

Review

Actual Trends in the Usability of Biochar as a High-Value Product of Biomass Obtained through Pyrolysis

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Abstract: This review comprehensively examines biochar, an essential material in an era of climate change for reducing carbon dioxide (CO₂) emissions into the atmosphere. It is inconspicuous, black, lightweight, and very porous, and is produced through the thermal conversion of biomass. Our literature review highlights biochar's expansive application possibilities. Firstly, its potential to improve soil quality and sequester CO₂ has been examined, as well as its utilization in iron and steel manufacturing to minimize the quantity of coke and ultimately reduce CO₂ emissions. In industrial manufacturing, the complete elimination of coke can promote environmental neutrality, which is achieved using biochar from biomass for its extrusion. Furthermore, biochar is becoming increasingly significant in modern energy storage technologies and as an important additive in Pickering emulsions, which are also employed in energy storage systems. Additionally, the use of carbon black is a broad topic, and this review illustrates where it can be successfully utilized, especially in environmentally sensitive areas.

Keywords: biochar; bio-coke; CO₂ sequestration; soil improvement; energy storage; Pickering emulsion



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1. Introduction

Pyrolysis is a well-known commercial technique for the production of charcoal from wood. However, this process is rather limited, as pyrolysis involves the conversion of any low-energy dense biomass into bio-oils (high-energy dense liquid), syngas (low-energy dense gas), and biochar (carbon-rich high-energy-dense solid) [1]. Pyrolysis conditions can be optimized to promote the synthesis of a given product, with slow pyrolysis at lower temperatures preferring higher charcoal yields and fast pyrolysis at higher temperatures favoring syngas production [2]. Charcoal and biochar are unique as they are created for an intended purpose rather than a composition or manufacturing process; charcoal is generated only for use as a fuel source, whereas biochar is produced primarily for non-fuel source uses [2,3]. Biochar has been used as a low-yield activated carbon, for the filtration of pollutants from wastewater and landfill leachate, for carbon sequestration, as a direct fuel source, in soil application for nutrient retention, to improve crop productivity, soil application for improved water holding capacity, reduce soil emissions, and improve soil cation exchange capacity [2,3].

Many factors influence the properties of biochar generated by the pyrolysis of biomass, including temperature, heating rate, feedstock type and content, particle size, and reactor parameters [2]. Biochar is comprised of all non-combustible ingredients of the feedstock (ash) and, thus, it is present after pyrolysis and gasification processes, while being independent of process temperature or feedstock. Biochar yield favors slow pyrolysis (300–700 °C) with heating rates ranging between 1–100 °C/s, and pyrolysis times varying from minutes to days [2,4,5]. Obviously, at high-temperatures biochar yield decreases. Additionally, biochar can be produced in other thermal biomass conversion processes such as torrefaction, hydrothermal carbonization (HTC), and in limited quantities during biomass gasification.

The ability to generate biochar via numerous processes and feedstocks, results in a plethora of chemical compositions and physical qualities. Investigations of biochar produced from a single feedstock revealed that the pyrolysis temperature, time, and oxygen exposure influence the quantity and quality of biochar produced. However, reports have shown that even though biochar production can be achieved via high-temperature pyrolysis, a lower carbon content product (of larger mass) is obtained during low-temperature pyrolysis. Hence, low- and high-temperature pyrolysis biochars have minimal differences in carbon sequestration [6].

As shown in Table 1, the carbon concentration of biochar can vary greatly depending on the feedstock used.

Table 1. Ultimate analysis of biochar from various biomass sources.

Biomass Type	Ultimate Analysis [wt%]									
	Carbon		Hydrogen		Oxygen		Nitrogen		Sulphur	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Agro-industrial residues	68.37	91.61	0.75	3.44	6.22	21.68	0.85	9.25	0.07	0.14
Grass	54.28	70.26	2.77	3.84	27.47	41.12	1.71	1.8	0.03	0.19
Olive husk and pit	69.95	94.39	0.53	5.62	4.31	18.77	0.39	2.59	0.04	0.04
Peanut shells	70.6	85.1	0.8	4.7	11.5	23.5	1	1.2	n/d	n/d
Straw	47.92	84.33	2.78	6.54	10	44.8	0.53	1.93	0.09	0.97
Wheat straw	73.05	88.11	2.28	3.85	8.05	22.03	0.72	1.45	0.11	0.13
Wood	64.55	92.99	0.7	6.13	2.99	23.89	0.01	3.1	0.02	1.01

Potassium (K) and chlorine (Cl) evaporate at relatively low pyrolysis temperatures, whereas calcium (Ca), silicon (Si), and magnesium (Mg) vaporize at higher temperatures. Regardless of pyrolysis temperature, the majority of feedstock phosphorus (P), sulphur (S), iron (Fe), and manganese (Mn) are present in the biochar product, as the dominant inorganic compounds [2]. Biochar nutritional contents are considerably greater when feedstocks are pyrolyzed at higher temperatures, albeit this is likely due to reduced biochar yields at higher temperatures. Nitrogen (N) concentrations, frequently decrease with increasing pyrolysis temperature, due to their liberation into the gaseous phase [7]. Therefore, a specific and desirable nutritional composition (N vs. P, K, Ca, and Mg) can be achieved by optimizing the pyrolysis temperature during biochar formation and selecting biomass material with higher concentrations of the above components.

Plant-derived feedstocks frequently yield biochar with reduced nutritional value due to N loss during the pyrolysis process and low nutrient values in the initial feedstock. Greater nutrient content in biochar is obtained from animal and human-generated feedstocks. However, previous studies have indicated that there are no statistically significant relationships between the nutrient content of the original feedstock and the generated biochar. As a result, the nutritional quality of biochar cannot be predicted from the starting material [5].

The pH of biochar varies greatly depending on the feedstock and pyrolysis type. According to the literature [7], biochar pH can range from 5.6 to 12.3 after the pyrolysis of hardwood feedstock at 700 °C, but in general, the majority of prepared biochar samples are alkaline (pH > 7.0). The relationship between pyrolysis temperature and biochar pH has been well established, in which elevated pyrolysis temperatures result in increased biochar alkalinity [8,9]. Increasing the pyrolysis temperature or exposure duration enhances the surface area and adsorption capacity of biochar [10]. Elimination of alkyl-CH₂, ester C=O, aromatic -CO, and phenolic -OH groups from aromatic carbons, as well as volatile organic matter at higher temperatures, enhances the micropore volume, and, hence, increases the surface area of biochar. This improves biochar's water-retention ability, soil nutrient retention, and microbial build-up. Although the pore structure of biochar generated from plant feedstocks has a better structure, biochar produced from manure feedstocks displays good fertilizer characteristics and heavy metal absorbability [2].

