9]
Corn cob	NR	NR	NR	90.3	1.3	5.6	0.6	0.1	4.31	[9]
Rice hulls	NR	NR	NR	89.7	1.4	6.6	1.0	0.1	41.35	[9]
Poultry litter	450–550	NR	NR	41–74	2.3–3.7	5.9–48.7	3.1–5.2	1.5–3.6	43.8–54.5	[129]
Starter turkey litter	450–550	NR	NR	72.1	3.6	20.2	2.4	0.5	24.6	[129]
Poultry litter	620	2	43–49	86.8	2.5	1.5	5.8	3.4	53.2	[46]
Swine manure	620	2	43–49	89.7	3.4	0	5.8	1.2	44.7	[46]
Wastepaper	750–950	NR	NR	46.7	6.2	46.9	0.1	0.1	15.4	[130]
Refuse derived fuel [†]	400–700	1	NR	76.5–87.3	1.3–6.1		1.4–1.7	0.3–0.8	26–42	[68]

[†]Municipal solid waste, minus recyclables.
daf: Dry ash-free weight; db: Dry weight; NR: Not reported; Tmax: Maximum temperature.

content increases. Char from waste feedstocks has a comparatively lower carbon content in both processes. It is striking that both dry pyrolysis and hydrothermal chars are significantly homogenized compared with the widely varying CHONS compositions of the original feedstocks (Tables 2, 5 & 6). However, this is only valid for the volatile fraction of the char (Tables 5 & 6); the ash content remains highly variable.

Retention of nutrients

Retention of nutrients in chars from dry pyrolysis has been found to be highly variable [131]. In general, chars from the wet and dry pyrolysis of waste feedstocks retain high levels of calcium, potassium and phosphorus. This was seen in animal manures [24,132] and with sewage sludge [133]. However, the question arises: how available are these nutrients for plants?

Shinogi demonstrated that by increasing the pyrolysis temperature from 250–800 °C, the P content of sewage sludge becomes concentrated within the dry char. However, the plant-available phosphorus, as characterized by the citrate extractable fraction, is decreased by more than 90% [134]. Acidic conditions facilitate the mobilization of nutrients and their uptake by plant roots. However, during wet pyrolysis, a low pH may also counteract the sorption of nutrients. Hydrochars from plant residues such as corn stover may result in low pH values of under 5 [135], and may affect the sorption capacity of nutrients, primarily in the case of phosphorus. Processing the same source material by dry pyrolysis resulted in a biochar with a pH value of 9.9, a high cation exchange capacity (CEC) and a high liming value. The phosphorus fertilizing effect of dry chars may also increase owing to thermolytical deliberation of organic bound phosphates from the feedstock [136]. Chars produced from sewage sludge at 550°C in dry pyrolysis significantly stimulated the growth of cherry tomato [133]. This growth stimulation was attributed mainly to improvements of plant

nitrogen and phosphorus nutrition. In contrast to phosphorus, though, almost half of the nitrogen of raw sewage sludge was volatilized at 450°C [65]. Nitrogen losses can be limited by low dry pyrolysis temperatures [9,137].

In HTC, dissolution of water-soluble minerals can be significant [138]; however, the nutrient content will also depend on the technique for dewatering the solid conversion product. The ratio between evaporation and mechanical dewatering governs the amount of plant nutrients that will be adsorbed/retained to the HTC chars surface. In both pyrolysis processes, nutrient concentrations in the feedstock and in the resulting solid and liquid phases need to be taken into account in the process design. The nutrient content in the solid will have to be adjusted for the application, while additional research on process combinations to recover nutrients from the liquid phase is needed.

Heavy metals

Heavy metals cannot be destroyed during pyrolysis, in contrast to organic compounds. Since they may have a toxic risk potential, the fate of heavy metals has to be followed. Their possible accumulation in the solid phase, especially if they can affect the food chain, has to be taken into account. There are some reassuring studies on the fate of metals in chars resulting from the dry pyrolysis of sewage sludge [64,34], animal wastes [129,139], and MSW [43,140,141]. Although metal concentrations associated with chars from carbonization of animal wastes and sewage sludge were detected, concentrations were relatively low when compared with chars resulting from the pyrolysis of MSW. In flash carbonization (FC) of sewage sludges, heavy metals with low boiling points (e.g., Hg, Cd, and Se) were eluted from the FC reactor, whereas those with high boiling points (e.g., Pb, Cd, Ni, Cu, Zn and Sr) were incorporated in the chars [9]. Metal concentrations in dry chars from biosolids were all significantly lower than the limits set for the exceptional quality biosolids,

suggesting unrestricted land application of carbonized sludge may be possible [64]. Again, research on the fate of heavy metals in HTC is rather limited.

Recent experimental results show that several types of char from wood met most of the limits set by the German Federal Soil Protection Act (Table 7) [142]. Only zinc exceeded the limit in all chars. However, for risk assessments, the loading rate is more important than the concentration of a pollutant. This means that an agricultural application is possible, as long as the loading of heavy metals is considered during periodical fertilization. In addition to the measurement of heavy metals concentrations, sequential extraction procedures should be performed in order to gain comprehensive knowledge about the mobility of heavy metal species in the soil [143].

Organic compounds

Since the chemistry of pyrolysis involves not only the decomposition of organic compounds, but also the formation of highly condensed aromatic structures, the discussion of organic compounds has two aspects: pyrolysis can destroy compounds present in the feedstock or produce them in the process. This is greatly influenced by the process and its conditions. Bridle *et al.* [34] reported that over 75% of polychlorinated biphenyls (PCBs) and over 85% of hexachlorobenzenes (HCBs) present in a sewage sludge were destroyed in slow pyrolysis at 450°C. Removal of wastewater-relevant organic pollutants by slow pyrolysis of sewage sludges has also been demonstrated by other authors [35,144]. While PAHs are known to form as the result of secondary thermochemical reactions at temperatures over 700°C, few evaluations of char for PAH or other organic compounds are available [13,15,145]. Investigation of five chars produced via slow pyrolysis showed background level dioxin concentrations and little PAH formation [306].

More systematic investigation of the destruction and formation of toxic organic substances in both processes is indispensable for designing pyrolysis processes and in evaluating potential applications for the solid, liquid and gaseous products.

Knowledge gaps in char characterization

In general, more comprehensive product characterization and reporting is needed to advance our understanding of processes, products and applications. This is an essential step in the search to relate char properties to effects in applications [146], and requires a concerted effort of key players across disciplines, producers and users, to choose the relevant characteristics and develop testing methods. Adequate characterization of the char before it is used in soil and plant experiments is necessary, especially for biochar applications, so that results can be generalized and predictors for expected effects in biochar applications developed. Seeing this need for a classification system, the International Biochar Initiative has started the process of developing guidelines for biochars [307]. Various authors have proposed classification systems for reporting and building on testing in other fields (e.g., charcoal, compost and biowaste/biosolids); a selection of important parameters is shown in Table 8 [147,148,307].

This list encompasses parameters relevant to many of the stages in the product chain from biomass to soil application: feedstock, production conditions, char composition and physical, chemical and biological characteristics. Owing to the heterogeneity of the input and the char itself, most of the parameters are sum parameters. The International Biochar Initiative Draft Guidelines for biochar [307] cover most of these parameters. Other applications will probably not require the soil-relevant parameters. However, it is critically important that the various groups working in this field are aware of the process and product variations, and requirements in the product chain. Feedstock, process conditions and efficiencies dictate char chemical composition. Communication between char producers and users must be developed in order to exploit the ability to influence char properties in the production process and ensure the quality of products. It is important to note that this is an iterative process, especially in biochar applications: while users try to understand how the char interacts with the soil and which properties are responsible for the interactions, the producers will continue to develop the processes, changing material properties.

Table 7. Heavy metal content of chars after thermochemical conversion of wood.

Process	Feedstock	Temperature (°C)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Wet pyrolysis	poplar	200	0.35	8.4	23.3	6.7	618
Wet pyrolysis	pine	210	0.16	1.4	15.8	5.7	603
Dry pyrolysis	pine	430	0.66	12.7	19.7	8.4	684
Gasification	poplar	800	0.23	16.5	190.3	15.5	742
Limits[†]			1.00	100.0	60.0	100.0	150

[†]Limits are from the German Soil Protection Act [142].
Data from [KERN, UNPUBLISHED DATA]

Table 8. Overview of proposed classification systems: feedstock, process and product characteristics to be reported.

	Parameter	Joseph <i>et al.</i> [†]	Okimori <i>et al.</i> [‡]	IBI draft guidelines [§]
Feedstock	Source, type and composition		×	×
	Type of pre-processing			×
Process conditions	T _{max} (°C)			×
	Time (h)			×
	Rate of heating			×
	Reactor pressure			×
	Solid yield (% g char/g feed, db)			×
	Type of post-processing			×
Chemical composition	Elemental composition (%)	×		C, N, P, K
	Molar H/C ratio			×
	Volatile content	×	×	
	Ash content	×	×	×
	Mineral N (mg/kg)	×		×
	Available P (mg/kg)			×
	Heavy metals			×
	Extractable (in water and/or solvents), DOC, phenols, chlorinated hydrocarbons, PAH, dioxins	× [¶]		× [¶]
Physical characteristics	Surface area	×	×	×
	Bulk density		×	×
	Particle size distribution			
	Pore volume (or pore size distribution: ratio macro/micropore volumes)	×	×	
	Chemical characteristics			
pH	×	×	×	
Liming value (% CaCO ₃)			×	
Electrical conductivity (µs/cm)	×		×	
Water-holding capacity		×		
Water drop penetration time				
Cation exchange capacity	×			
Calorific value				
Biological tests	Biodegradability			
	Earthworm avoidance/attraction			×
	Germination inhibition			×

[†]Data from [147].
[‡]Data from [148].
[§]Data from [307].
[¶]Water-soluble fraction.
^{*}Relevant local standards should be used.
db: Dry weight; DOC: Dissolved organic carbon; H/C: Hydrogen to carbon ratio; IBI: International Biochar Initiative; PAH: Polycyclic aromatic hydrocarbon;
T_{max}: Maximum temperature.

Application of char in soils

Much research effort has been expended in recent years to show that returning carbon to the soil in the form of char can sequester carbon and increase soil fertility. This application as biochar could quickly capture a large proportion of biomass production capacity if it were to be included in the carbon trading schemes, such as of the Clean Development Mechanism (CDM) in the Kyoto Protocol [149]. Its suitability as a carbon sequestration strategy will depend on the overall

carbon balance of the production process and the long-term stability of char in soils [20]. Reliable and reproducible methods are needed to assess the sequestered CO₂ equivalents over the product life cycle with due diligence. In addition to the variability in production and biochar properties, the soil, climatic and management conditions may vary widely from location to location and will influence char recalcitrance significantly. In addition, biochar application may possess additional carbon mitigation potential owing to

indirect effects; for example, increases in soil organic carbon (SOC), and decreases in GHG emissions and fertilizer use should be considered in addition to the direct benefits of carbon sequestration (Figure 4).

From these considerations some fundamental issues arise that need to be resolved before the true carbon mitigation potential of biochar can be quantified. These issues are especially relevant for evaluating hydrochar's suitability in soil applications.

First, the time frame over which carbon must remain 'sequestered' has to be decided upon; for example, all biochar that is stable for a century could be regarded as sequestered in terms of climate mitigation. This time frame must be related to other pathways that claim to sequester carbon; for example in the form of wood (e.g., furniture and reforestation) or SOC (e.g., restoration of bogs).

Second, a reliable method to determine the true carbon sequestration potential has to be decided upon. Two pathways could theoretically be considered:

- Direct accounting: based on the amount of carbon that was applied to a soil. The fraction of the applied carbon that will remain after an agreed time period is calculated from the absolute amount of carbon applied to the soil and a 'minimum-C-sequestered' factor. These factors need to be obtained from a broad range of experimental results (various chars, soils, crops and climates);
- Comparative accounting: based on measurements of the SOC in char-amended and reference plots. Such an approach will account for possible carbon losses associated with char use. However, this change has to be assured over the complete sequestration timeframe.

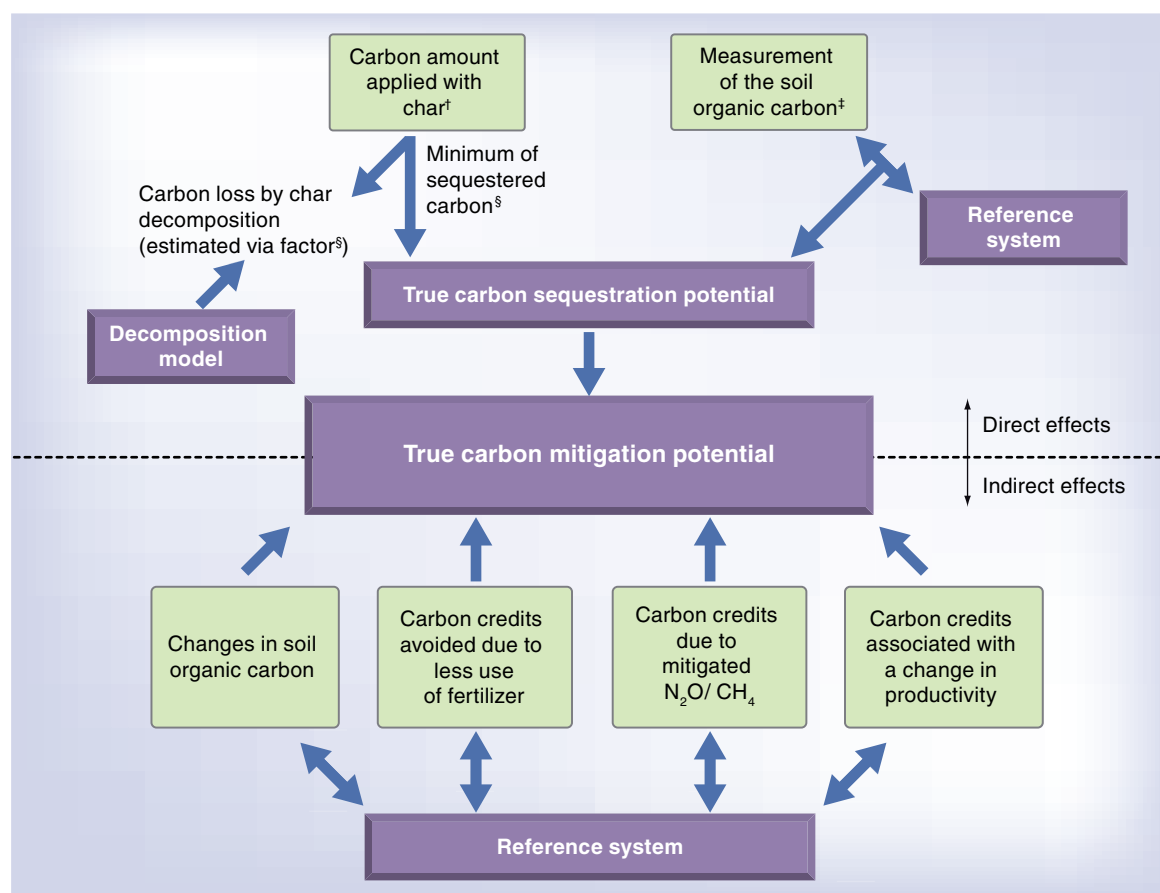


Figure 4. Factors influencing the true carbon mitigation potential of char application. Determination of this true carbon mitigation potential requires a well-defined timeframe, over which the carbon is regarded to be 'sequestered' and it crucially depends on suitable reference systems.