This variation in properties is caused by both the biomass type, and preparation conditions, and makes biochar highly adaptable. Furthermore, understanding the impact of biomass characteristics, as well as the circumstances and type of thermal conversion, on the properties of biochar allows control of certain properties and the development of materials for specific purposes. Biochar is currently being used in a variety of industries. Its application is no longer limited to the production of sorbents, but is expanding into completely new areas of science and industry. We chose to present selected directions for the use of biochar as a material for reducing CO₂ emissions due to the growing interest in the possibilities for the often novel use of biochar. This review article discusses the environmentally friendly applications of biochar such as CO₂ sequestration, agricultural use, energy storage, coking, and hydrothermal carbonization (HTC).

2. Application of Biochar

2.1. Biochar in CO₂ Sequestration and Soil Improvement

Biochar is produced by a pyrolysis process, and involves the heating of materials to temperatures above 300 °C, in the absence of oxygen. This procedure can be employed to transform biomass into a time-stable form of biochar that is generally resistant to the breakdown process [3]. Additionally, this enhances the stabilization of organic matter in the soil, where CO₂ is maintained for a longer period of time, and simultaneously provides numerous benefits associated with improved soil quality [11]. These benefits include greater water and, as a result, nutrient retention, and increased crop yields (Figure 1). Currently, the utilization of biochar for reducing or absorbing CO₂ emissions is uncommon, which is due to the high cost of pyrolysis equipment and its restricted availability. However, according to estimates provided by industry professionals, the rollout of biomass pyrolysis facilities on a wider scale has already begun and will continue to rise for the following ten years [12].

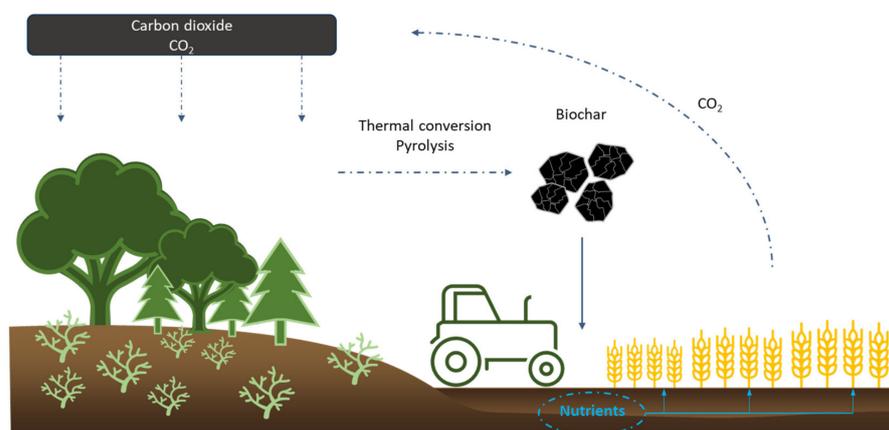


Figure 1. Utilization of biochar in CO₂ sequestration and soil improvement.

Reports have shown that the amount of CO₂ sequestered by one tonne of biochar can range from 2.1 to 4.8 Mg, depending on the life cycle of the biochar formed from a particular crop [13]. These estimates consider crop cultivation, biochar production by pyrolysis, carbon sequestration by biochar to enhance soil quality, and the generation of electricity by harnessing the energy emitted from the pyrolysis process. Biochar's porous nature makes it suitable for use in both large quantities and as a component of extended-release fertilizers [14]. Hence, in the case of fertilization, the quantity of biochar utilized per hectare can be reduced and determined based on fertilization needs. It is believed that biochar is a more stable substance than organic matter deposited in the soil, which should translate into a longer-term CO₂ accumulation rate. It is important to note that the rate of biochar decomposition in the soil varies depends on the raw material type employed for the pyrolysis process and temperature conditions. The availability of biomass in a specific region is another factor that determines biochar efficiency in terms of both the decrease and uptake of CO₂.

It is predicted that the amount of CO₂ that can be sequestered in the world's soils can be increased to 2–5 billion Mg of CO₂ (GtCO₂) every year by the year 2050, with a total potential of 104–130 GtCO₂ by the end of the century. More optimistic projections of sequestration rates can be found in the literature, with estimates of total potential ranging from 78 to 477 GtCO₂. Additionally, predictions of sequestration rates as high as 35 GtCO₂ each year have been presented [15,16].

The manufacturing of biochar necessitates the utilization of biomass in and of itself, which in turn requires land to first grow the feedstock and then storage of the generated biochar. However, due to issues regarding biomass cultivation for biochar production, such as competition for land, the use of waste biomass is essential. Additionally, owing to biochar's degradation rate in soil being slower than organic matter, it is possible to utilize it as a supplement in levels as low as 30 to 60 Mg/ha. Therefore, this approach is capable of exhibiting a significantly larger impact on soil carbon sequestration than biochar. Furthermore, in addition to biochar's capacity to sequester carbon, it is also possible to generate other forms of energy, such as electricity, during the manufacturing process. The energy output potential of biochar production is estimated as 5–14 GJ/Mg of CO₂ removed, assuming an energy content of 16.4–35.3 MJ/kg of raw material [17], and 10–20% of the energy costs and energy losses of pyrolysis facilities, respectively [18].

The amount of readily available biomass for biochar production plays a significant role in the potential of biochar as a material for the sequestration of CO₂. Nevertheless, small-scale and mobile biomass pyrolysis facilities may expand the applications of this approach and further lower costs. These potentials stem from the possibility of biochar being manufactured at the biomass waste production location, which helps minimize material transportation. According to reported studies, the expected costs of producing biochar range from 18 to 320 EUR/Mg of CO₂ [18]. The economic gains linked to the utilization of biochar may outweigh certain expenditures, but the fluctuation of this balance may depend on location.

Biochar can not only potentially affect soil carbon sequestration but also the modification of its physicochemical and biological aspects [19,20]. As previously stated, the type of biomass material employed for biochar generation, as well as the various processes and conditions under which it is produced, can result in a variety of qualities. The addition of biochar to the soil improves nutrient retention and increased plant growth [21]. This stems from biochar increasing the soil's pH, electric conductivity (EC), organic carbon (C), total nitrogen (TN), accessible phosphorus (P), and cation-exchange capacity (CEC) due to the presence of organic matter and nutrients [22]. It causes the soil becomes alkaline within properties. According to the literature [23], biochar application influences the toxicity, transport, and fate of several heavy metals in the soil due to the soil's increased absorption capacity. The availability of plant nutrients and ash provided by biochar, as well as its large surface area, porosity, and ability to act as a medium for microorganisms, are some of the

reasons biochar-treated soils have better soil properties and plant's ability to absorb more nutrients [24].