†Direct accounting.

‡Comparative accounting.

§Any 'carbon-sequestration factor' must be assessed conservatively (i.e., the fraction of char that is decomposed should be overestimated rather than underestimated).

In addition to the assessment of the true carbon sequestration potential, several indirect effects of char application have to be taken into account, such as fertilizer use, N₂O and CH₄ emissions, change in SOC and increased productivity. These changes have to be determined in comparison to a nonamended reference system. Naturally, the choice of a proper reference system is decisive for the accuracy of quantifying these indirect effects. The sum of the true carbon sequestration potential and the indirect effects represents the true carbon mitigation potential (see Figure 4). This section summarizes the research on these direct and indirect effects for biochar from dry pyrolysis and highlights the questions still open for hydrochar.

▪ Stability of biochar & hydrochar in soils

Char from natural fires is usually the oldest carbon pool present in ecosystems prone to fire [150,151]. Lehmann *et al.* conservatively assessed mean residence times (MRT) for naturally generated char in Australian woodlands to be 1300–2600 years (range: 718–9259 years [151]). The long-term stability of biochar has been shown in Terra preta soils, which contain considerable amounts of carbon; most of which is 500–2000 years old, sometimes up to 7000 years (¹⁴C dating, [19,152]). Considerable biochar stocks of 50 t C ha⁻¹ have been found down to 1-m depth in such soils, despite the climatic conditions strongly favoring decomposition and the lack of additional biochar additions in the last 450 years [19,153]. However, MRT assessments from natural ecosystems or Terra preta soils can only deliver orders of magnitude in accuracy, since there is no way to quantify the initial (repeated) biochar input to obtain straightforward mass balances [20].

Despite the fact that biochar contributes the longest-living organic carbon pool in soils [21,154,155], biochar cannot be considered inert. It will ultimately be decomposed and mineralized over sufficiently long time scales; otherwise the world's carbon stocks would finally end up in biochar [20,156].

Hydrochar, with its less aromatic structure and higher percentage of labile carbon species, will probably decompose faster than char from dry pyrolysis but less quickly than uncarbonized material [157]. While Kuzakov *et al.* calculated mean MRTs of approximately 2000 years from their 3.2-year incubation study in the laboratory with ¹⁴C-labeled char from dry pyrolysis [21], Steinbeiss *et al.* reported MRTs between 4 and 29 years for two ¹³C-labeled hydrochars made from glucose (without nitrogen) and yeast (5% nitrogen) in a 4-month incubation study [158]. However, the latter study probably underestimated the 'true' MRT of hydrochar. Chars usually show two decay phases that can be approximated with a double-exponential decay

curve [20]. First, labile carbon substances on the surfaces of the chars are decomposed and the outer surfaces are oxidized (which increases the cation exchange capacity in the case of biochar) [159,160]. Thereafter, the decay of the more recalcitrant fraction continues much more slowly (see Figure 11.9 in [20]).

However, the 'true' long-term MRT is hard to capture with a short-term study: the shorter the incubation time and data set, the larger the underestimation of char stability will be. Lehmann *et al.* showed that the MRTs of the recalcitrant fraction, calculated from the same data set, can range from 57 years (using only the first 2 years of a 100-year data set) to 2307 years (using the entire 100-year data set) [20]. Thus, long-term studies are still required for a variety of different chars before MRTs can be reliably estimated and tied to char properties, another reason why a systematic analytical characterization of the properties of biochar/hydrochar is urgently needed (Table 8) [147].

Physical or biological forces such as freeze–thaw or swelling–shrinking of clay minerals, or in-growth of plant roots and fungal hyphae into char particles, may shatter larger particles into smaller ones. This exposes surfaces and increases the total surface area so that the char can be further oxidized or degraded. In old biochar-containing soils, biochar particles are very small (e.g., Terra preta or chernozems); most of the biochar is included within micro-aggregates where they appear to be protected from further decomposition [150,161]. Ploughing and priming by addition of labile carbon substrates (cometabolization) increased biochar decomposition slightly [20,21,156]. White-rot fungi, whose preferred substrate is lignin, and other basidiomycetes were able to slowly decompose lignite, sub-bituminous coal and biochar via excretion of exoenzymes, such as laccase, manganese-peroxidase or phenol-oxidase [162,163]. A nitrogen-rich hydrochar was preferentially decomposed by fungi [158], and considerably stimulated root colonization of arbuscular mycorrhizal fungi in mixtures of up to 20% (by volume) beet-root hydrochar chips was reported [25]. Therefore, fungi will probably be the dominant char decomposers; however, it is unknown to what extent their activity will impact char stability in soils in the long-term.

Other means of char loss from soils include surface erosion or transport to the subsoil, either as small particles with the rain water, or through dissolution as (highly aromatic) dissolved organic carbon (DOC). Further mechanisms of char movement from the surface to deeper layers include bioturbation, kryoturbation or anthropogenic management [156,164,165]. The nonmineralization carbon losses due to erosion or relocation to deeper soil layers can be considerable and quick: Major *et al.* reported a migration rate of 379 kg C ha⁻¹ year⁻¹ from biochar

application of 116 t ha⁻¹ to the top 10 cm of a grassland soil downward to 15–30-cm depth during a 2-year study in Columbia [165]. Conversely, respiratory biochar-C losses or losses via DOC were rather small (2.2 and 1%, respectively) [165]. The movement of char (components) to other ecosystems may have significant effects on its stability; the rate of mineralization in deeper layers may be insignificant compared with that of top soils.

▪ Carbon sequestration potential: soil carbon priming or buildup?

An intriguing fact of the Terra preta soils is the significantly increased SOC stocks besides the black carbon, compared with adjacent Ferralsols [19]. By contrast Wardle *et al.* reported an increased mass loss of organic matter over 10 years in mesh bags with a char mixture when compared with those without [166]; the pH increase associated with charcoal may have promoted microbial decomposition of the acid litter. Therefore, addition of biochar or hydrochar to soils or litter layers must be carefully investigated with regard to possible priming effects that endanger the existing old soil carbon pool. However, in Terra preta soils, the increased SOC contents do not indicate a long-term SOC loss due to biochar presence [19,150,161].

Biochar and hydrochar seem to promote fungal growth, such as arbuscular mycorrhiza [25,167]. These fungi produce the protein glomalin which, as a binding agent, significantly promotes soil aggregation [168,169]. Thus, both chars may, in the long-term, increase the production of nonbiochar SOC by fungal promotion [25], or by formation of organo-mineral complexes and aggregates [20].

The net outcome of the two opposite mechanisms ‘labile carbon fraction induces SOC priming’ and ‘fungal stimulation and soil aggregation protect SOC’ is unknown; it may vary with ecosystem or hydrochar properties. Hence, field studies are urgently required (Figure 4).

▪ Influence of char on soil fertility and crop yields

Change of soil characteristics with biochar & hydrochar

Biochar application or the presence of charcoal in soils has demonstrated several beneficial effects on soil physicochemical properties. Its presence could:

- Enhance the water-holding capacity (WHC) (see Figure 5C), aeration and hydraulic conductivity of soils [153,170];
- Reduce the tensile strength of hard-setting soils [171,172];
- Increase the CEC of soils [153,159,173], resulting in an improved nutrient retention or higher nutrient use efficiency [174];

- Stimulate growth, activity and the metabolic efficiency of the microbial biomass [174,175], including arbuscular mycorrhiza [167,176,25] and N₂-fixing rhizobiota [177];
- Attract earthworm activity [172,178,179].

However, biochar application to soils is not a straightforward road to happiness; results of ‘no (significant) change’ have also been obtained.

Hydrochar will affect soil properties based on the same basic principles, ‘soil physics and chemistry’, ‘water’, ‘nutrients’ and ‘microbial activity’. It will very likely reduce the tensile strength, increase the hydraulic conductivity and enhance the soil WHC. Hydrochars will not have the same large internal surfaces as biochars, owing to the lower production temperature [37,72]. Therefore, water retention curves of hydrochar–soil mixtures may be different to biochar–soil mixtures and resemble that of peat- or compost-additions to soils.

The WHC of hydrochar is usually greater than that of mineral soils; for example fresh wet hydrochar, pressed wet hydrochar and oven-dried hydrochar (105°C) produced from the same feedstock (sugar beet reminder) showed WHCs of 6.6 ± 0.2 g H₂O g⁻¹, 5.9 ± 0.4 g H₂O g⁻¹ and 1.6 ± 0.1 g H₂O per g⁻¹ dry hydrochar, respectively (n = 4/char) [180]. The WHC was considerably reduced after the hydrochar had been fully dried, but not after water had been removed by pressing. Some hydrochars do become hydrophobic when oven- or completely air-dried. Keeping hydrochar at suitable moisture for use in soil without inducing fungal degradation may be a challenge.

The majority of hydrochars are more acidic than many biochars, which are often alkaline, owing to their ash content. Hence, the ‘liming value’ that alkaline biochars can have, reducing, for example, the Al toxicity in acidic soils [19,181,182], may not be associated with acidic hydrochars. Thus, the effect of the two char products on soil biology may vary greatly.

It is likely that hydrochars will undergo ageing processes similar to biochars, where the number of functional groups on the biochar surface increases over time [159,160]; however, large numbers of carboxylic groups on the hydrochar surfaces already exist that can theoretically increase the CEC of soils, improving ‘nutrients’. To our knowledge, this has not yet been investigated.

Soil fertility & crop yield

For various biochars, it is well documented that their application can improve crop yields [183]. However, a yield increase is not guaranteed [184,185]. The following pattern emerges from the recent body of biochar literature. Biochar application can increase yields:

- In degraded or low-fertility soils rather than at already-fertile sites [186,171,184];
- In tropical soils [181,184] rather than in temperate soils [185,178];
- In combination with NPK fertilizers or nutrient-releasing substances rather than without extra nutrient supply [171,179,181,186];
- When the chars themselves were sources of nutrients (e.g., biochar from poultry litter [172]).

However, nutrient supply, pH and other soil parameter changes alone are not always sufficient to fully

explain the observed positive or negative biochar effects on yields [184,185]. At 'low' application rates (where 'low' is relative) the effect of biochar on yields was even sometimes negative, with 'nitrogen immobilization' by the high-carbon additive being an often-cited explanation [171,183]. However, patterns may change when more sources become available.

Hydrochars often exhibit higher labile carbon fractions such as carbohydrates and carboxylates than biochars [157]. Labile carbon in hydrochars could thus initially induce nitrogen deficiency by nitrogen immobilization, particularly in chars from nitrogen-poor

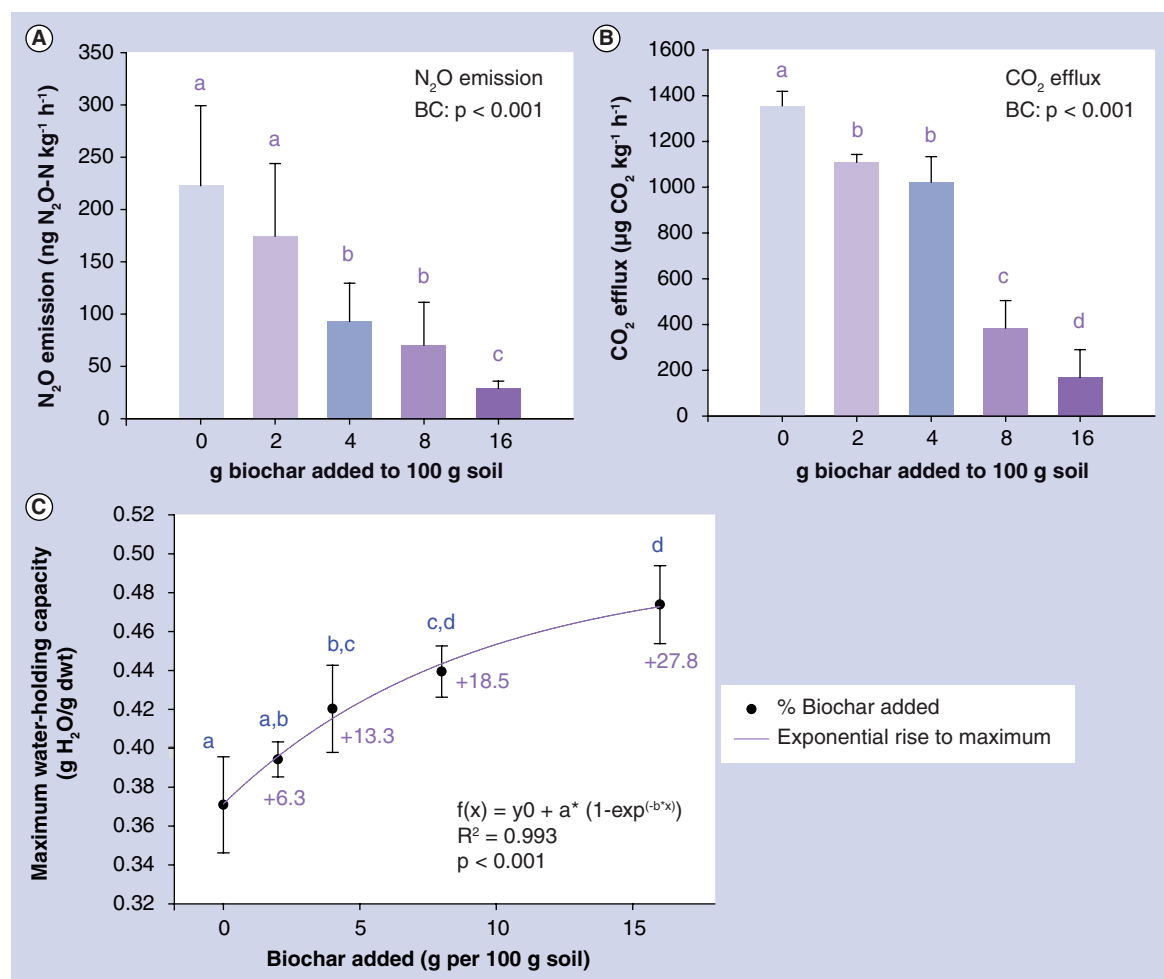


Figure 5. Reduction of (A) N₂O emissions and (B) CO₂ efflux (mean ± standard deviation, n = 4) from a sandy loam brown earth mixed with increasing amounts of biochar (peanut hull from Eprida, USA) and set to 65% of the maximum water-holding capacity of the respective mixture. Since the water-holding capacity increased significantly with increasing amounts of biochar (C; in purple: percentage increase compared with the control), the absolute amount of water added to the biochar mixtures was increasingly higher than that added to the control. Letters indicate significant differences between treatments (A, B and C: one-way analysis of variance and Student-Newman-Keuls all pairwise test procedure; statistics and curve fitting: SigmaPlot 11.0). The flux measurement was performed 4 weeks after mixing soil and biochar and incubating it at 22 ± 1°C in the laboratory, and 1 day after addition of 50 µg N g⁻¹ soil of a NH₄⁺NO₃⁻ solution to stimulate denitrification. Jar incubations and GC analyses of the gas samples for N₂O and CO₂ were carried out as described in [194].

feedstock. Conversely, the large labile carbon fraction may initiate microbial growth and stimulate soil-char nutrient cycling after a lag phase, as observed for some biochars [175,182,187].

With freshly produced hydrochars mixed with soil, we observed a preferential growth of fungi (basidiomycetes); Rillig *et al.* recently described a strong stimulation of arbuscular mycorrhizal root colonization [25]. Hence, depending on the type of fungus it may thus be possible to create purpose-optimized ‘designer hydrochars’ that, for example, stimulate symbiotic fungi to help establish young trees after planting. However, experimental data are currently lacking.