Biochar can play an important role in the establishment of a sustainable agricultural system owing to its ability to enhance soil quality. Several applications and positive impacts of biochar amendment have been evaluated as an effective approach to reclaim contaminated soil [25] and achieve high crop yields while minimizing environmental impact. The beneficial effect of biochar on plant development and soil quality shows that is an effective strategy to overcome nutrient deficits, making it an appropriate technique for improving farm-scale nutrient cycles. The two characteristics that distinguish biochar amendment from other organic materials are its high stability against decay, which allows for extended time-periods in the soil, while providing long-term benefits to the soil, and its greater ability to retain nutrients. Additionally, biochar reduces the soil's pH and improves the quality of soil, promoting water retention, cation exchange cations, and increase microorganism content [26]. Such phenomena depend on the initial parameters of the soil. In the case of a strongly alkaline nature, an acidic biochar will lower the pH of the soil. However, the effect of this phenomenon depends mainly on the physical properties of the soil, i.e., water capacity and permeability of layers, and the degree of advancement of soil-forming processes (transformation from parent rock to soil solution).

The addition of biochar to the soil enhances the availability of basic cations as well as the amounts of P and total N [27,28]. In the short to medium term, the alkaline pH and mineral contents of biochar (ash content, including N, P, K, and trace minerals) can often provide significant agronomic benefits to many soils. When a higher pH biochar is placed on the soil, it becomes less acidic [8]. In the case of low pH soil, addition of acidic biochar may intensify the acidity of soil. Biochar's pH can be regulated by the kind of feedstock, production temperature, and production time. Another beneficial aspect of biochar is the reduction of greenhouse gas emissions in soil [29] such as methane and nitrous oxide emissions from agricultural soil, which may possess climate mitigation impacts. The addition of biochar to the soil in varying concentrations 2–60% (*w/w*) [30] effectively reduces CO₂ production, nitrous oxide production at levels greater than 20% (*w/w*), and ambient methane oxidation at all levels above unamended soil.

Extensive research has been conducted on the avoidance of "diffuse water pollution" through ammonium sorption or the mediation of the dynamics of a soil solution containing nitrate, P, and other nutrients. Biochar application to soil can surpass a variety of soil limitations, including high Al availability [31], soil structure, and nutrient availability, as well as bioavailability of organic [32] and inorganic pollutants, cation-exchange capacity (CEC), and nutrient retention [33,34]. Biochar can also adsorb pesticides, fertilizers, and minerals in the soil, preventing their transfer into the surface or groundwater and preventing subsequent deterioration of these waters as a result of agricultural activity. Biochar can lead to improved soil fertility and crop output, particularly in low-nutrient soils [35]. However, in the case of soils with high fertility, no discernible improvement in yield is observed, and even plant growth inhibition occurs. The effect of biochar addition on plant productivity is also affected by the amount added. Any soil amendment application rates must be based on substantial field testing. However, currently, there is insufficient data to propose broad recommendations. Furthermore, because biochar materials vary widely in their properties, the nature of the specific biochar material (e.g., pH and ash content) determines the application rate. Several studies have found that the use of biochar at rates of 5–50 Mg/ha with appropriate nutrient management increases crop yields. In contrast, an experiment conducted in the United States found that the application of peanut hull and pine chip biochar at rates of 11 and 22 Mg/ha reduces corn yields below those obtained in the control plots with standard fertilizer management [36]. To avoid the harmful effects of biochar, the rate at which it is applied must be controlled appropriately.

The current fight against climate change will dictate Europe's and the world's future. Therefore, according to European climate law, EU must reduce emissions by at least 55% by 2030. To accomplish such a necessary goal and create a neutral climate by 2050, EU

member states are drafting new legislation. To ensure that EU policies are in accordance with the climate targets agreed upon by the Council and the European Parliament, the Fit for 55 packages is a set of proposals to revise and update EU legislation and also to implement new initiatives. The Fit for 55 packages was submitted to the Council in July 2021. These proposals were first presented and discussed at a technical level within the Council's working parties responsible for the policy area concerned. Most of the packages the Council adopted are a general approach to the proposal in June 2022. This is to lay the foundation for an agreement on the proposals among the 27 member states. The set of recommendations intends to create a framework for achieving the following EU climate objectives:

- Guarantees a reasonable and equitable transition;
- Ensures a level playing field concerning third-world countries while preserving and enhancing the creativity and competitiveness of EU industry;
- Economic operators;
- Supports EU's role as a worldwide leader in the battle against climate change.

In the Fit for 55 packages, the different aspects were discussed in detail, such as energy taxation, energy efficiency, renewable energy, social climate fund, alternative fuels infrastructure, greener fuels in shipping, sustainable aviation fuels, CO₂ emission standards for cars and vans, emissions and removals from land use, member states' emissions reduction targets, carbon border adjustment mechanism, and EU emissions trading system.

The Commission has proposed a set of changes to the existing EU's emissions trading system that should result in an overall emission reduction in sectors concerned of 61% by 2030 compared with 2005, by including mainly emissions from maritime transport in the EU ETS and implementation of global carbon offsetting and a reduction scheme for international aviation. The proposal increases the EU-level greenhouse gas emissions reduction target from 29% to 40%, compared with 2005, and updates the national targets accordingly. The calculation method for determining the national targets remains based on GDP per capita with a limited number of targeted corrections to address cost-efficiency concerns. For the reduction of emissions and removals from land use, land use change, and forestry, the revision of rules proposes to set an EU-level target for net removals of greenhouse gases of at least 310 million Mg of CO₂ equivalent by 2030, which is distributed among the member states as binding targets. Furthermore, the rules on CO₂ emissions for cars and vans have been revised, by increasing EU-wide reduction targets for 2030 and sets a new target of 100% by 2035. Therefore, from 2035 it will no longer be possible to place cars or vans with an internal combustion engine on the market in EU. In addition, this increases the current EU level target of at least 32% of renewable energy sources in the overall energy mix to at least 40% by 2030.

It also proposes the introduction or enhancement of sectorial sub-targets and measures across sectors, with a specific focus on sectors where progress with integrating renewables has been slower to date, in particular the transportation, buildings, and industry. For sustainable aviation fuels (both advanced biofuels and electrofuels) the potential to significantly reduce aircraft emissions is clear. However, this potential is largely untapped as such fuels represent only 0.05% of the total fuel consumption in the aviation sector. Hence, it is imperative to gain great insight into the amplified effects of global warming in light of changes to EU regulations.

There are four main Carbon Capture methods, pre-combustion capture, post-combustion capture [37], oxyfuel combustion [38], and chemical looping combustion [39]. Chemical methods are based either on adsorption or absorption; physical methods, including membrane filtration or chemical looping combustion, enhance oil and gas recovery; and biological mitigation through terrestrial plants, and algae are all common CO₂ management techniques. However, the aforementioned approaches exhibit some drawbacks. For example, evaporative losses, high energy requirements for solvent recycling, and corrosion, all affect chemical systems that use solvents such as amines to separate CO₂ from industrial

off-gas, and result in high operating costs. In the case of physical methods, large pressure decreases are easily caused by membrane technology failure, etc.

A solution to such issues may be the application of biosequestration of Industrial CO₂ off-gas. In addition to the removal of carbon from the atmosphere, carbon biosequestration offers various advantages, such as increased water retention, fostering fertility, and boosting primary output. Microalgae have the potential to reduce air pollution and slow down global warming by using NO_x as a source of nitrogen and converting solar energy into chemical energy through CO₂ fixation. Additionally, they can increase the production of biomass (such as animal feed, functional foods, nutraceuticals) and biofuels, as well as high-value goods (algal extracts for use in cosmetics, carotenoids production such as β-Carotene and astaxanthin, and phycobilin pigments phycocyanin, and antibiotics production etc.).

Reports have shown that microalgae use CO₂ as a source of carbon and transform it into organic carbon to create cellular components such as lipids and carbohydrates [40,41]. Moreover, due to their higher growth and photosynthesis rates microalgae [42] are more effective at storing CO₂ than terrestrial plants [43]. Depending on the growth parameters (such as temperature, light, pH, and nutrient availability), species of microalgae, CO₂ concentration, and harmful contaminants in the flue gas, microalgae can fix CO₂ and produce biomass. A mechanism for concentrating carbon and a photosynthesis process is both involved in the sequestration of CO₂ by microalgae, which has been reported in the literature [44]. Interestingly, flue gases and wastewater from other industrial processes may be used to meet the high CO₂ and nutritional needs of microalgae, offering environmental benefits while decreasing the cost of biomass production [45]. The utilization of waste is one of the effective solutions for global warming mitigation and minimizing environmental damage.

Remarkably, microalgae that grow using flue gases may be further processed into a variety of fuel products. For example, bioethanol and biobutanol by fermentation, bio-oil by thermochemical conversion, green diesel and gasoline by direct catalytic hydrothermal liquefaction, biodiesel by transesterification, and biomethane by anaerobic digestion. The lipid composition in microalgae consists of above 70% triglycerides, and can be solvent extracted and further transesterified with alcohol to produce biodiesel. The end products of this chemical process are glycerol (undesired) and fatty acid methyl esters (FAMES). There are two methods to obtain FAMES, (a) direct transesterification of wet microalgae under supercritical conditions in the absence of a catalyst, and most often reported (b) the utilization of either sodium or potassium hydroxide as a catalyst [41]. These techniques are in the early stages of research and require further exploration. Additionally, microalgal research for industrial flue gas biosequestration recently started to attract attention and is considered a hot research topic [46]. Currently, it is believed that in the light of FIT for 55 packages, biosequestration will achieve policy support to develop an economically viable process.

Published studies [47] revealed that creative technical solutions can be employed to scale up production, boost output, and lower costs of algae-based bioenergy generation. Consequently, it is anticipated that an affordable and efficient commercial manufacturing algal bioenergy technology will be developed in the near future. Therefore, CO₂ fixation via microalgae is a potential and promising method for CCS, with a clear prospective for industrial flue gas biosequestration.

2.2. Biochars in Iron and Steel Industries

Iron and steel production due to its economic potential and importance for the economy, the steel industry is one of the strategic industries [48]. Iron and steel production is considered a key indicator of domestic prosperity [49] and plays a leading role in the global market economy [50]. Currently, China leads with more than 50% of the world's iron and steel supplies [51].

Steel products are the basic industrial material used by most sectors of the national economy [52] and are widely employed in major industries such as energy, transport,

construction, agriculture, light and heavy industries, etc. [53] Steel is vital for economic development and urbanization, and is essential in terms of sustainable development [54]. However, the iron and steel industry is one of the most energy-consuming [55] and emission-intensive industries in the world [56,57]. The effect of energy and environmental pressure in terms of carbon emissions and carbon neutrality [58,59], has allowed the iron and steel industry to improve energy efficiency [60], reduction of carbon emissions [61], and promotion of sustainable development [62].

Globally, low-carbon [63,64] and energy-efficient production techniques are implemented in steel companies [65,66], but each iron and steel plant has its own production specificity, which requires customized decarbonization strategies [67,68]. According to reports [69,70], the transition to obtaining sustainable production towards low-carbon production processes in the steel industry is difficult and involves long and complex development, including radical innovations and large-scale tests [71]. These industries focus on intense operations to reduce CO₂ emissions, while research is advancing in many different areas, and mainly focuses on the possibility of complete or partial replacement of fossil carbon with biochar [72]. The specifics of the steel industry specifications hinder the replacement of coal in metallurgical processes; hence, it is important to create methodologies and technologies that enable companies to produce the appropriate type of biochar [73] with the appropriate properties [74].

According to Shukla [65], there are economic and technological reasons for replacing fossil fuels with biomass-based renewable fuels in varied metallurgical processes, especially biochar, which is a suitable substitute for conventional carbon in the aerobic method of steel production [65]. Nevertheless, it should be noted that raw biomass (e.g., due to its high moisture content, low carbon content and low calorific value) is not suitable for direct use in metallurgical processes and requires thermal conversion, [75] e.g., pyrolysis [76,77] or torrefaction [78,79] into biochar [76]. Additionally, the variety of biomass types affects the reactivity of the biochar resulting from the thermal conversion process [80].

Brazil is the leading global producer and consumer of biochar [81], where as much as 75% of its production goes to the steel industry [82] (Figure 2). The advantageous nature of biochar in metallurgical processes is primarily determined by its quality [83,84], which must adhere to the requirements of the steel industry (Table 2) [82,85].

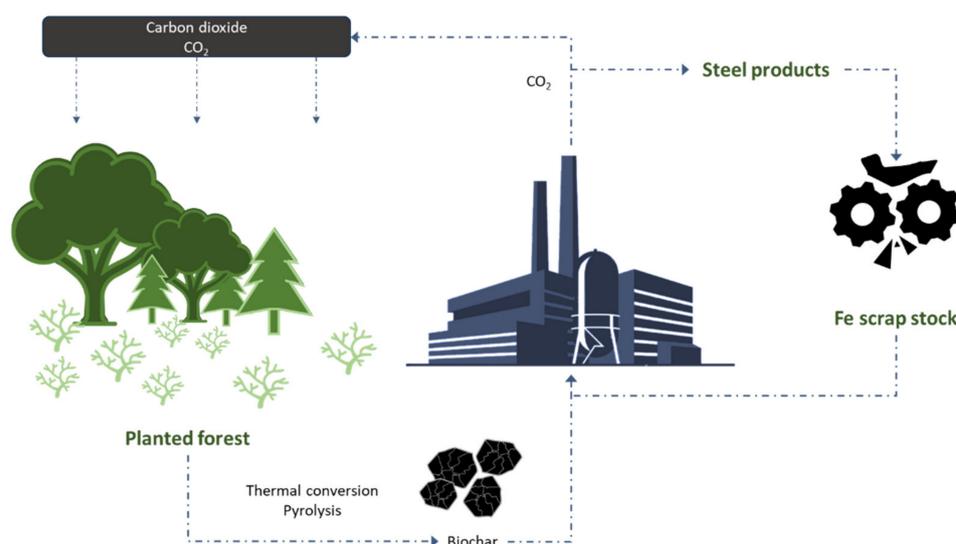


Figure 2. Utilization of biochar in iron and steel industries.