The behavior of nutrients in the production process and in soil application is still an open question. Char from dry pyrolysis has been found to lose some of the initial feedstock nutrients (e.g., via volatilization), or the nutrients may become unavailable to plants by inclusion in aromatic stable structures [185,188], while hydrochar, with its lower production temperature, may retain more nutrients in a plant-available form, either in the hydrochar itself, or in the aqueous phase. We have previously discussed some of these results. In the face of declining phosphorus deposits worldwide, the conservation of plant nutrients from residual materials for agricultural use may become one of the most interesting features of char in soil applications. In the current quest for the most beneficial SOC- and fertility-increasing management practices [189], it may be highly promising to consider SOC-increasing soil additives such as chars [18].

▪ GHG emissions from soils containing biochar

When char is applied to soils, it is crucial to quantify the subsequent fluxes of all GHGs (CO_2 , N_2O and CH_4) because any positive carbon sequestration effect could be diminished, or even reversed, if the emissions of other potent GHGs increase after char application. For CO_2 emissions from soils, the possibility of ‘priming’ of old SOC was discussed earlier in this review. Hence, the following section mainly deals with nitrous oxide (N_2O) and methane (CH_4) fluxes.

Sources & sinks of N_2O

Nitrous oxide is a potent GHG and absorbs, integrated over 100 years, 298-times more infrared radiation than CO_2 [149]. It is predominantly produced during heterotrophic denitrification of NO_3^- to N_2 as a gaseous intermediate, and usually to a lesser extent by nitrification of NH_4^+ to NO_3^- as a by-product (see reviews [190,191]). Rates of N_2O emission from agricultural soils are particularly high after:

- Nitrogen-rich fertilizers have been applied, in particular in the presence of labile carbon (e.g., manures and slurries);

- When aerobic soils experience anaerobicity (e.g., after a heavy rainfall or irrigation);
- During freeze–thaw cycles in spring.

Neglecting N_2O emissions may cause considerable misinterpretation of the real carbon- (i.e. CO_2 -equivalent-)sink capacity of an ecosystem, be it agricultural [192] or semi-natural [193]. Conversely, if N_2O emissions are significantly *reduced* by biochar application, this would considerably improve the GHG balance of biochar-grown agricultural products.

Effect of biochar soil application on N_2O emissions

Rondon *et al.* [205] reported reduced N_2O emissions after biochar application. Since then, more reports of reduced N_2O emissions in the presence of biochar have followed (Table 9). We also observed a significant reduction of soil N_2O emissions with biochar, both without plants (Figure 5) [194], and in the presence of plants [KAMMANN, UNPUBLISHED DATA]. The effects of hydrochar on N_2O formation in soils are even less investigated, let alone understood. In the short term, we observed significant reductions of N_2O emissions in unfertilized loamy and sandy soils when hydrochar has been added, compared with pure-soil controls [KAMMANN & RO, UNPUBLISHED DATA].

Mechanisms of N_2O suppression

Although biochar application led mostly to reduced N_2O emissions [182], the mechanisms of N_2O suppression are not well understood, nor have they been specifically studied. The following mechanisms might be involved:

- Decrease in anaerobic microsites in soil. Char addition can improve the soil aeration and lower the soil bulk density [8, 72, 153, 171]. Hence, the presence of chars can probably reduce anaerobic microsites in soils that are involved in N_2O formation via denitrification [191];
- Change in soil pH. Biochar may reduce N_2O fluxes via pH increases because many biochars from dry pyrolysis are alkaline. When soils become less acidic

Table 9. Overview of the effect on greenhouse gas flux associated with biochar or charcoal applications.

Greenhouse gas flux	Effect	Ref.
N_2O emission	+	[182,208]
	-	[37,179,182,197,205,209,210]
CH_4 uptake	+	[182]
	-	[206,209]
CH_4 emission	-	[182]
CO_2 efflux (soil respiration)	+	[181,175,165,211]
	-	[182,209,211]

+; Indicates an increase in the GHG flux; -; Indicates a reduction in the GHG flux.

(e.g., by liming) more NO_3^- is completely reduced to N_2 (i.e., the $\text{N}_2\text{O}/\text{N}_2$ ratio declines) [195,196]. Yanai *et al.* reported that charcoal amendments reduced the N_2O emissions by 89% [197]; however, simply adding the alkaline ashes or the dominant ions associated with the biochar (K^+ , Cl^- , SO_4^{2-}) did not reduce N_2O emissions. Here, biochars and hydrochars may have opposing effects owing to their pH, with the hydrochars being often acidic and the biochar often alkaline. However, the acidic nature of the hydrochar seems to be lessened when it is combined with soil [25];

- N immobilization in soil. Labile carbon compounds in fresh biochar, or in particular in fresh hydrochar may lead to a temporary nitrogen immobilization in soils, thereby reducing NO_3^- or NH_4^+ available for denitrification and nitrification and hence for N_2O formation, respectively. However, a reduction of N_2O emissions due to nitrogen immobilization will probably not be permanent, demanding long-term studies;
- Stimulation of plant growth. It has long been known that plant growth can reduce the nitrogen availability to soil (de)nitrifiers [198–200], which is one of the reasons for the use of catch crops. If plant growth is indeed stimulated by biochar, then a larger amount of nitrogen might be fixed within the plant biomass, allowing less mineral nitrogen for N_2O formation;
- Change in nitrogen transformation pathways in soil. Biochar may have the potential to change N transformation pathways in soils. Van Zwieten *et al.* reported that at the start of incubations of four different biochars, NH_4^+ concentrations were reduced; at the end of the incubations, however, NO_3^- concentrations were significantly increased in all cases where biochar reduced N_2O emissions [182]. Therefore, soil N transformations clearly changed owing to biochar addition. However, for hydrochar, more or less nothing is known;
- Chemical reduction of N_2O . Biochars with their large porous surfaces may even chemically lead to N_2O reduction, for example, via metallic or metal oxide catalysers on biochar surfaces such as TiO_2 [182]. If this is one of the main mechanisms, it may be more strongly associated with biochars than hydrochars because of the larger internal surfaces per g of biochar.

For the effect of chars on N_2O emissions, many open questions remain: do all chars have this reducing effect on N_2O emissions? Why does it occur and is the mechanism behind it universal? Could one or both chars also lead to a stimulation of N_2O emissions under certain circumstances? Most importantly, does the reduction prevail even after years in the field? To

answer these questions, long-term field studies with a focus on process-oriented measurements (e.g., involving ^{15}N -labeling-tracing techniques) are urgently required.

Sources & sinks of CH_4

Methane production by methanogenic archaea will occur when organic material starts to decay anaerobically; for example, in swamps, bogs, rice paddies, landfills or within ruminant animals. By contrast, methane oxidation by aerobic methanotrophic bacteria (i.e., CH_4 uptake and hence CH_4 sink capacity) takes place in almost every soil under oxic conditions [201]. Interestingly, it is well-established that anthropogenic disturbances such as forest clear-cutting, agricultural management (e.g. ploughing) or, in particular, N-(NH_4^+ -) fertilization diminish soil CH_4 sinks globally [202–204], for reasons that are not yet fully understood.

Effect of biochar soil application on CH_4 fluxes

The effect that biochar or hydrochar additions to soils may have on CH_4 production or CH_4 oxidation is almost completely unknown. Van Zwieten *et al.* [182] mention that CH_4 production declined to zero in the presence of biochar in a grass stand and in a soybean field, and that CH_4 uptake in a poor acidic tropical soil increased by 200 $\text{mg CH}_4 \text{ m}^{-2}$ per year compared with the controls [205]. Priem and Christensen [206] reported that CH_4 uptake rates declined in a savannah that had recently been burned. Terra preta studies do not provide clues since, to our knowledge, no GHG fluxes have been measured so far.

Mechanisms of CH_4 flux changes after char application

Changes in CH_4 fluxes due to char amendment will be the same as outlined for N_2O : reduced soil compaction and improved soil aeration may stimulate CH_4 consumption, since O_2 and CH_4 diffusion are regulated by the ‘key factor,’ soil water content [207]. Increases in the soil pH (via biochar) in acidic soils may enhance CH_4 uptake rates. In highly nitrogen-loaded ecosystems, inhibition of CH_4 oxidation may occur [204]. In such ecosystems, immobilization of nitrogen by biochar or hydrochar application may lead to a faster recovery of the CH_4 sink capacity of those soils. Although it has been cited and re-cited in many reviews, beneficial changes of CH_4 fluxes between biochar-amended soils and the atmosphere clearly leave much room for further research – the issue is far from being resolved.

In summary, the results of the various investigations present a mixed picture (Table 9) [165,175,179,181,182,197,205,206,208–211]. As mentioned in the section on char characteristics, research targeted at relating char properties to soil interactions is needed (Table 8).

▪ Best practice considerations for biochar/hydrochar soil application

To date, standardized best practice guidelines for the application of both char types have not been established. Challenges that have to be considered for dry char include its 'dustiness' and its very low packing density [183]. Major and Husk [178] estimated that, in a commercial larger biochar field trial in Canada, approximately 30% was lost during transport and incorporation. Since black carbon fine particles and soot have considerable greenhouse potential [149], dust loss must be avoided. In addition, the risk of spontaneous combustion or dust explosions in the presence of open fire has to be considered [183].

To ease the application of biochar to agricultural sites and minimize losses when working with machinery, several strategies have been suggested [183], including a preliminary mixing of the bio- or hydrochar with compost, liquid manures or slurries; or wetting a dry char with water, followed by management practices such as ploughing, discing or deep-banded application. Strategies of mixing or composting the biochar or hydrochar with a nutrient-carrier substance such as green waste (composting), slurry or manure will have the positive side effect of 'loading' the char with nutrients.

In contrast to biochar, hydrochar is wet when it leaves its production process; therefore, it may be easier to apply to soils without dust losses. However, it may be necessary to find a 'water content window' (probably between 10 and 15% water content) where the hydrochar is neither at risk of dust formation nor quick fungal degradation. To date, no guidelines or experiences towards the water content of hydrochar for storage, handling and field application exist.

Other applications of char

Char-based materials possess extraordinary properties that partly exceed those of current standards. Chars from both wet and dry pyrolysis have numerous applications in crucial fields, such as sustainable energy or environmental protection. Feedstocks under current investigation vary from well-defined substrates to heterogeneous residues and waste streams. One of the most appealing features of HTC is that it is a green and scalable process, which can be used to tailor design carbon and hybrid nanostructures with practical applications on a price base that is mostly well below any number of corresponding petrochemical processes. Advantages of such HTC-based materials over those produced via the classical dry pyrolysis process include:

- The fact that the carbon precursors can be used without additional drying;
- The temperature at which they are produced is relatively mild (180–250°C);

- The activation step may not be necessary for adsorbing some pollutants;

- Less steps are usually necessary until the final product is obtained.

▪ Activated carbon adsorbents

One of the most important traditional application fields for chars from dry pyrolysis is, without a doubt, adsorption, especially for water purification purposes. Chars normally need an activation step in order to increase their sorption capacity, thus becoming 'activated carbon'. The sorption properties of activated carbons are extremely versatile and can be used for the removal of a variety of inorganic and organic contaminants from water such as heavy metals [212], arsenates [213], organic dyes [214], as well as many other toxic substances [215]. **Table 10** [216–230] shows a list of different agricultural waste materials used in making activated carbon, activation methods, and the adsorption applications.

Activation increases the surface area and pore size. There are two methods: physical and chemical activation. Physical activation involves the activation of the char in the presence of activating agents such as CO₂ or steam. During chemical activation, the raw materials or chars are impregnated or mixed with chemical activating agents. Many activating agents can be used in chemical activation, such as potassium salts, sodium hydroxide, magnesium chloride, calcium chloride and zinc chloride (**Table 10**). The impregnated or mixed materials are then heat-treated in inert environments at various temperatures. Mechanisms for the chemical activation processes have been proposed by [231]. A one-step chemical activation process is possible with dry pyrolysis, where the raw material is dosed or soaked with activating agents and the mixture is dried, and then pyrolyzed [216].

Sorbents for the removal of heavy metals from water have also been successfully designed via the hydrothermal process without an activation step. Incorporation of very small amounts of carboxylic groups containing organic monomers, such as acrylic acid, in the carbon structure produces functional high surface area materials, which were successfully tested as adsorbents for cadmium and lead, achieving higher capacities than standard synthetic ion exchange resins and other types of sorption materials [225]. Such a material is a hybrid between a biomass-based hydrochar and acrylic acid from petrochemistry; however, the major fraction is based on sustainable resources.

▪ Generation of nanostructured materials

The HTC process allows the generation of a variety of nanostructured carbon materials designed to fulfill a specific function. The structure, size and functionality

Table 10. Examples of source materials and applications for activated carbons from dry and wet pyrolysis.

Source materials	Activation methods	Applications [†]	Ref.
Coconut tree sawdust, silk cotton hull, sago industry waste, banana pith, maize cob	Temperature not reported, H ₂ SO ₄	Rhodamine-B, Congo red, methylene blue, methyl violet, malachite green, Hg (II), Ni (II)	[217]
Sewage sludge	600–950°C, spent car oil	H ₂ S	[218]
Dairy manure	200–350°C	Pb (II), atrazine	[219]
<i>Delonix regia</i> tree pods	160°C, H ₂ SO ₄	Crystal violet dye	[220]
Hydrolytic product of sawdust	550–800°C, steam, CO ₂ , KOH	H ₂ storage	[221]
Bean-pods waste	600°C, steam	As (III), As (V), Mn	[222]
Olive mill waste, sewage sludge	500–800°C, ZnCl ₂	Humic acid	[223]
Sewage sludge	440–950°C, ZnCl ₂ , H ₂ SO ₄	H ₂ S	[216]
Bagasse	850°C, H ₂ SO ₄	Cd (II), Zn (II)	[224]
Coir pith	700°C	Congo Red	[226]
Broiler litter and cake	800°C, steam	Cu (II)	[227]
Sewage sludge	550°C, ZnCl ₂	Toluene, methyl-ethyl-ketone, 1,1,2-trichloroethylene	[228]
Cattle-manure compost	ZnCl ₂ , 400–900°C	Phenol	[230]
Carbohydrate plus acrylic acid	Non-activated HTC	Cd (II), Pb (II)	[225]
Japanese cedar	HTC at 350°C with addition of hydrogen peroxide	Phenol	[230]

[†]Compounds investigated for adsorption. HTC: Hydrothermal carbonization.

of the hydrochar can be varied by changing the carbonization time, feedstock type and concentration, as well as by using additives and stabilizers. Soluble, nonstructural carbohydrates produce micrometer-sized, spherically shaped particles with numerous polar oxygenated functionalities from the original carbohydrate or additives. The presence of such surface groups offers the possibility of further functionalization and makes the materials more hydrophilic and highly dispersible in water [96,102]. Through the choice of feedstock or addition of certain compounds (so-called ‘doping’), the type of functional groups on the hydrochar can be controlled; for example, the hydrochar adsorbent discussed above was improved by ‘carbon-doping’ – the addition of organic monomers containing carboxylic groups to the reaction solution.

For biomass without structural crystalline cellulose scaffolding, hydrophilic and water-dispersible carbonaceous spherical nanoparticles in the size range of 20–200 nm were obtained [106]. Such carbon nanoparticles might represent an alternative to the current carbon blacks, or end up in novel applications, such as

reinforcement in concrete or pavements. For biomass made from crystalline cellulose, an ‘inverted’ structure was found, with the carbon being the continuous phase, penetrated by a sponge-like continuous system of nanopores (representing the majority volume). In addition, these products are hydrophilic owing to the presence of approximately 20 weight% functional oxygenated groups, and can be easily wetted with water. Such structures are ideal for water binding, capillarity, and ion exchange [106].

The carbon spheres produced during the HTC process can also be profitably used as sacrificial templates for the production of new materials. The addition of metal salts to carbohydrate solutions results in a very simple and scalable all-in-one pathway towards hollow metal oxide spheres that can be used in electrochemical or other applications [232]. The removal of carbon directly results in hollow spheres of the corresponding metal oxide (e.g. SnO, NiO, Co₃O₄, CeO₂ and MgO) [102].

The micrometer-sized hollow spheres shown in **Figure 6** enable easy handling in terms of separation or device formation in comparison with their nanosized

constituents, while their mesoporosity provides a high surface area network that can be easily penetrated by electrolytes.

Similar to the HTC-generated materials, activated carbon materials from dry pyrolysis can also be used as templates for the generation of hollow metal oxide spheres (TiO_2 , Nd_2O_3 , SiO_2 and Al_2O_3) [233], or hollow fibers ($\text{ZrO}_2/\text{TiO}_2$) [234]). However, these applications require the use of solvents in contrast to the aqueous HTC process. A further advantage of HTC is that it can produce metal oxides not accessible by traditional sol-gel processes.

▪ Catalysis

Carbon materials can be used as catalyst supports or as catalysts on their own, owing to their high stability at elevated temperatures and against harsh reaction conditions. In addition to the well-established use of activated carbon as a catalyst in the production of fine chemicals [235,236], a large number of new applications using carbon as a catalyst, both in the liquid and gas phases, have been reported [237].

A particular role in this field is played by carbon nanocomposites obtained by impregnation of the activated carbon from dry pyrolysis with various metal precursors, followed by reduction. Among all the different nanomaterials produced in this simple route, carbon materials loaded with noble metal such as Pt and Pd have gained particular importance owing to their versatility in different catalytic reactions, such as hydrogenation [238], hydrodechlorination [239] and various other coupling reactions [36].

An advantage of hydrochars in this application is their polarity and the functional groups on their surface, which makes further modification easier; for example, noble metal salts such as Pd^0 can be reduced *in situ* by the aldehyde groups of the carbohydrates, resulting in hydrochars loaded with metallic nanoparticles. These hydrophobic nanoparticles will be preferentially located in the hydrophobic center of the carbon sphere [240]. This system proved to be a successful catalyst for the selective hydrogenation of phenol to cyclohexanone. Such selective binding and enrichment bring technical catalytic systems closer to the performance of natural enzymes.

The coupling of TiO_2 and activated carbons from dry pyrolysis has long been employed to degrade various dissolved organic pollutants photocatalytically under UV light [241,242] or with oxidants (e.g., ozone or H_2O_2) [243]. The same principle can be used with HTC; for example, a nanocomposite was produced by simultaneous hydrothermal treatment of Ti isopropoxyde and glucose. This carbon-doped titanium dioxide (C@TiO_2) has a high surface area able to absorb a high amount

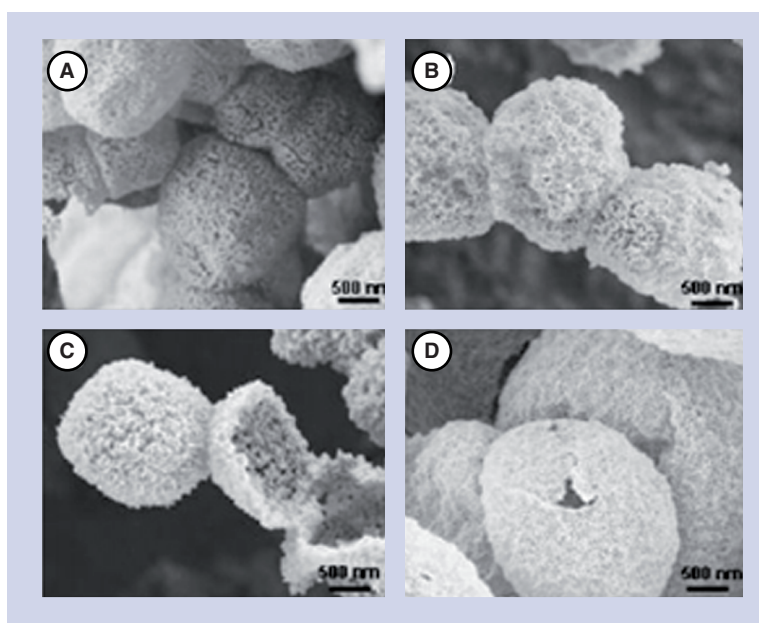


Figure 6. Scanning electron micrographs (SEMs) of (A) NiO , (B) Co_3O_4 , (C) CeO_2 , and (D) MgO hollow spheres [102].

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of photoenergy in the visible range, effectively driving photochemical degradation reactions of organic dyes and pollutants [244].

The addition of nitrogen-containing functional groups (N-doping) to hydrochar can produce carbon materials with surface functionality that is tuned with temperature in order to meet various application requirements; for example, x-ray photoelectron spectroscopy has shown that hydrochar produced hydrothermally at 180°C has amine functionality at the surface and, once heated at higher temperatures, the functionality changes towards pyridinic nitrogen (N incorporated within a graphitic structure) (Figure 7A). Another advantage is that such materials exhibit high surface areas with a well defined mesoporosity (Figure 7B). These materials successfully catalyzed various reactions selectively and at high conversions [244].

▪ CO_2 sorption

Microporous materials such as activated carbons and, in particular nitrogen-doped carbon materials, show great potential for adsorbing CO_2 at relatively high temperatures ($150\text{--}500^\circ\text{C}$) [245]. The capture of CO_2 in the gas phase with low cost, highly selective solid sorbents is another important strategy to reduce CO_2 emissions, in addition to the direct sequestration of CO_2 as a solid in biochar [246]. Such designed materials were recently produced hydrothermally, either directly using nitrogen-containing carbohydrates as precursors

(e.g., chitosane, glucoseamine, algae or crustacean bio-waste [247,248]) or using a mixture of carbohydrates and nitrogen-containing natural precursors (e.g., glucose and ovalbumine protein [96]). The performance of these designed materials can be improved even further by grafting branched amino groups onto their surface [249].

▪ Energy production & storage

Various applications exist for carbon materials in the field of fuel cells: as a solid phase for hydrogen storage [250], as catalysts in low temperature fuel cells to enhance the rates of the hydrogen oxidation and oxygen reduction reactions [251], or as the fuel itself [252,253]. The fuel cell efficiency can be increased using carbon colloids as a fuel, since electrochemical oxidation of a solid depends on the absolute surface area and its surface structure. For indirect carbon fuel cells operating in water at ambient temperatures, design of carbon colloid fuels prepared by the HTC process shows promising potential [252,253]. Such a hydrochar proved to be even more reactive than various natural coals, since it features a chemical structure mainly composed of aliphatic and olefinic building units, which are highly reductive and reactive, while the amount of conjugated aromatic rings is remarkably low. The micrometer-sized spherical particles dispersed in water additionally offer a more accessible surface for the heterogeneous oxidation process.

Another field where hydrochar may bring an advantage is in electrochemical energy storage with lithium-ion batteries and supercapacitors. Their high energy or power densities, portability and promising cycling life are the core of future technologies [254,255]. Graphite and activated carbon are still the most used materials

for lithium-ion batteries and for supercapacitors, respectively [256,257]. However, improved anode materials are still being sought, with improved storage capacity and thermal stability over commercial graphite. Among these, Sn- and Si-based electrodes have gained particular attention owing to their properties of forming alloys with Li, thus, resulting in very high theoretical capacities. However, the use of such materials is still hindered by the low electric conductivity and poor cycling life. In order to overcome such problems, researchers recently started to combine both materials, Sn/Si and C, in one single electrode with improved performance [258]. HTC provides suitable functional groups for binding the carbon layer to the surface of Si or Sn. Thus, a Si/SiO₂/C nanocomposite produced by HTC of preformed silicon showed excellent cycling performance, and high rate capability [102,259,260].

Furthermore, improvements in the cathode in Li ion batteries are also still required. Using a hydrothermal carbon coating technique, LiFePO₄/C cathodes in lithium cells were prepared, showing excellent electrochemical performance [253].

These scientific advances are still far from producing any competitive commercial energy-producing and storage device; however, these experiments already prove that carbon colloids derived from hydrothermally treated biomass can indeed act as a potential fuel for decentral energy generation with an overall zero-emission balance of CO₂.

Regulations for land application of chars

To date, there are no regulations in the US or EU that are specific to the land application of char. However,

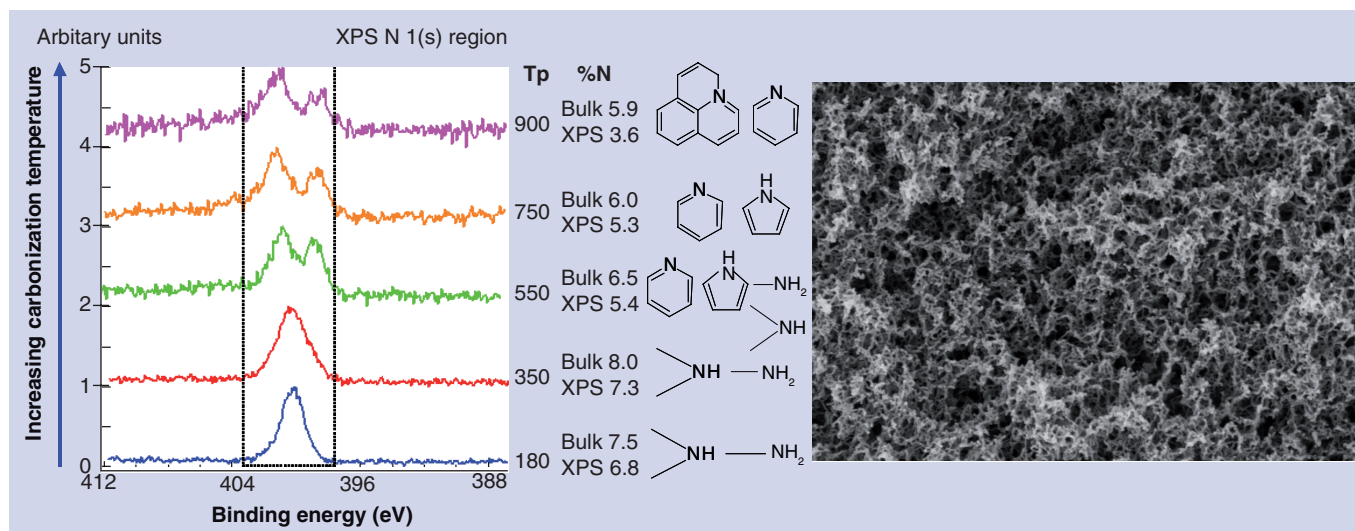


Figure 7. (A) x-ray photoelectron spectroscopy spectra of the N-doped materials obtained upon hydrothermal treatment of glucose and albumine at different temperatures, showing the change in the surface functionality. (B) Scanning electron micrograph of the hydrothermal carbon aerogel obtained from glucose and albumin.

land application of soil amendments such as biosolids (originating from sewage sludges), compost and fertilizer are regulated. It is hypothesized that regulations governing the application of biochar will be at least as stringent as those controlling the application of these products. Therefore, this section summarizes the current regulations as an orientation aid for developing char processes and applications. However, it is important to note that new regulations associated with national environmental initiatives or international carbon trading schemes may drive future biochar regulations.

▪ Regulations in the USA

The US regulations that may apply to land application of char are probably those currently in place for land application of biosolids (regulated federally) or other soil amendments (e.g., fertilizer and compost), which may vary from state-to-state.

Land application of biosolids is regulated federally by the so-called Part 503 rule [261], which requires that sewage sludge be processed (or stabilized) for pathogen destruction, vector attraction reduction and odor minimization prior to land application. Based on the biosolids properties, they are classified into four quality categories and restrictions are placed on the type of receiving land (e.g., agricultural land, lawns and home gardens) and on crop harvesting, animal grazing and public contact associated with these areas. The required pathogen and vector attraction reduction, as well as allowable metal concentrations vary for each category; the highest classification, exceptional quality, has the most stringent metal concentration limits (Table 11) and can be applied with few restrictions.

Biochar application may also be governed by rules associated with land application of composts, which are set by state environmental or department of transportation (DOT) agencies [262,308], and thus, limits/restrictions vary from state-to-state. The limits suggested by compost-quality guidelines include soluble salt concentrations, pH, particle size, heavy metal concentrations, odor, respiration rate, foreign material, pathogen limits and PCB levels [262,309,310]. In some states, the carbon:nitrogen ratio, feedstock source, cation exchange capacity, sulfide, application rate; and nutrient and organic matter concentrations are also regulated [308].

There are few regulations governing fertilizer application in the US. Restrictions depend on the fertilizer source. Nutrient and metal levels are generally restricted, although fertilizers originating from recovered organic materials (i.e., yard waste and food waste) may have more stringent restrictions (see those associated with compost application [305]). Fertilizers composed of biosolids must adhere to the Part 503 rule.

▪ Regulations in the EU

The standards that may apply to biochar use vary based on the individual country within the EU as well as on the regulations in play. An overview of various European standards for composts is given in Table 11 in addition to US standards for biosolids and relevant German standards. The values vary considerably between countries and application. In the following section, the four German federal ordinances that may apply for biochar application are discussed.

Biochar is likely to be classified as either a fertilizer or as soil-ameliorating agent for agriculture use under current German legislation. Although soil-ameliorating agents (or soil improvers) do not have any nutrients, they have a positive influence on the biological, chemical or physical status of the soil to improve the effect of fertilizers and are, therefore, regulated by the fertilizer law [263]. The limits of potential pollutants are regulated in the corresponding ordinance [264], and listed in Table 11. The maximum annual input allowed is determined by the nutrient content. Currently, only ashes derived from natural wood are permitted as soil improvers.

If biochar is applied as part of a compost or mixture with compost, the Biowaste Ordinance [265] must be considered in addition to [264]. All components in the mixture must meet the limits for heavy metals and organic pollutants set by the German Fertiliser Ordinance [264] individually (Table 11) [142,261,264,265,266,303]. There is a maximum application limit for compost of 20 tons per hectare in 3 years. If the heavy metal and organic pollutant content is very low, it is possible to get exceptions from the responsible authorities.

To avoid any restrictions in application quantity, it may be possible to use biochar to build a “root-penetrable soil layer” according to the Soil Protection Ordinance [266], as long as the limits for the metal and organic pollutants in the Sewage Sludge Ordinance [267] are met. The Sewage Sludge Ordinance includes limits on metal concentrations in the sludge itself, as well as on background values for metals in soil. Sludge application is only allowed on soils with metal concentrations below the soil limit values. There is a maximum limit of 5 tons sludge per hectare in 3 years.

Conclusions

Carbonization of biomass residue and waste materials has great potential to become an environmentally sound conversion process for the production of a wide variety of products. However, process and product development are still in their infancy for these feedstocks, and accordingly, there are many aspects that require additional research. Filling the current research gaps is necessary before the process can be designed and exploited

Table 11. Metal pollutant limits for land application of compost or biosolids.