Table 2. Quality criteria for biochar and coke intended for the steel industry [82].

Parameters	Coke	Blast Furnace Coke	Charcoal	Steel Quality Charcoal
Fixed carbon (%)	88–92	88	65–75	74–77
Volatile matter (%)	7.8–11	1	25–35	22–25
Ash (%)	0.1–0.5	10–12	2–5	1–1.5
Alkalis	low	Low	High	<20%
Resistance to compression (kg/cm ²)	-	130–160	10–80	50–100

Currently, there are two main production routes for iron and steel, namely the blast furnace–basic oxygen furnace (BF-BOF) and the electric arc furnace (EAF). Approximately 75% of the global steel is produced in an integrated BF-BOF steel production process [86].

In the steel industry, coal is used at several stages of steel production, including during the carbon reduction stage, where it acts as a carbon source in iron oxide reduction reactions [80]. Therefore, the use of biochar is an attractive alternative to coal and coke [87,88]. In many countries (e.g., Australia and Sweden), a large-scale study was conducted on the use of biochar in iron production, where promising results were obtained [89]. According to Fan et al. [62], in Brazil, 60 small blast furnaces completely replaced coke and carbon with biochar. The authors stated that Japanese, German, and Finnish sites displayed results that justified the environmental and economic benefits of the utilization of biochar in the blast furnace process. At the same time, they suggested that although the rate of coke substitution in a blast furnace reached only approximately 25%, this was still economically justified considering the future coke prices and pollutant emissions [60].

The main possibilities for using biomass in the iron and steel industry include [90]:

- (i) Cokemaking for the production of bio-coke;
- (ii) Sintering process for the production of bio-sinter;
- (iii) Pelletizing/briquetting for the production of bio-composites and/or bio-briquettes;
- (iv) Partial replacement of nut coke, coke or PC in the blast furnace;
- (v) Bio-carburization of steel in ladle furnace.

Reducing greenhouse gas emissions generated through steel production is an important issue in many countries [91,92], including Sweden, where the reduction of emissions from the use of coke in blast furnaces is the biggest challenge. This is partly because it is the main energy carrier, but it is also a reducing agent from which other alternatives are very limited [93,94].

ArcelorMittal is another company aims to achieve 30% reduction of Europe’s carbon emissions by 2030, in support of the Green Deal concept adopted by the European Commission. This goal is incorporated in the company’s plan to achieve climate neutrality in Europe by 2050. ArcelorMittal has proposed a three-pronged pathway to achieve this goal. One of the proposed pathways is the utilization of raw materials such as biomass in metallurgical processes instead of fossil fuels, which will diminish the emissivity of metallurgy. The initiatives implemented or planned by ArcelorMittal in Europe in this respect include “Torero”, a project worth EUR 40 million, which assumes the production of biochar from wood waste. The produced biochar is intended to replace fossil fuels currently used in blast furnace technology. The first such project was created in Ghent [95].

The results of the research conducted by Gul et al. [96] indicated that the most attractive option for the use of biochar was blast furnaces [96], namely:

- Coking coal (charcoal substitution rate: 2–10%);
- Blast Furnace tuyere injection (charcoal substitution rate: 0–100%);
- Blast Furnace nut coke (charcoal substitution rate: 50–100%);
- Blast furnace briquettes (charcoal substitution rate: 0–100%);
- Sintering solid fuel (charcoal substitution rate: 50–100%).

Bianco and others [97] showed that carbon could also be replaced by biochar in an electric arc furnace, both at the loading and injection stages, to facilitate foaming.

In addition to the benefits of biochar in metallurgical processes, certain issues and limitations should be highlighted [98]. Numerous studies have indicated that the primary negative aspects of biochar usage in metallurgical processes are the impact of ash content from biochar on slag chemistry and the introduction into the process of elements, which hinders the formation of air pollutants (e.g., Cl, S) and is critical for steel quality (e.g., P). In the case of the physical properties, low compressive strength and density may require the processing of biochar, such as pelleting or briquetting, to create a suitable material for an electric arc furnace [99].

To summarize, the use of biochar from the thermal conversion of biomass in the iron and steel industry could replace 20% of the energy from coke, which has environmental benefits such as part of the carbon emitted in the process would come from a renewable source and used to balance carbon emissions from non-renewable fossil fuels [100]. Studies regarding the general suitability of biochar in iron and steel production showed that this should be supported by countries with sufficient, sustainable national biomass resources, and support national policies [101]. The countries that could successfully use biochar in metallurgical processes include Sweden, Canada, China, USA, and France, as well as Finland, Australia, Poland, Brazil, and Russia [102]. Furthermore, the studies proved that the use of biochar as a reducing agent in metallurgical processes significantly reduces CO₂ emissions. At the same time, the metallurgy industry has the opportunity to adapt to established environmental regulations and constraints.

The undeniable energy crisis and rising fuel prices make biochar a substitute for coal in the production of pig iron and steel environmentally and economically. One of the main limitations preventing the transition to steel production using products from thermal biomass conversion seems to be the costly biomass and limited access [77]. The literature has shown that reducing agents based on biochar produced in the torrefaction process has the best performance properties [74]. Research studies have proved that the physical quality of the material is the basic criterion for the proper selection of biochar for applications in the steel industry [82,85]. Brazil extensively employs biochar, which replaces coke in the steel industry, in blast furnaces, the iron reduction process for the production of pig iron [103,104]. According to reports, the insufficient supply of biochar and poor sinter quality of raw biomass is the most concerning limitation for widespread use in sinter production [105]. Despite biomass-based biochar possessing a huge potential in reducing greenhouse gas emissions as a substitute for fossil carbon in steel production, it remains a challenge [106,107].

2.3. Usability of Carbonite Materials in Cokemaking

Virtually all industries related to processing and goods production promote the emission of pollutants. Additionally, the metallurgical sector, which includes the coke-making industry should also be taken into account. This stems from increased society's ecological awareness and the limitations and stringent regulations applied to industrial pollutants emissions.