Country	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Se (mg/kg)	Mb (mg/kg)	Ti (mg/kg)	PAH (mg/kg)	PCB (mg/kg)	PCDD/PCDF (ng/kg)
Austria (composted MO)	4	150	400	500	4	1000	6	0.2						
Belgium (composted SSMA)	1	70	90	120	0.7	280								
Denmark (composted MO)	1.2			120	1.2	45	3							
France (composted MO)	8			800	8	200								
Germany (composted MO)	1.5	100	100	150	1	400								
Spain (compost)	40	750	1750	1200	25	400	NR	NR						
Germany (fertilizer ordinance)	40	1.5	2	70	150	1	80	1000			1			
Germany (sewage sludge ordinance)	10/5 [†]	900	800	900	8	200	2500/2000 [†]						0.2 [‡]	100 TEF
USA (maximum concentration in biosolids)	75	85	[§]	4300	840	57	420	7500	100	75				
USA (concentration limits for exceptional quality biosolids)	41	39	[§]	1500	300	17	420	2800	36	[¶]				

Adapted from [142,261,264–266,303].

[†]The lower limit is for soils with a clay content below 5% or below pH 5.[‡]For the six PCB indicator congeners 28, 52, 101, 138, 153, 180.[§]The chromium standard was removed in 1995 (see Committee on Toxicants and Pathogens in Biosolids Applied to Land 2002).[¶]No limit for molybdenum.

PAH: Polycyclic aromatic hydrocarbon; PCB: polychlorinated biphenyl; PCDD/PCDF: Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans; MO: Mixed organics; NR: Not reported; SSMA: Source separated mixed organics; TEF: Toxicity equivalent factor.

to produce char for specifically intended applications. **Box 1** highlights specific activities for further research. The general challenges are summarized here.

Fundamental and systematic investigations are still required before the suitability of pyrolysis and char-based concepts for the sanitation and waste sector can be evaluated. These investigations have to address first and foremost the physicochemical characteristics of the conversion products (e.g., organic and inorganic; gaseous,

liquid and solid) and their fates, in order to develop process combinations for treating all three phases, as well as developing applications for the resulting chars.

Many years of research have shown that biochar from dry pyrolysis has great potential to significantly reduce CO₂ emissions via soil application for carbon sequestration and soil amelioration. If biochar is to be included into a carbon trading scheme, fundamental issues still need to be resolved in order to quantify the

Box 1. Overview of future research areas.

Char production

- Determine which initial feedstock properties significantly influence the hydrothermal carbonization (HTC) process energetics and final product composition and yield
- Develop a feasible process model to describe the HTC of biomass, both qualitatively and quantitatively
- Relate feedstock properties and process conditions to char characteristics
- Assess life cycle impacts for char production systems vs alternative technologies for the treatment of waste streams, especially considering the respective by-products and transportation requirements
- Develop scenarios for evaluating the efficiencies of the two pyrolysis processes under various conditions, individually and comparatively, to find the most suitable carbonization treatment for various feedstocks, intended applications and pertinent boundary conditions

Characteristics of char & by-products

- Determine the chemical structure of various hydrochars and its relevance to various applications such as soil amendment, carbon-sequestration and activated carbon precursor
- Develop a classification system for char characterization based on process and product parameters, which can be used to estimate the suitability of the char for the desired application
- Determine how char characteristics affect soil conditions (e. g., pH, cation exchange capacity, water-holding capacity, recalcitrance of applied carbon and impacts on soil organic carbon mineralization) and plant growth
- Characterize water phase from HTC in terms of water quality parameters and individual chemicals
- Determine the fate of environmentally important chemicals during HTC processes such as metals, polycyclic aromatic hydrocarbons, dioxins and nutrients

Biochar applications

Stability in soil

- Perform long-term field and laboratory studies to systematically quantify the fractions of sequestered and decomposed char over agreed time frames for a broad variety of different chars, soils, cropping systems and climates
- Identify the main char-decomposing mechanisms and microorganisms
- Estimate the water pollution potential of the decomposition products
- Connect the stability results to char properties to enable 'forecasts' for new types of char
- Obtain minimum-carbon-sequestration factors based on field experiments to build a basis for the inclusion into carbon trading schemes

Soil fertility

- Investigate changing soil properties due to char application for a broad variety of chars, soils, cropping systems and climates
- Identify key mechanisms of crop yield increase and soil amelioration
- Design biochars for different situations (e.g., soils, crops and climates) and develop processes suitable to produce such chars in an environmentally sound manner

Indirect effects of carbon mitigation

- Investigate the effect of char application to different soils, cropping systems and climates to include the indirect effects of char application, to avoid the danger of missing negative effects (e.g., soil organic carbon loss and increased greenhouse gas emissions), and add possible positive effects (e.g., soil organic carbon build-up and reduced greenhouse gas emissions)
- Identify key process mechanisms of GHG-flux changes, if general patterns emerge, to enable general predictions

Other applications

- Investigate how the various constituents of the biomass residuals affect potential products and their properties
- Identify process limiting factors for scale-up

Communication networks between stakeholders

- Facilitate communication between char researchers, producers and users in order to exploit the ability to influence char properties in the production process and ensure the quality of products

Regulations

- Revise legislation to create an investment-friendly framework for the secure use of clean, ecologically compatible chars either in agriculture or as materials or fuel to implement intelligent, sustainable material and energy flows

Key term

'Designer'chars: specifically designed carbonaceous materials.

carbon mitigation effects. These include the time frame over which carbon must remain 'sequestered' and the choice of a method for the assessment of such 'sequestered' carbon. Currently, the results of the extensive investigations still do not give a consistent picture in many aspects, ranging from plant growth stimulation to GHG emissions.

Better quantification and reporting of char characteristics is an important step in understanding this variability in experimental results. The fact that the characteristics of char depend highly on feedstock and process conditions is often not adequately taken into account in experimental investigations. Further research is necessary to identify important characteristics for soil amendment and their effects in the soil in order to provide a basis for the design and choice of suitable processes to achieve a high-quality char for soil amendment.

To this end, communication between char producers and users must be improved in order to exploit the ability to influence char properties in the production process and ensure the quality of products. However,

not only the char–soil interactions in the final stage of the product life cycle are of interest. The overall impacts on health and environment in all stages of the life cycle must be evaluated. Further development of both chars must be accompanied by comprehensive analyses of processes, products, by-products and their fates and impacts along the life cycle. This is especially important for complex feedstocks such as heterogeneous organic residues. In addition to the fate of the carbon bound in the char and mobile organic compounds, the fate of the inorganic constituents (e.g., nutrients and heavy metals) in the original feedstock must be determined, both in the process and in the application.

It is important to note that this is an iterative process – especially in biochar applications – since the complex soil interactions are not well understood and which product properties will produce the most benefit are not clear. Progress in this area must flow into work on process development in wet and dry pyrolysis, so that methods for designing new material properties can be tuned to produce the chars with the desired attributes, for instance, nutrient content.

Executive summary**Feedstocks**

- Hydrothermal char production processes require a water content that exceeds the one feasible in dry pyrolysis. This considerably widens the spectrum of potential feedstocks to a variety of the nontraditional renewable wet agricultural residues and municipal waste streams for beneficial waste use.
- The overall suitability of thermochemical conversion processes for these wet residual streams will ultimately be dependent on combined management concepts that encompass their collection, the treatment of by-products in the water phase and the recovery of nutrients, besides the production of economically viable products.

Chemistry & energetics

- The chemistry of hydrothermal carbonization (HTC) offers a huge potential to influence product characteristics on demand and thereby produce purpose-optimized 'designer' chars.
- HTC reactions show a comparable calorific nature to those of dry pyrolysis; however, there are significant differences in the process design and energetic requirements involved in running the process.
- Detailed ecological and economical analyses of the products and by-products of HTC need still to be made,

Char characteristics

- Hydrochar has substantially different characteristics than char from dry pyrolysis. However, the characteristics of both products, depend highly on feedstock and process conditions. HTC usually achieves a higher solid yield than dry pyrolysis, but does not produce energy gases as in dry pyrolysis.
- Better quantification, reporting and standardization of char characteristics and production conditions are required in order to understand the wide variability found in experimental investigations.

Chars in soil amelioration

- Hydrochar with a high number of carboxyl groups could have soil-ameliorating properties. Such hydrochars may be useful for increasing the carbon content of degraded soils and improving plant nutrition.
- However, compared to biochars from dry pyrolysis, knowledge on hydrochar use in soils is in its infancy. Thus, possible toxic effects or risks have to be carefully evaluated.
- Hydrochar may be more stable than normal soil organic matter, but less stable than biochar from dry pyrolysis. Knowledge on its property-related long-term stability in soils is lacking.
- It is unknown to date if hydrochar may reduce emissions of the potent greenhouse gas N₂O from soils in the same way as biochar.

Other applications

- The HTC process allows the generation of a variety of tailor-designed hydrophilic nanostructured carbon and hybrid materials. They have been successfully demonstrated in a number of applications as adsorbents, catalysts, ion exchangers and in energy storage.

Indeed, sustainable nutrient recycling may in the end govern hydrochar use in agriculture. In the current quest for the most beneficial SOC- and fertility-increasing management practices, it may be highly promising to consider SOC-increasing soil additives such as chars. In the light of a growing world population, decreasing fertile agricultural areas worldwide and global change on our heels, it would be inexcusable not to investigate the promising ‘designer’ char mitigation option.

Future perspective

The large potential for converting residual materials into a char that can be used for such a variety of applications will spur coordinated effort between producers, users and regulators of char to close the current knowledge gap on the relationship between char properties, end use application and environmental impact. With

the experience from continuing laboratory experiments and field trials, decisive properties of char will be understood, allowing processes to be designed to achieve the required product characteristics. Simultaneously, regulations for the production and various applications of carbonaceous materials will be developed, which need to consider the complexity of benefits and difficulties connected with environmental quality.

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The authors have no relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript. This includes employment, consultancies, honoraria, stock ownership or options, expert testimony, grants or patents received or pending, or royalties.

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Bibliography

Papers of special note have been highlighted as:

■ of interest

■ ■ of considerable interest

- 1 Perlack R, Wright L, Turhollow A *et al.* *Biomass as a feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply*. US Department of Energy, DC, USA (2005).
- 2 *Energie aus Biomasse – Grundlagen, Techniken, Verfahren (2nd Edition)*. Kaltschmitt M, Hartmann H, Hofbauer H (Eds). Springer Verlag, Berlin, Germany (2009).
- 3 Larkum A. Limitations and prospects of natural photosynthesis for bioenergy production. *Curr. Opin. Biotech.* 21(3), 271–276 (2010).
- 4 Pratt K, Moran D. Evaluating the cost-effectiveness of global biochar mitigation potential. *Biomass Bioenerg.* 34(8), 1149–1158 (2010).
- 5 Mathews JA. Carbon-negative biofuels. *Energy Policy* 36(3), 940–945 (2008).
- 6 Whitman T, Lehmann J. Biochar – one way forward for soil carbon in offset mechanisms in Africa? *Environ. Sci. Policy.* 12(7), 1024–1027 (2009).
- 7 *Biochar for Environmental Management*. Lehmann J, Joseph S (Eds). Earthscan, London, UK (2009).
- 8 Sohi S, Krull E, Lopez-Capel E, Bol R. A review of biochar and its use and function in soil. *Adv. Agron.* 105, 47–82 (2010).
- 9 Antal MJ, Gronli M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* 42(8), 1619–1640 (2003).
- ■ **Comprehensive review paper that outlines the current knowledge of charcoal production and properties.**
- 10 *IUPAC Compendium of Chemical Terminology (2nd Edition)*. McNaught AD, Wilkinson A (Eds). Blackwell Science, Oxford, UK (1997).
- 11 Fitzer E, Kochling K, Boehm HP, Marsh H. Recommended terminology for the description of carbon as a solid (IUPAC Recommendations 1995). *Pure Appl. Chem.* 67(3), 473–506 (1995).
- 12 Lehmann J, Joseph S. Biochar for environmental management – an introduction. In: *Biochar for Environmental Management: Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 1–12 (2009).
- 13 Verheijen F, Diafas I, Jeffery S, Bastos A, Velde MVD. *Biochar Application to Soils: A Critical Scientific Review of Effects on Soil Properties, Processes and Functions*. EC Joint Research Centre, Brussels, Belgium, Report No. EUR 24099 EN – 2010 (2010).
- 14 *Amazonian Dark Earths: Explorations in Space and Time*. Glaser B, Woods WI (Eds). Springer Verlag, Berlin, Germany (2004).
- 15 Sohi S, Lopez-Capel E, Krull E, Bol R. *Biochar, Climate Change and Soil: A Review to Guide Future Research*. Commonwealth Scientific and Industrial Research Organisation, Science Report No. 05/09 (2009).
- 16 Funke A, Ziegler F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuel. Bioprod. Bior.* 4(2), 160–177 (2010).
- 17 Hu B, Wang K, Wu L *et al.* Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* 22(7), 813–828 (2010).
- 18 Lal R. Challenges and opportunities in soil organic matter research. *Eur. J. Soil Sci.* 60, 158–169 (2009).
- 19 Glaser B, Haumaier L, Guggenberger G, Zech W. The ‘Terra preta’ phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwissenschaften* 88(1), 37–41 (2001).
- ■ **Best introduction to Terra preta soils; brief and still highly current.**
- 20 Lehmann J, Czimczik C, Laird D, Sohi S. Stability of biochar in soil. In: *Biochar for Environmental Management – Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 183–205 (2009).
- ■ **More than just a good review; it comprises conceptual knowledge and recommendations for key research concerning char stability in soils.**
- 21 Kuzyakov Y, Subbotina I, Chen H, Bogomolova I, Xu X. Black carbon decomposition and incorporation into soil microbial biomass estimated by ¹⁴C labeling. *Soil Biol. Biochem.* 41(2), 210–219 (2009).
- **Longest of the laboratory studies under controlled conditions dealing with biochar stability in soil mixtures.**
- 22 Wang Q, Li H, Chen L, Huang X. Monodispersed hard carbon spherules with uniform nanopores. *Carbon* 39, 2211–2214 (2001).

- 23 Titirici M, Antonietti M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem. Soc. Rev.* 39, 103–116 (2010).
- 24 Ro KS, Novak J, Bae S, Flora JRV, Berge ND. Greenhouse gas emission from soil amended with biochar made from hydrothermally carbonizing swine solids. Presented at: *American Chemical Society National Meeting*, San Francisco, CA, USA, 21–25 March 2010.
- 25 Rillig MC, Wagner M, Salem M et al. Material derived from hydrothermal carbonization: Effects on plant growth and arbuscular mycorrhiza. *Appl. Soil Ecol.* 45, 238–242 (2010).
- 26 Bridgwater AV. Pyrolysis – state of the art. In: *Success & Visions for Bioenergy: Thermal Processing of Biomass for Bioenergy, Biofuels and Bioproducts*. Bridgwater AV (Ed.). CPL Press, Newbury, Berks, UK (2007).
- 27 Bugge G. *Industrie der Holzdestillations-Produkte*. Theodor Steinkopff, Dresden and Leipzig, Germany (1927).
- 28 Nowak A. *Chemische Holzverwertung*. Hartleben, Vienna, Austria (1932).
- 29 Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. *Renew. Sust. Energ. Rev.* 4, 1–73 (2000).
- 30 Higan C, Burgt MVD. *Gasification*. Gulf Professional Publishing, Amsterdam, The Netherlands (2003).
- 31 Behrendt F, Neubauer Y, Oevermann M, Wilmes B, Zobel N. Direct liquefaction of biomass. *Chem. Eng. Technol.* 31(5), 667–677 (2008).
- 32 Peterson AA, Vogel F, Lachance RP, Froeling M, Antal MJ. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy Environ. Sci.* 1, 32–65 (2008).
- 33 Liu H, Neubauer Y. Gasification. In: *High Temperature Processes in Chemical Engineering*. Lackner M (Ed.). ProcessEng Engineering GmbH, Vienna, Austria (2010).
- 34 Bridle T, Hammerton I, Hertle C. Control of heavy-metals and organochlorines using the oil from sludge process. *Water Sci. Technol.* 22(12), 249–258 (1990).
- 35 Sütterlin H, Tritler R, Bojanowski S, Stadbauer E, Kümmerer K. Fate of benzalkonium chloride in a sewage sludge low temperature conversion process investigated by LC–LC/ESI–MS/MS. *CLEAN – Soil Air Water* 35(1), 81–87 (2007).
- 36 Seki M. Recent advances in Pd/C-catalyzed coupling reactions. *Chem. Inform.* 37(52), 2975–2992 (2006).
- 37 Lehmann J. Bio-energy in the black. *Front. Ecol. Env.* 5(7), 381–387 (2007).
- **Fine overview concerning the hopes and perspectives that may make char techniques as potential sustainable global warming mitigation tools so interesting.**
- 38 CEC. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources. *Official Journal of the European Union* L140/16 (2009).
- 39 Schuchardt F. [Organische reststoffe aus landwirtschaft, agrarindustrie und kommunen. In: *Energie und Rohstoffe aus landwirtschaftlichen Reststoffen – Hydrothermale Carbonisierung ein geeignetes Verfahren?*] BMELV, Berlin, Germany (2009).
- 40 Smeets E, Faaij A, Dees M et al. A review and harmonization of biomass resource assessments. *Proceedings of the 17th European Biomass Conference and Exhibition*. Hamburg, Germany, 29 June–3 July 2009.
- 41 Ragland KW, Aerts DJ, Baker AJ. Properties of wood for combustion analysis. *Bioresour. Technol.* 37(2), 161–168 (1991).
- 42 Khalil R, Mészáros E, Grönlund M et al. Thermal analysis of energy crops: part I: The applicability of a macro-thermobalance for biomass studies. *J. Anal. Appl. Pyrol.* 81(1), 52–59 (2008).
- 43 Tchobanoglous G, Theisen H, Vigil S. *Integrated Solid Waste Management: Engineering Principles and Management Issues*. McGraw-Hill, NY, USA (1993).
- 44 Vesilind P, Worrell W, Reinhart D. *Solid Waste Engineering*. Brooks/Cole, Pacific Grove, CA, USA (2002).
- 45 Gordillo G, Annamalai K, Carlin N. Adiabatic fixed-bed gasification of coal, dairy biomass, and feedlot biomass using an air–steam mixture as an oxidizing agent. *Renew. Energ.* 34(12), 2789–2797 (2009).
- 46 Ro KS, Cantrell KB, Hunt PG. High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Ind. Eng. Chem. Res.* 49(20), 10125–10131 (2010).
- 47 Thomé-Kozmiensky K. [*Biologische Abfallbehandlung*]. EF – Verlag für Energie und Umwelttechnik, Berlin, Germany (1995).
- 48 Tchobanoglous G, Stensel DH. In: *Wastewater Engineering: Treatment and Reuse: Metcalf & Eddy Inc. (4th Edition)*. Burton FL (Ed.). McGraw-Hill, NY, USA (2003).
- 49 Yeoman S, Sterritt R, Rudd T, Lester J. Particle-size fractionation and metal distribution in sewage sludges. *Water Air Soil Poll.* 45(1–2), 27–42 (1989).
- 50 Cantrell K, Ro K, Mahajan D, Anjom M, Hunt PG. Role of thermochemical conversion in livestock waste-to-energy treatments: obstacles and opportunities. *Ind. Eng. Chem. Res.* 46(26), 8918–8927 (2007).
- 51 Ro KS, Cantrell K, Elliott D, Hunt PG. Catalytic wet gasification of municipal and animal wastes. *Ind. Eng. Chem. Res.* 46(26), 8839–8845 (2007).
- 52 *Global Atlas of Excreta, Wastewater Sludge, and Biosolids Management: Moving Forward the Sustainable and Welcome Uses of a Global Resource*. LeBlanc R, Matthews P, Richard RP (Eds.). United Nations Human Settlements Programme (UN-HABITAT), Nairobi, Kenya (2008).
- 53 European Commission Environment. Urban waste water treatment – Commission Directive 98/15/EC amending Council Directive 98/271/EEC. (1998).
- 54 Fyttili D, Zabanitoulou A. Utilization of sewage sludge in EU application of old and new methods – a review. *Renew. Sust. Energ. Rev.* 12(1), 116–140 (2008).
- 55 Esrey S. Towards a recycling society: ecological sanitation – closing the loop to food security. *Water Sci. Technol.* 43(4), 177–187 (2001).
- 56 Suzuki A, Nakamura T, Yokoyama S, Ogi T, Koguchi K. Conversion of sewage-sludge to heavy oil by direct thermochemical liquefaction. *J. Chem. Eng. Jpn* 21(3), 288–293 (1988).
- 57 Campbell H, Bridle T. Conversion of sludge to oil – a novel-approach to sludge management – reply. *Water Sci. Technol.* 21(12), 1632–1632 (1989).
- 58 He P, Gu G, Shao L, Zhang Y. Research on low temperature thermo-chemical conversion to oil process for sewage sludge. *Water Sci. Technol.* 42(3–4), 301–308 (2000).
- 59 Bridle T, Skrypski-Mantele S. Experience and lessons learned from sewage sludge pyrolysis in Australia. *Water Sci. Technol.* 49(10), 217–223 (2004).
- 60 Badosz T, Block K. Removal of hydrogen sulfide on composite sewage sludge-industrial sludge-based adsorbents. *Ind. Eng. Chem. Res.* 45(10), 3666–3672 (2006).

- 61 Rio S, Le Coq L, Faur C, Lecomte D, Le Cloirec P. Preparation of adsorbents from sewage sludge by steam activation for industrial emission treatment. *Process Saf. Environ.* 84(B4), 258–264 (2006).
- 62 Rozada F, Otero M, Garcia A, Moran A. Application in fixed-bed systems of adsorbents obtained from sewage sludge and discarded tyres. *Dyes Pigm.* 72(1), 47–56 (2007).
- 63 Liu C, Tang Z, Chen Y, Su S, Jiang W. Characterization of mesoporous activated carbons prepared by pyrolysis of sewage sludge with pyrolusite. *Bioresour. Technol.* 101(3), 1097–1101 (2010).
- 64 Yoshida T, Antal M. Sewage sludge carbonization for Terra preta applications. *Energ. Fuels.* 23, 5454–5459 (2009).
- 65 Bridle T, Pritchard D. Energy and nutrient recovery from sewage sludge via pyrolysis. *Water Sci. Technol.* 50(9), 169–175 (2004).
- 66 Sanchez M, Lindao E, Margaleff D, Martinez O, Moran A. Biofuels and biochar production from pyrolysis of sewage sludge. *J. Residuals Sci. Tech.* 6(1), 35–41 (2009).
- 67 Bogner J, Ahmed M, Diaz C *et al.* Waste management. In: *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* (Eds). Cambridge University Press, Cambridge, UK (2007).
- 68 Buah WK, Cunliffe AM, Williams PT. Characterization of products from the pyrolysis of municipal solid waste. *Process Saf. Environ.* 85(B5), 450–457 (2007).
- 69 Chang YH, Chen WC, Chang NB. Comparative evaluation of RDF and MSW incineration. *J. Hazard. Mater.* 58(1–3), 33–45 (1998).
- 70 Caputo AC, Pelagagge PM. RDF production plants: I design and costs. *Appl. Therm. Eng.* 22(4), 423–437 (2002).
- 71 Luo SY, Xiao B, Hu ZQ, Liu SM. Effect of particle size on pyrolysis of single-component municipal solid waste in fixed bed reactor. *Int. J. Hydrogen Energ.* 35(1), 93–97 (2010).
- 72 Downie A, Crosky A, Munroe P. Physical properties of biochar. In: *Biochar for environmental management – science and technology.* Lehmann J, Joseph S (Eds). Earthscan, London, UK, 13–32 (2009).
- 73 Hofbauer H, Kaltschmitt M, Nussbaumer T. [*Energie aus Biomasse – Grundlagen, Techniken, Verfahren.*] Kaltschmitt M, Hartmann H, Hofbauer H (Eds). Springer Verlag, Berlin, Germany, 375–406 (2009).
- 74 Groenli MG, Varhegyi G, Di Blasi C. Thermogravimetric analysis and devolatilization kinetics of wood. *Ind. Eng. Chem. Res.* 41, 4201–4208 (2002).
- 75 Mok WSL, Antal MJ, Szabo P, Varhegyi G, Zelei B. Formation of charcoal from biomass in a sealed reactor. *Ind. Eng. Chem. Res.* 31, 1162–1166 (1992).
- 76 Bobleter O. Hydrothermal degradation of polymers derived from plants. *Prog. Polym. Sci.* 19, 797–841 (1994).
- 77 Landais P, Michels R, Elie M. Are time and temperature the only constraints to the simulation of organic matter maturation? *Org. Geochem.* 22, 617–630 (1994).
- 78 Ruyter HP. Coalification model. *Fuel* 61(12), 1182–1187 (1982).
- 79 Venderbosch RH, Sander C. Hydroconversion of wet biomass: a review. Report GAVE-9919. SenterNovem, Utrecht, The Netherlands (2000).
- 80 Fang Z, Fang C. Complete dissolution and hydrolysis of wood in hot water. *AIChE J.* 54(10), 2751–2758 (2008).
- 81 Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* 91, 87–102 (2003).
- 82 Hatcher PG, Clifford DJ. The organic geochemistry of coal: from plant materials to coal. *Org. Geochem.* 27, 251–274 (1997).
- 83 Hashaikh R, Fang Z, Butler IS, Hawari J, Kozinski JA. Hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion. *Fuel.* 86(10–11), 1614–1622 (2007).
- 84 Funke A, Ziegler F. Hydrothermal carbonization of biomass: a literature survey focusing on its technical application and prospects. Presented at: *17th European Biomass Conference and Exhibition.* Hamburg, Germany, 1037–1050 (2009).
- 85 Bergius F. [*Die Anwendung hoher Drücke bei chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle.*] Wilhelm Knapp, Halle a. d. Saale, 41–58 (1913).
- 86 Schuhmacher JP, Huntjens FJ, van Krevelen DW. Chemical structure and properties of coal XXVI – studies on artificial coalification. *Fuel* 39, 223–234 (1960).
- 87 Sugimoto Y, Miki Y. Chemical structure of artificial coals obtained from cellulose, wood and peat. *Proceedings of the 9th International Conference on Coal Science ICCS '97.* Ziegler A, van Heek KH, Klein J, Wanzl W (Eds). 1, 187–190 (1997).
- 88 van Krevelen DW. *Coal: Typology – Physics – Chemistry – Constitution (3rd Edition).* Elsevier, Amsterdam 837–846 (1993).
- 89 Friedl A, Padouvas E, Rotter H, Varmuza K. Prediction of heating values of biomass fuel from elemental composition. *Anal. Chim. Acta.* 544, 191–198 (2005).
- 90 Crelling JC, Hagemann HW, Sauter DH *et al.* Coal. In: *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley VCH, Weinheim, Germany 5–6 (2006).
- 91 Oden S, Unnerstad A. Über die Nassverkohlung des Torfes. *Brennstoff-Chemie.* 5, 249–253 (1924).
- 92 Sun X, Li Y. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. *Angew. Chem. Int. Ed.* 43, 597–601 (2004).
- 93 Cui X, Antonietti M, Yu S. Structural effects of iron oxide nanoparticles and iron ions on the hydrothermal carbonization of starch and rice carbohydrates. *Small* 2, 756–759 (2006).
- 94 Yao C, Shin Y, Wang L *et al.* Hydrothermal dehydration of aqueous fructose solutions in a closed system. *J. Phys. Chem. C* 111, 15141–15145 (2007).
- 95 Sevilla M, Fuertes A. Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chem-Eur. J.* 15(16), 4195–4203 (2009).
- 96 Baccile N, Laurent G, Babonneau F *et al.* Structural characterization of hydrothermal carbon spheres by advanced solid-state MAS ¹³C NMR investigations. *J. Phys. Chem.* 113, 9644–9654 (2009).
- 97 Shafizadeh F. Introduction to pyrolysis of biomass. *J. Anal. Appl. Pyrolysis.* 3, 283–305 (1982).
- 98 Siskin M, Katritzky AK. Reactivity of organic compounds in hot water: geochemical and technological implications. *Science* 254, 231–237 (1991).
- 99 100 Yu Y, Lou X, Wu HW. Some recent advances in hydrolysis of biomass in hot-compressed, water and its comparisons with other hydrolysis methods. *Energ. Fuel.* 22(1), 46–60 (2008).
- 100 Lichtenthaler FW. Towards improving the utility of ketoses as organic raw materials. *Carbohydr. Res.* 313, 69–89 (1998).
- 101 Kabyemela BM, Adschiri T, Malaluan RM, Arai K. Glucose and fructose decomposition in subcritical and supercritical water: detailed reaction pathway, mechanisms, and kinetics. *Ind. Eng. Chem. Res.* 38, 2888–2895 (1999).