The implementation of stricter legal regulations regarding ecological aspects, such as EU Fit for Regulations 55, has resulted in increased penalties for CO₂ emissions. In contrast, there remains a high demand for coking coals for the production of various types of coke over many different sectors, but at the same time, their overall production is insufficient to meet the supply.

Therefore, to overcome these issues the utilization of biomass-origin additives should be examined, which can be applied in the preparation of cokemaking blends (Figure 3). Furthermore, the employment of bio-additives and the replacement of fossil carbons in coke production may result in the reduction of CO₂ emissions, and thus the limitation of raw material costs of coke production [108]. These costs are mainly in conjunction with coal supply and blend preparation, and influence steel production in which the applied coke is responsible for 1.8 Mg CO₂ per 1 Mg emission of the finished steel product. Furthermore, the steel sector generates 7% share of total global CO₂ emissions [109]. However, among

the various issues related to the application of raw biomass in coking blends, it depends on the coking parameters of the coke blend and the quality of the product. This is due to the presence of bio-additives during the cokemaking process limiting the formation of a plastometric layer. While the passage of the plastometric layer through the coking blend, a large amount of volatile matter parts is released, which promotes significant shrinkage and the formation of weak bonds between the carbon grains and grains of biomass particles. This phenomenon in combination with the release of elemental oxygen from combustible matter causes a deterioration of plastometric layer formation [110].

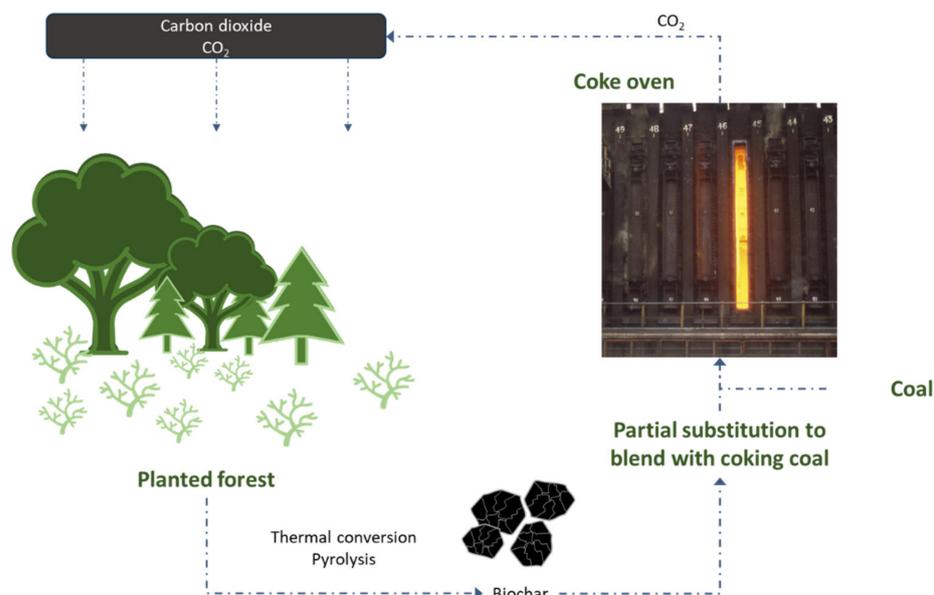


Figure 3. Utilization of biochar in cokemaking.

Reports have described that a few percent share of raw biomass in the coke blend negatively impacts the quality of coke by simultaneously increasing its reactivity and reducing its mechanical strength [111]. Therefore, to introduce a greater share of bio-component without promoting deterioration of the quality of the final product, bio-coke, pre-processes of biomass must be examined to form a product similar to coal, such as biochar.

One of the most commonly available charcoals on the market is wood-charcoal. Charcoal is a raw material applied in various sectors of activity including its use as an adsorbent in water and gas filters, medicine, cosmetology, food industry, and the energy used as a raw material for the production of utility heat. One of the main ones its consumers, with an annual consumption of 1 million tons in 2020 is the European Union. Charcoal/bicarbonates are produced from various kinds of biomass, and its technological parameters depend on biomass type, initial pre-processing, and carbonization process conditions. The important process factors include process temperature, raw material heating rates, and construction of the applied reactor [112]. Changes in the process parameters, such as process temperature and pressure, alter the physical parameters, including a decrease in real density and an increase in the porosity of the produced biochar [113].

In comparison to raw biomass, the fuel produced in this way has a higher content of combustible substances, lower content of volatile substances, and higher calorific value. Moreover, the aforementioned effects are possible to achieve at relatively low temperatures. For example, the subjection of walnut shells without pre-processing to torrefaction at a temperature above 200 °C, results in increased calorific value of the produced biochar, from 17 to 27 MJ/kg compared to raw biomass [114]. Hence, in order to use the produced biochar as a component of the coal blend, it should be properly processed, which depends on the availability of the raw material and the expected share in the coke blend. This issue is important because, ideally, the produced biocoke should contain as much organic carbon

as possible. The value of its share can be determined using the special coefficient so-called fixed carbon (FC).

A higher FC parameter value indicates that a greater amount of biomass-derived substance remains in the structure of the manufactured coke. Therefore, biocoke with a higher share of renewable components is more ecological. The literature [115] has shown that biochars, due to their high specific surface and porosity, and their much larger total volume, are characterized by a relatively high reactivity. This dependence has been confirmed in reports, showing the relationship between the degree of coke reactivity and the size of the specific surface area assessed using the multilayer gas-phase adsorption model on the adsorbent surface, i.e., the Brunauer, Emmet, and Teller ((BET) isotherm) and microscopic analyses [116]. However, under the conditions associated with bio-coke production, excessive reactivity causes a significant reduction in mechanical strength, which, as mentioned above, is one of the main technological challenges related to designing blends with appropriate coking properties [117]. Additionally, from a technological point of view, biochar must be susceptible to homogenization with the coking blend and its specific content, which would allow compaction of the expected technological parameters.

The usage of highly dense biochar than biomass is beneficial because the compaction of the coke blend significantly improves the quality of coke and the production capacity of the coking chamber coking battery [118]. Therefore, when composing a blend containing carbonized biomass (biochar), it is important to identify its proper share in the blend, which allows for the production of bio-coke with parameters acceptable and expected by the industry. In contrast to the raw biomass, the effect of the addition of biochar with a similar share of the coking parameters of the coke blend, and the quality of the produced coke reduces the possibility of deterioration of the bio-coke's quality. This stems from the raw biomass containing a higher content of elemental oxygen, which limits the mobility of structural carbon particles to a greater extent, lowering their plasticity. It allows its incorporation into the coal blend at a higher percentage share. However, any component that is non-typical to coking coal deteriorates its quality.

In practice, the obtaining of coke of appropriate quality is usually based on analysis of the effectiveness of the charge preparation operation. The analysis is carried out based on coke production of unchanged quality from impoverished with containing cheaper coals of lower quality or non-carbon additives, and at the same time of worse quality coke blend. This can be achieved by optimization of the recipe and increased charge density [119]. Operational and motor activities of this type allow for the diminishment of quality deterioration of the coal blend. However, from a financial and ecological point of view, an increase in the proportion of biochar in the coke blend is desirable and justified.

The presence of biochar deteriorates the coking properties, i.e., reduction of the blend's dilatation, which modifies certain parameters, including enhanced reactivity [113,119]. The obtaining of a higher dilatation value results in a coking blend with better cokemaking properties and greater quality of coke. Therefore, various aspects depend primarily on the preparation method of the bio-additive to the blend, such as grain size, the amount in the charge, and the coke blend's properties. Changing the coking properties by modifying the composition of the coke blend results in significant differences in the quality of the produced bio-coke.

Currently, researchers focus on the issue of using various additives with varying degrees of thermal processing, which are a component of coke blends. According to reference [116], the application of certain additives to the coking charge in the form of biochar made from rice and coke hulls, causes deterioration of the coke quality concerning the coal reference blend through increased reactivity and lowering the mechanical strength. In the case of coke husks biochar, its introduction of up to 15% allows for the generation of bio-coke with reactivity (CRI = 55.1%) and post-reaction strength (CSR = 29.8%) at levels dedicated to the workability of the bio-coke acceptable for blast furnace applications, i.e., CSR = 50–74% and CRI 19–30%. The report obtained a similar level with a share of 10–15% of the biomass in the blend [118]. However, the biomass was partially com-

pressed/briquetted. Specific studies claimed that in terms of the quality of the produced bio-coke, the introduction of 3% of the additive was considered a safe level [119]. However, in this case, the criterion adopted by the authors was of key importance [113].

In addition to the proportion and degree of processing, grain size of the added biomass and the density of the coal charge significantly impact the quality of the bio-coke. However, it was shown that an increase in the charge density from 634 to 750 kg/m³ resulted in an 82% increase in the mechanical strength of coke at ambient temperature from 9.39 to 17.08 MPa [110]. Furthermore, it was confirmed that apart from the bulk density, the particle size distribution of the used bio-component was important. When 5% charcoal was used with a particle size of 125–250 µm, an increase in coke strength compared to the reference blend was observed. These results were confirmed by microscopic analyses of bio-coke, and showed that the soft coke mass penetrated the spaces of the bio-carbon while passing through the plastic state after its solidification, and contributed to the improvement of cold resistance bio-coke. Additionally, washing and coating can be implemented limiting the negative impact of the bio-component on coke quality, i.e., with kaolin before the introduction to the cokemaking blend. Other investigators indicated that such action promotes reduced reactivity of the bio-coke and increases its share in the blend. Generally, the issue of biocarbonisates utilization in composing coke blends is significant from a technological and ecological stand-point and can be undertaken on a laboratory and large-scale.

Contrary to raw biomass, biochar can be introduced in a higher proportion to the coking blend. However, when composing the blend with a bio-carbon additive, the number of technological coefficients should be considered, i.e., properties of the obtained biochar (in relation to unprocessed raw biomass), distribution of biochar grains, percentage of biochar in the coke blend, the degree of homogenization of the blend with the additive, and the method of blend charging in the cokemaking chamber. Achieving these goals allow for the production of bio-coke with quality parameters corresponding to the technical requirements or close to the values expected and accepted by the industrial sector.

2.4. The Use of Biochar in Energy Storage Technologies

A way of storing energy in SC is based on the reversible electrostatic accumulation of ions on the electrode surface and the formation of a so-called electrical double layer. According to the basic Helmholtz model, the charge separation phenomenon occurs at the electrode-electrolyte interface due to electrode polarization. Ions of the opposite sign disperse at the electrolyte condensate to form a condensed layer several nanometres long in a plane parallel to the electrode surface. Due to the developed specific surface area of SC electrodes, they are capable to store much more energy (on the order of several thousand farads) than conventional dielectric capacitors. Furthermore, they have a higher power density and longer life compared to batteries. Another undeniable advantage is their ability to store and deliver energy in a very short time period, in some cases even less than a minute, which translates into short charging times. However, one drawback is their low energy density, which results in short operating times, so their role is short-lived, high-power energy storage devices in support of batteries or fuel cells. Hybrid vehicles use such batteries as a source of power for starting and climbing, and for recovering energy after braking. An interesting solution is the use of supercapacitors in cranes and hoists, where they supply or recover power when lifting or lowering a load, respectively. A well-known example is SCs as a source of electricity in public transport vehicles (Figure 4).

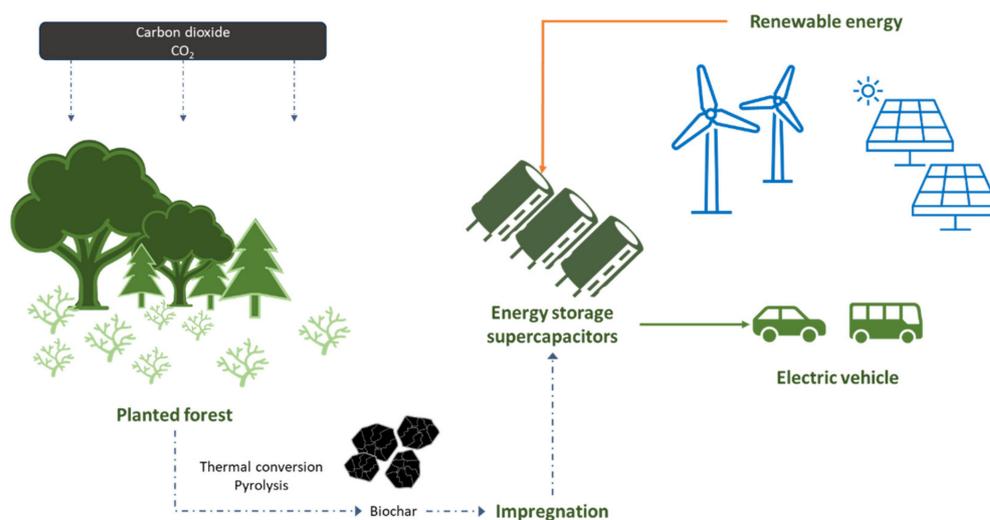


Figure 4. Utilization of biochar in energy storage technologies.