- 102 Titirici MM, Antonietti A, Baccile N. Hydrothermal carbon from biomass: a comparison of the local structure from poly- to monosaccharides and pentoses/hexoses. *Green Chem.* 10, 1204–1212 (2008).
- 103 Kuster BFM. 5-hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch/Staerke.* 42, 314–321 (1990).
- 104 Lewkowski J. Synthesis, chemistry and applications of 5-hydroxymethylfurfural and its derivatives. *Arkiwoc.* 17–54 (2001).
- 105 Karayildirim T, Sinag A, Kruse A. Char and coke formation as unwanted side reaction of the hydrothermal biomass gasification. *Chem. Eng. Technol.* 31, 1561–1568 (2008).
- 106 Titirici MM, Thomas A, Yu S, Müller J, Antonietti M. A direct synthesis of mesoporous carbons with bicontinuous pore morphology from crude plant material by hydrothermal carbonization. *Chem. Mater.* 19, 4205–4212 (2007).
- 107 Masselter S, Zemann A, Bobleter O. Analysis of lignin degradation products by capillary electrophoresis. *Chromatographia* 40, 51–57 (1995).
- 108 Evans RJ, Milne TA. Molecular characterization of the pyrolysis of biomass. 1. Fundamentals. *Energ. Fuel.* 1, 123–137 (1987).
- 109 Antal MJ, Croiset E, Dai X et al. High-yield biomass charcoal. *Energ. Fuel* 10, 652–658 (1996).
- 110 Monthieux M, Landais P, Monin J. Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia. *Org. Geochem.* 8, 275–292 (1985).
- 111 Gaunt JL, Lehmann J. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Technol.* 42(11), 4152–4158 (2008).
- 112 Roberts KG, Gloy BA, Joseph S, Scott NR, Lehmann J. Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. *Environ. Sci. Technol.* 44(2), 827–833 (2010).
- 113 Klason P, von Heidenstam G, Norlin E. Untersuchungen zur Holzverkohlung. *Angew. Chem. Int. Ed.* 25, 1205–1214 (1909).
- 114 Geissler C, Belau L. [Zum Verhalten der stabilen Kohlenstoffisotope bei der Inkohlung.] *Z. Angew. Chem.* 17, 13–17 (1971).
- 115 Häggglund, SE. *Vatkolning av Torv.* AB Svensk Torvförädling, Lund. (1960).
- 116 Prins MJ. Thermodynamic analysis of biomass gasification and torrefaction Eindhoven: Technische Universiteit Eindhoven (2005).
- 117 Mok WSL, Antal MJ. Effects of pressure on biomass pyrolysis. II. Heats of reaction of cellulose pyrolysis. *Thermochim. Acta* 68, 165–186 (1983).
- 118 Kunihisa KS, Ogawa H. Acid hydrolysis of cellulose in a differential scanning calorimeter. *J. Thermal. Anal.* 30, 49–59 (1985).
- 119 Erlach B, Tsatsaronis G. Upgrading of biomass by hydrothermal carbonisation: analysis of an industrial-scale plant design. Presented at: *The 23rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems.* Lausanne, Switzerland, 14–17 June 2010.
- 120 Sehn W, Gerber H. Pyrolyse mit flammenloser oxidation kombinieren. *BWK – Das Energie-Fachmagazin.* 10, 22–26 (2007).
- 121 Mursito AT, Hirajima T, Sasaki K. Upgrading and dewatering of raw tropical peat by hydrothermal treatment. *Fuel* 89(3), 635–641 (2010).
- 122 Bridgwater AV, Toft AJ, Brammer JG. A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion. *Renew. Sus. Energ. Rev.* 6(3), 181–246 (2002).
- 123 Fischer Z, Bienkowski P. Some remarks about the effect of smoke from charcoal kilns on soil degradation. *Environ. Monit. Assess.* 58, 349–358 (1999).
- 124 Berger S. Entwicklung und technische Umsetzung der Mechanisch/Thermischen Entwässerung zum Einsatz als Vortrocknungsstufe in braunkohlegefeuerten Kraftwerken. Shaker Verlag: Aachen (2001).
- 125 Myreen B. PDF – new peat technology. *Energ. Digest.* 11, 14–18 (1982).
- 126 Lehmann J. A handful of carbon. *Nature* 447(7141), 143–144 (2007).
- 127 Hammes K, Schmidt MWI, Smernik RJ et al. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochem. Cycles* 21, GB3016 (2007).
- 128 Tsukashima H. The infrared spectra of artificial coal made from submerged wood at Uozu, Toyama Prefecture, Japan. *Bull. Chem. Soc. Jpn.* 39(3), 460–465 (1966).
- 129 Agblevor FA, Beis S, Kim SS, Tarrant R, Mante NO. Biocrude oils from the fast pyrolysis of poultry litter and hardwood. *Waste Manag.* 30(2), 298–307 (2010).
- Describes the pyrolysis of poultry litter that includes measurements of important char characteristics.
- 130 Zheng J, Jin Y, Chi Y et al. Pyrolysis characteristics of organic components of municipal solid waste at high heating rates. *Waste Manag.* 29(3), 1089–1094 (2009).
- 131 Chan KY, Xu ZH. Biochar – nutrient properties and their enhancement. In: *Biochar for Environmental Management: Science and Technology.* Lehmann J, Joseph S (Eds). Earthscan, London, UK, 67–84 (2009).
- 132 Kim S, Agblevor FA, Lim J. Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *J. Ind. Eng. Chem.* 15(2), 247–252 (2009).
- 133 Hossain M, Strezov V, Chan K, Nelson P. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere* 78(9), 1167–1171 (2010).
- 134 Shinogi Y. Nutrient leaching from carbon products of sludge. *ASAE/CSAE Annual International Meeting.* Ottawa, ON, Canada, Paper Number 044063 (2004).
- 135 Fuertes A, Arbestain M, Sevilla M et al. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. *Aust. J. Soil Res.* 48(7), 618–626 (2010).
- 136 Knicker H. How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochemistry* 85(1), 91–118 (2007).
- 137 Shinogi Y, Kanri Y. Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. *Bioresour. Technol.* 90(3), 241–247 (2003).
- 138 Wild T. Demineralisierung und mechanisch/thermische Entwässerung von Braunkohlen und Biobrennstoffen. Shaker Verlag: Aachen (2006).
- 139 Koutcheiko S, Monreal C, Kodama H, McCracken T, Kotlyar L. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresour. Technol.* 98(13), 2459–2464 (2007).
- 140 McIntyre A, Papic M. Pyrolysis of municipal solid waste. *Can. J. Chem. Eng.* 52, 263–272 (1974).

- 141 Vassilev SV, Braekman-Danheux C. Characterization of refuse-derived char from municipal solid waste – 2. Occurrence, abundance and source of trace elements. *Fuel Process. Technol.* 59(2–3), 135–161 (1999).
- Describes the dry pyrolysis of municipal solid waste that includes detailed analysis of trace elements (e.g., metals) found in the char and compares them to coal samples.
- 142 German Federal Law on Soil Protection (BBodSchG), Law for the protection against harmful structural changes of the soil and for the remediation of contaminated land as of 03/17/98, last amended through article 3 G as of 12/09/04. *Federal Law Gazette* 3214 (2004).
- 143 Hwang IH, Matsuo T, Tanaka N, Sasaki Y, Tanaami K. Characterization of char derived from various types of solid wastes from the standpoint of fuel recovery and pretreatment before landfilling. *Waste Manage.* 27(9), 1155–1166 (2007).
- 144 Lutz H, Romeiro GA, Damasceno RN, Kutubuddin M, Bayer E. Low temperature conversion of some Brazilian municipal and industrial sludges. *Bioresour. Technol.* 74(2), 103–107 (2000).
- 145 Garcia-Perez M. *The formation of polyaromatic hydrocarbons and dioxins during pyrolysis*. Report WSUEEP08-010. Washington State University, WA, USA (2008).
- 146 McLaughlin H, Anderson PS, Shields FE, Reed TB. All biochars are not created equal and how to tell them apart. Presented at: *North American Biochars Conference*. Boulder, CO, USA, 9–12 August 2009.
- 147 Joseph S, Peacocke C, Lehmann J, Munroe P. Developing a Biochar classification and test methods. In: *Biochar for Environmental Management – Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 107–126 (2009).
- 148 Okimori Y, Ogawa M, Takahashi F. Potential of CO₂ emission reductions by carbonizing biomass waste from industrial tree plantation in South Sumatra, Indonesia. *Mitig. Adapt. Strateg. Glob. Change.* 8(3), 261–280 (2003).
- 149 IPCC. *Climate Change 2007 – The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC*. Cambridge University Press, Cambridge, UK (2007).
- 150 Schmidt MWI, Skjemstad JO, Gehrt E, Kögel-Knabner I. Charred organic carbon in German chernozemic soils. *Europ. J. Soil Sci.* 50(2), 351–365 (1999).
- 151 Lehmann J, Skjemstad J, Sohi S *et al.* Australian climate-carbon cycle feedback reduced by soil black carbon. *Nature Geosci.* 1(12), 832–835 (2008).
- 152 Neves EG, Petersen JB, Bartone RN, Silva CAD. Historical and socio-cultural origins of Amazonian Dark Earths. In: *Amazonian Dark Earths: Origin, Properties, Management*. Lehmann J, Kern DC, Glaser B, Woods WI (Eds). Kluwer Academic Publishers, Dordrecht, The Netherlands, 29–50 (2003).
- 153 Glaser B, Lehmann J, Zech W. Ameliorating physical and chemical properties of highly weathered soils in the Tropics with charcoal – a review. *Biol. Fertil. Soils.* 35, 219–230 (2002).
- 154 Cheng C, Lehmann J, Thies JE, Burton SD. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* 113(G02027), DOI:10.1029/2007JG000642 (2008) (Epub).
- 155 Nguyen B, Lehmann J, Kinyangi J *et al.* Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89(3), 295–308 (2008).
- 156 Hammes K, Schmidt M. Changes of biochar in soil. In: *Biochar for Environmental Management – Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 169–181 (2009).
- 157 Cao X, Ro KS, Chappell M, Li Y, Mao J. Chemical structure of swine-manure chars with different carbonization conditions using advanced solid-state ¹³C NMR spectroscopy. In Print. *Energ. Fuel* (2011).
- 158 Steinbeiss S, Gleixner G, Antonietti M. Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol. Biochem.* 41(6), 1301–1310 (2009).
- Only available laboratory study on hydrochar stability to date.
- 159 Cheng C, Lehmann J, Thies JE, Burton AJ, Engelhard M. Oxidation of black carbon by biotic and abiotic processes. *Organic Geochem.* 37, 1477–1488 (2006).
- 160 Cheng C, Lehmann J. Ageing of black carbon along a temperature gradient. *Chemosphere* 75(8), 1021–1027 (2009).
- 161 Brodowski S, John B, Flessa H, Amelung W. Aggregate-occluded black carbon in soil. *Europ. J. Soil Sci.* 57(4), 539–546 (2006).
- 162 Wengel M, Kothe E, Schmidt CM, Heide K, Gleixner G. Degradation of organic matter from black shales and charcoal by the wood-rotting fungus *Schizophyllum commune* and release of DOC and heavy metals in the aqueous phase. *Sci. Total Environ.* 367(1), 383–393 (2006).
- 163 Czimczik CI, Masiello CA. Controls on black carbon storage in soils. *Global Biogeochem. Cycles.* 21(3), GB3005 (2007).
- 164 Nguyen BT, Lehmann J. Black carbon decomposition under varying water regimes. *Organic Geochem.* 40(8), 846–853 (2009).
- 165 Major J, Lehmann J, Rondon M, Goodale C. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biol.* 16(4), 1366–1379 (2010).
- 166 Wardle DA, Nilsson M, Zackrisson O. Fire-derived charcoal causes loss of forest humus. *Science* 320(5876), 629 (2008).
- 167 Warnock D, Lehmann J, Kuyper T, Rillig M. Mycorrhizal responses to biochar in soil – concepts and mechanisms. *PlantSoil* 300(1), 9–20 (2007).
- 168 Wright S, Upadhyaya A. A survey of soils for aggregate stability and glomalin, a glycoprotein produced by hyphae of arbuscular mycorrhizal fungi. *PlantSoil* 198(1), 97–107 (1998).
- 169 Rillig M, Caldwell B, Wösten H, Sollins P. Role of proteins in soil carbon and nitrogen storage: controls on persistence. *Biogeochemistry* 85(1), 25–44 (2007).
- 170 Oguntunde PG, Abiodun BJ, Ajayi AE, van de Giesen N. Effects of charcoal production on soil physical properties in Ghana. *J. Plant Nutr. Soil Sci.* 171(4), 591–596 (2008).
- 171 Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph S. Agronomic values of greenwaste biochar as a soil amendment. *Austr. J. Soil Res.* 45(8), 629–634 (2007).
- 172 Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph S. Using poultry litter biochars as soil amendments. *Austr. J. Soil Res.* 46(5), 437–444 (2008).
- 173 Liang B, Lehmann J, Solomon D *et al.* Black carbon increases cation exchange capacity in soils. *SSSAJ* 70, 1719–1730 (2006).
- 174 Steiner C, Glaser B, Teixeira WG *et al.* Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *J. Plant Nutr. Soil Sci.* 171(6), 893–899 (2008).
- 175 Kolb SE, Fermanich KJ, Dornbush ME. Effect of charcoal quantity on microbial biomass and activity in temperate soils. *SSSAJ* 73(4), 1173–1181 (2009).
- 176 Thies J, Rillig MC. Characteristics of biochar: biological properties. In: *Biochar for Environmental Management: Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 85–105 (2009).

- 177 Rondon M, Lehmann J, Ramírez J, Hurtado M. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biol. Fertil. Soils* 43(6), 699–708 (2007).
- 178 Major J, Husk B. *Commercial scale agricultural biochar field trial in Québec, Canada, over two years: Effects of biochar on soil fertility, biology, crop productivity and quality*. Experimental Report, BlueLeaf Inc., QC, USA 1–38 (2010).
- 179 van Zwieten L, Kimber S, Morris S et al. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil* 327(1), 235–246 (2010).
- 180 Kammann C. Zwischenbericht zum Stand der Arbeiten im Projekt “Risikobewertung des Einsatzes von Biokohle in temperaten Böden - ein Weg zur dauerhaften C-Sequestrierung?” Environment and Geology, Germany. 1–26 (2010).
- 181 Steiner C, Teixeira M, Zech W. Soil respiration curves as soil fertility indicators in perennial central Amazonian plantations treated with charcoal, and mineral or organic fertilisers. *Tropical Sci.* 47(4), 218–230 (2007).
- 182 van Zwieten L, Singh B, Joseph S et al. Biochar and emissions of non-CO₂ greenhouse gases from soil. In: *Biochar for Environmental Management – Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 227–249 (2009).
- Provides the most extended actual overview over GHG-flux changes with biochar addition, and theoretical considerations regarding why and how they may change with biochar application.
- 183 Blackwell P, Riethmuller G, Collins M. Biochar application to soil. In: *Biochar for Environmental Management: Science and Technology*. Lehmann J, Joseph S (Eds). Earthscan, London, UK, 207–226 (2009).
- Provides a comprehensive overview concerning the current knowledge on biochar effects in agriculture and associated challenges.
- 184 Kimetu J, Lehmann J, Ngoze S et al. Reversibility of soil productivity decline with organic matter of differing quality along a degradation gradient. *Ecosystems* 11(5), 726–739 (2008).
- 185 Gaskin JW, Speir RA, Harris K et al. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. *Agron. J.* 102(2), 623–633 (2010).
- 186 Oguntunde PG, Fosu M, Ajayi AE, Giesen N. Effects of charcoal production on maize yield, chemical properties and texture of soil. *Biol. Fertil. Soils.* 39(4), 295–299 (2004).
- 187 Novak J, Busscher W, Watts D et al. Short-term CO₂ mineralization after additions of biochar and switchgrass to a Typic Kandiuult. *Geoderma.* 154(3–4), 281–288 (2010).
- 188 Cao X, Harris W. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Biores. Technol.* 101(14), 5222–5228 (2010).
- 189 Lal R. Soil carbon sequestration impacts on global climate change and food security. *Science* 304(5677), 1623–1627 (2004).
- 190 Firestone MK, Davidson EA, Andreae MO, Schimel DS. Microbiological basis of NO and N₂O production and consumption in soil. In: *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. John Wiley & Sons Ltd., Chichester, UK, 7–21 (1989).
- 191 Granli T, Bøckmann OC. Nitrous oxide from agriculture. *Norwegian Journal of Agricultural Sciences.* Suppl 12, 1–128 (1994).
- 192 Crutzen PJ, Mosier AR, Smith KA, Winiwarter W. N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Physics* 8, 389–395 (2007).
- 193 Kammann C, Müller C, Grünhage L, Jäger H. Elevated CO₂ stimulates N₂O emissions in permanent grassland. *Soil Biol. Biochem.* 40(9), 2194–2205 (2008).
- 194 Kammann C, Ryan M, Ratering S et al. Treibhausgas-Emissionen (CO₂, N₂O, CH₄) nach Biochar-Applikation (poster presentation). Presented at: *Aktiver Klimaschutz und Anpassungsstrategien an den Klimawandel – Beiträge der Agrar – und Forstwirtschaft*. Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (BEMLV) and Johann Heinrich von Thünen Institute (vTI), Volkswagenhalle Braunschweig, 128 (2009).
- 195 Šimek M, Cooper J. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Europ. J. Soil Sci.* 53, 345–354 (2002).
- 196 Clough TJ, Kelliher FM, Sherlock RR, Ford CD. Lime and soil moisture effects on nitrous oxide emissions from a urine patch. *SSSAJ* 68, 1600–1609 (2004).
- 197 Yanai Y, Toyota K, Okazaki M. Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* 53(2), 181–188 (2007).
- 198 Smith MS, Tiedje JM. The effect of roots on soil denitrification 1. *SSSAJ.* 43(5), 951–955 (1979).
- 199 Klemmedtsen L, Svensson BH, Rosswall T. Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants. *Plant Soil.* 99, 303–319 (1987).
- 200 Mosier AR, Duxbury JM, Freney JR, Heinemeyer O, Minami K. Nitrous oxide emissions from agricultural fields: assessment, measurement and mitigation. *Plant Soil* 181, 95–108 (1997).
- 201 Conrad R. Microbial ecology of methanogens and methanotrophs. In: *Adv. Agronomy* 96, 1–63 (2007).
- 202 Powlson DS, Goulding KWT, Willison TW, Webster CP, Hütsch BW. The effect of agriculture on methane oxidation in soil. *Nutrient Cyc. Agroecosys.* 49(1–3), 59–70 (1997).
- 203 Bradford MA, Ineson P, Wookey PA, Lappin-Scott HM. Soil CH₄ oxidation: response to forest clearcutting and thinning. *Soil Biol. Biochem.* 32(7), 1035–1038 (2000).
- 204 Veldkamp E, Weitz AM, Keller M. Management effects on methane fluxes in humid tropical pasture soils. *Soil Biol. Biochem.* 33(11), 1493–1499 (2001).
- 205 Rondon M, Ramirez JA, Lehmann J. Charcoal additions reduce net emissions of greenhouse gases to the atmosphere. In: *Proceedings of the 3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration in Agriculture and Forestry*. University of Delaware, Baltimore, MD, USA, 21–24 March 2005.
- 206 Priem A, Christensen S. Methane uptake by a selection of soils in Ghana with different land use. *J. Geophys. Res.* 104(D19), 23617–23622 (1999).
- 207 Castro MS, Mellilo JM, Steudler PA, Chapman JW. Soil moisture as a predictor of methane uptake by temperate forest soils. *Can. J. Forest Res.* 24, 1805–1810 (1994).
- 208 Clough T, Bertram JE, Ray JL et al. Unweathered wood biochar impact on nitrous oxide emissions from a bovine-urine-amended pasture soil. *SSSAJ* 74, 852–860 (2010).
- 209 Spokas K, Koskinen W, Baker J, Reicosky D. Impacts of woodchip biochar additions on greenhouse gas production and sorption/ degradation of two herbicides in a Minnesota soil. *Chemosphere* 77(4), 574–581 (2009).
- 210 Singh BP, Hatton BJ, Singh B, Cowie AL, Kathuria A. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* 39(4), 1224 (2010).

- 211 van Zwieten L, Kimber S, Morris S *et al.* Influence of biochars on flux of N₂O and CO₂ from Ferrosol. *Aust. J. Soil Res.* 48(7), 555–568 (2010).
- 212 Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.* 97(1–3), 219–243 (2003).
- 213 Mohan D, Pittman J. Arsenic removal from water/wastewater using adsorbents – a critical review. *J. Hazard. Mater.* 142(1–2), 1–53 (2007).
- 214 Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol.* 97(9), 1061–1085 (2006).
- 215 Radovic LR. *Chemistry and Physics of Carbon*. CRC Press, USA (2004).
- 216 Lu GQ, Lau DD. Characterisation of sewage sludge-derived adsorbents for H₂S removal. Part 2: surface and pore structural evolution in chemical activation. *Gas Sep. Purif.* 10(2), 103–111 (1996).
- 217 Kadirvelu K, Kavipriya M, Karthika C *et al.* Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour. Technol.* 87(1), 129–132 (2003).
- 218 Bagreev A, Bandosz T. Efficient hydrogen sulfide adsorbents obtained by pyrolysis of sewage sludge derived fertilizer modified with spent mineral oil. *Environ. Sci. Technol.* 38, 345–351 (2004).
- 219 Cao X, Ma L, Cao B, Harris W. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* 43(9), 3285–3291 (2009).
- 220 Ramakrishnan M, Nagarajan S. Utilization of waste biomass for the removal of basic dye from water. *World Appl. Sci. J.* 5, 114–120 (2009).
- 221 Cheng F, Llang J, Zhao J, Tao Z, Chen J. Biomass waste-derived microporous carbons with controlled texture and enhanced hydrogen uptake. *Chem. Mater.* 20, 1889–1895 (2008).
- 222 Budinova T, Savova D, Tsyntsarski B *et al.* Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions. *Appl. Surf. Sci.* 255, 4650–4657 (2009).
- 223 Gokee C, Guneyssu S, Aydin S, Arayici S. Comparison of activated carbon and pyrolyzed biomass for removal of humic acid from aqueous solution. *Open Environ. Pollut. Toxicol. J.* 1, 43–48 (2009).
- 224 Mohan D, Singh K. Single- and multi-component adsorption of cadmium and zinc activated carbon derived from bagasse – an agricultural waste. *Water Res.* 36, 2304–2318 (2002).
- 225 Demir-Cakan R, Baccile N, Antonietti M, Titirici M. Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid. *Chem. Mater.* 21(3), 484–490 (2009).
- 226 Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments.* 54, 47–58 (2002).
- 227 Lima I, Marshall W. Granular activated carbons from broiler manure: physical, chemical and adsorptive properties. *Bioresour. Technol.* 96, 699–706 (2005).
- 228 Chiang P, You J. Use of sewage sludge for manufacturing adsorbents. *Canadian J. Chem. Eng.* 65(6), 922–927 (1987).
- 229 Qian Q, Machida M, Tatsumoto H. Preparation of activated carbons from cattle-manure compost by zinc chloride activation. *Bioresour. Technol.* 98, 353–360 (2007).
- 230 Mochidzuki K, Sato N, Sakoda A. Production and characterization of carbonaceous adsorbents from biomass wastes by aqueous phase carbonization. *Adsorption* 11, 669–673 (2005).
- 231 Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A. Understanding chemical reactions between carbons and NaOH and KOH – an insight into the chemical activation mechanism. *Carbon* 41, 267–275 (2003).
- 232 Titirici M, Antonietti M, Thomas A. A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach. *Chem. Mater.* 18(16), 3808–3812 (2006).
- 233 Lei Z, Li J, Ke Y *et al.* Two-step templating route to macroporous or hollow sphere oxides. *J. Mater. Chem.* 11(12), 2930–2933 (2001).
- 234 Wu B, Yuan R, Fu X. Structural characterization and photocatalytic activity of hollow binary ZrO₂/TiO₂ oxide fibers. *J. Solid State Chem.* 182(3), 560–565 (2009).
- 235 Schneider W, Diller W. Phosgene. In: *Ullmann's Encyclopedia of Industrial Chemistry (6th Edition)*. Wiley-VCH, Weinheim (2002).
- 236 *The Catalyst Technical Handbook – Be Selective*. Johnson Matthey Catalysts, NJ, USA (2005).
- 237 Serp P, Figueiredo JL. *Carbon Materials for Catalysis*. Wiley, NJ, USA (2008).
- 238 Du R, Zhu C, Zhang P, Fan R. Selective hydrogenation of aromatic aminoketones by Pd/C catalysis. *Synthetic Commun.* 38(17), 2889 (2008).
- 239 Amorim C, Yuan G, Patterson PM, Keane MA. Catalytic hydrodechlorination over Pd supported on amorphous and structured carbon. *J. Catal.* 234(2), 268–281 (2005).
- 240 Makowski P, Cakan RD, Antonietti M, Goettmann F, Titirici M. Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon. *Chem. Commun.* 8, 999–1001 (2008).
- 241 Matos J, Laine J, Herrmann J. Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon. *Applied Catalysis B: Environmental.* 18(3–4), 281–291 (1998).
- 242 Mozia S, Toyoda M, Inagaki M, Tryba B, Morawski AW. Application of carbon-coated TiO₂ for decomposition of methylene blue in a photocatalytic membrane reactor. *J. Hazard. Mater.* 140(1–2), 369–375 (2007).
- 243 Gottschalk C, Libra JA, Saupe A. *Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and Its Applications*. Wiley-VCH, Weinheim (2010).
- 244 Zhao L, Chen X, Wang X, *et al.* One-step solvothermal synthesis of a carbon@TiO₂ dyade structure effectively promoting visible-light photocatalysis. *Adv. Mater.* 22(30), 3317–3321 (2010).
- 245 Lee KB, Beaver MG, Caram HS, Sircar S. Reversible chemisorbents for carbon dioxide and their potential applications. *Ind. Eng. Chem. Res.* 47(21), 8048–8062 (2008).
- 246 Day D, Evans R, Lee J, Reicosky D. Economical CO₂, SO_x, and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. *Energy* 30(14), 2558–2579 (2005).
- 247 Zhao L, Baccile N, Gross S *et al.* Sustainable nitrogen-doped carbonaceous materials from biomass derivatives. *Carbon* 48(13), 3778–3787 (2010).
- 248 White RJ, Antonietti M, Titirici M. Naturally inspired nitrogen doped porous carbon. *J. Mater. Chem.* 19(45), 8645–8650 (2009).
- 249 Zhao L, Bacsik Z, Hedin N *et al.* Carbon dioxide capture on amine-rich carbonaceous materials derived from glucose. *ChemSusChem.* 3(7), 840–845 (2010).

- 250 Ströbel R, Garche J, Moseley P, Jörissen L, Wolf G. Hydrogen storage by carbon materials. *J. Power Sources*. 159(2), 781–801 (2006).
- 251 Antolini E. Formation, microstructural characteristics and stability of carbon supported platinum catalysts for low temperature fuel cells. *J. Mater. Sci.* 38(14), 2995–3005 (2003).
- 252 Paraknowitsch JP, Thomas A, Antonietti M. Carbon colloids prepared by hydrothermal carbonization as efficient fuel for indirect carbon fuel cells. *Chem. Mater.* 21(7), 1170–1172 (2009).
- 253 Murugan AV, Muraliganth T, Manthiram A. One-pot microwave-hydrothermal synthesis and characterization of carbon-coated LiMPO[sub 4] (M = Mn, Fe, and Co) Cathodes. *J. Electrochem. Soc.* 156(2), A79–A83 (2009).
- 254 Béguin F, Frackowiak E. Electrochemical Energy Storage. In: *Adsorption by Carbons*. Bottani E, Tascon J (Eds). Elsevier, Amsterdam, 593–629 (2008).
- 255 Béguin F, Frackowiak E. *Carbons for Electrochemical Energy Storage and Conversion Systems (1st Edition)*. CRC Press, USA (2009).
- 256 Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* 39(6), 937–950 (2001).
- 257 Pandolfo A, Hollenkamp A. Carbon properties and their role in supercapacitors. *J. Power Sources*. 157(1), 11–27 (2006).
- 258 Scrosati B, Garche J. Lithium batteries: Status, prospects and future. *J. Power Sources*. 195(9), 2419–2430 (2010).
- 259 Demir CR, Titirici M, Antonietti M et al. Hydrothermal carbon spheres containing silicon nanoparticles: synthesis and lithium storage performance. *Chem. Commun. (Camb.)*. (32), 3759–3761 (2008).
- 260 Demir Cakan R, Titirici M, Antonietti M et al. Hydrothermal carbon spheres containing silicon nanoparticles: synthesis and lithium storage performance. *Chem. Commun. (Camb.)*. (32), 3759–3761 (2008).
- 261 US EPA. *A Plain English Guide to the EPA Part 503 Biosolids Rule*. EPA/832/R-93/003. US EPA, Office of Wastewater Management, DC, USA (1994). Available at: www.epa.gov/owm/mtb/biosolids/503pe
- 262 US EPA. Decision-Maker's Guide to Solid Waste Management, Second Edition. US EPA, Municipal and Industrial Solid Waste Division, DC, USA (1995). Available at: www.p2pays.org/ref/03/02021/02021.pdf
- 263 German Fertiliser Law (DüV), Law about the application of fertilisers, soil additives, growing media and plant additives in accordance to good practice as of 1/10/06, last amended through article 18 G as of 7/31/09. *Federal Law Gazette* 2585 (2009).
- 264 German Fertiliser Ordinance (DüMV), Ordinance about the placing of fertilisers, soil additives, growing media and plant additives on the market. *Federal Law Gazette* 2524 (2008).
- 265 German Biowaste Ordinance (BioAbfV), Ordinance about the utilisation of biowastes on soils used in agriculture, forestry and gardening as of September 21, 1998, last amended through article 5 V as of 10/20/06. *Federal Law Gazette* 2298 (2006).
- 266 German Federal Ordinance on Soil Protection and Contaminated Land (BBodSchV) as of 07/12/19999, last amended through article 2 V as of 12/23/2004. *Federal Law Gazette* 3758 (2004).
- 267 German Federal Sewage Sludge Ordinance (AbfKlärV) as of 4/15/1992, last amended through article 19 as of 7/29/09. *Federal Law Gazette* 2542 (1992).
- **Websites**
- 301 US Energy Information Administration. World Carbon Dioxide Emissions from the Consumption and Flaring of Fossil Fuels (Million Metric Tons of Carbon Dioxide), 1980–2006 (2008). www.eia.doe.gov/pub/international/ieal
- 302 International Biochar Initiative (IBI). Frequently Asked Questions about Biochar. www.biochar-international.org/biochar/faqs (Accessed 15 October 2010)
- 303 Reichenbach J. ISTEAC StudyReport: Collection and Composition of Source Separated Biowaste in Different Settings in Germany 2005. www.wadef.com/projects/isteac/StudyReport__Biowaste_Separation_Effects.Work_Results.pdf (Accessed 15 October 2010)
- 304 Barker J, Zublena JP, Walls FR. *Animal and Poultry Manure: Production & Characterization*. North Carolina A&T State University Cooperative Extension 2001. www.bae.ncsu.edu/programs/extension/manure/awm/program/barker/a&pmp&c/cover_page_apmp&c.html
- 305 USEPA. Background Document for the Final Comprehensive Procurement Guideline (CPG) IV and Final recovered Materials Advisory Notice (RMAN) IV 2004. www.epa.gov/wastes/conserve/tools/cpg/pdf/cpg4final_docket.pdf (Accessed 15 October 2010)
- 306 Granatstein C, Kruger C, Collins H, Galinato S, Garcia-Perez M, Yoder J. Use of Biochar from the Pyrolysis of Waste Organic Material as a Soil Amendment 2009. http://afrsweb.usda.gov/research/publications/publications.htm?seq_no_115=245778 (Accessed 15 October 2010).
- 307 International Biochar Initiative. Draft Guidelines for a Safe Biochar Industry 2009. http://cees.colorado.edu/docs/characterization/IBI%20Working%20Draft%20Characterisation_Draft_V9_Charaterization_Paper_NABC2009.doc (Accessed 15 October 2010).
- 308 EPA. Compost Use on State Highway Applications. Composting Council Research and Education Foundation and US Composting Council. www.epa.gov/osw/conserve/rrr/composting/highway
- 309 CalRecycle. Compost Quality Standards 2004. www.calrecycle.ca.gov/organics/products/Quality/CQStandards.htm (Accessed 15 October 2010)
- 310 Ohio Administrative Code. Chapter 3745–3727 Solid Waste and Infectious Waste Regulations. <http://codes.ohio.gov/oac/3745–3727–46>.