In most cases, storage is not in procurement the min challenge associated with using of renewable energy sources to generate usage power. It is recognized that the best energy storage devices are lithium-ion batteries, electrochemical capacitors, which sometimes referred to as supercapacitors (SCs). These electrochemical devices store electricity with two methods: chemical change and accumulation of electrostatic charge. The second one is applied in the area where the electrode meets the electrolyte. Although the latter applies the electrochemical capacitor concept, the former involves the conversion of chemical reaction energy into electrical energy [120].

This concept has been tested by China and involves the rapid charging of electrochemical capacitors at special charging stations located at stops several kilometres apart. For many years, SC's very high application potential has led to intense research into improving this technology. Furthermore, it is hoped that the idea of using electrochemical capacitors to power mobile devices will come to fruition [120]. In both types of energy storage units, different types of carbon materials are used as electrode materials. Batteries use high-quality natural or synthetic graphite as anodes, while supercapacitors employ activated carbon with high activity (capacity) as electrodes. The raw material for good quality activated carbons can include various types of biomass, such as waste materials, i.e., fruit stones or shells, bark and wood chips, and biomass of animal origin. The material obtained by pyrolysis of the mentioned organic materials, upon subjection to an activation and modification process, can meet all the criteria related to their use in SC electrodes. Additionally, other organic wastes, such as plastics can be utilized as the starting material for pyrolysis. This allows for the practical management of a variety of organic wastes, which upon pyrolysis provide a carbon residue with qualities that are amenable to activation and modification in order to enhance their active surface area. SC has two identical electrodes that are electrically separated from each other by a porous membrane-separator, which is a thin, porous plastic film. The separator does not act as a dielectric, but merely prevents direct electrical short-circuiting of the two carbon electrodes. Thus, it does not present any obstacle to ions, allowing them to pass to the respective electrodes after voltage is applied. Each electrode, which is a mass of activated carbon, is in contact (saturated) with a liquid electrolyte, which is commonly a sulphuric acid solution. The use of SCs in combination with other energy sources, e.g., batteries or fuel cells, when the components are properly selected and combined, creates a system with high energy and power values, increasing efficiency and lifespan. The combined utilization of batteries and SCs may lead to a future breakthrough in electromobility.

Carbon nanostructures are characterized by their mesoporous structure and are associated with a high capacitance. They have been tested as potential SC electrode materials [121]. Significant qualities related to these materials, such as strong electrical conductivity and

stability do not go hand in hand with a reasonable price and, harmful chemicals are disposed while in production. As a result, the use of biochar from biomass has emerged as a cheap and easily accessible carbon source for SC electrodes [122]. Research on opportunity of using SC carbon material obtained from pyrolysis of biomass (ash wood) as an electrode material has been carried out by Canadian team [123]. They observed that the presence of non-electrified areas with the possibility of the availability of electricity only from renewable (solar, wind) or combustion generators. The structure and surface morphology of char obtained from biomass determines the functional properties of the electrode. One of the key requirements of these materials is their large surface area. However, the size of the specific surface area is not associated with a useful (proper) active surface area. The most important aspect is the pore size that allows easy access to electrolyte ions, facilitating the formation of an electrical double layer in which the actual charge is stored. Studies have discovered that natural nanotube structures are present in biochar, what significantly increases the specific surface area. This approach promotes management of waste biomass, which is considerably large and originates from natural disasters [124].

Waste ash wood was processed with carbonization at 600, 700, and 900 °C, which is then shredded and, after sieving, activated in a dilute nitric acid solution for 24 h at 95 °C with periodic stirring [123]. The resulting suspension was filtered, washed with demineralized water, and dried at 130 °C. The obtained char was subjected to tests to determine its suitability as an SC electrode material. Observations have shown that waste ash wood is a promising material for electrodes with a quality similar to that obtained from full-grade raw material [124]. Canadian researchers expanded their study in order to identify opportunities for increasing the energy storage capacity of SCs without increasing cost and improving the performance of their electrodes. Inexpensive and high-performance materials for SC electrodes were extensively investigated for this purpose. The subject of the study was the most commonly used carbon in SC electrodes in different forms. For example, biochar from charred wood residues has a unique pore morphology, and its physical and electrochemical properties are highly dependent on the type of source biomass, carbonization conditions, and subsequent activation methods. One of the criteria for SC electrode material is adequate electrical conductivity, which can be achieved using by various methods. One approach is simple activation with silver ions, which results in a composite material with surface functional groups containing silver, and exhibits high electrical conductivity that improves the overall conductivity of the resulting composite material [124].

Activated char with unique properties is a very useful carbon active material for various applications such as ea. catalytic media, removal of pollutants, electrodes, capacitors, gas storage [125]. Currently, the production of activated carbon materials, especially from low-cost and natural bio-precursors (biomass), is considered an attractive research topic in advanced materials science. A series of reports related with the application of activated carbons in this area are available [122,125,126]. The creation of a consolidated compilation of applications of activated carbons derived from biomass provides a useful database for those interested in this topic. A literature review showed that activated char derived specifically from biomass can be specifically employed as electrodes in electrochemical power devices. In particular, carbon derived from pyrolyzed peanut shells show a maximum specific capacity of 4765 mAh/g, demonstrating suitability for lithium-ion batteries. For example, char obtained from coconut shells and waste coffee grounds activated with $ZnCl_2$ in suitable electrolytes display a capacity of 368 F/g [127]. A previously published review related to ongoing research has confirmed that biomass-derived carbons are economically and commercially promising raw materials for obtaining electrodes for electricity storage units [127].

Char can also be obtained from different origin materials such as cedar wood, characterized by high carbon content and high degree of order without additional processing and modification [128]. Detailed studies have shown that the produced biocarbon has a carbon content of 98%, and oxygen is the only detectable impurity in a highly ordered microp-

orous texture characterized by alternating regular microporous areas and narrow porous areas. In addition, the porous biocarbon monolith has a high BET specific surface area of approximately $400 \text{ m}^2/\text{g}$. Electrochemical measurements have shown that electrodes prepared from biocarbon have a potential of approximately 1.3 V and are characterized by fast charge–discharge cycles with a capacitance of approximately 14 F/g. Simple activation of biochar with dilute nitric acid at room temperature leads to a 7-fold increase in capacitance, to a level of 115 F/g [128]. Preliminary lifetime studies indicate that supercapacitors using electrodes from the tested biochar, original, and activated in nitric acid, are stable for 5000 cycles without loss of performance. Therefore, wood biochar has great potential due to its low cost and can act as a good quality SC electrode material with satisfactory performance while being environmentally benign [128–131].

Activation by low-temperature oxygen plasma is a useful method for the effective activation of biochar and has been detailed in ref. [132]. Plasma activation is a non-toxic, energy-efficient, and fast ($<15 \text{ }^\circ\text{C}$ and 5 min) approach compared to conventional chemical activation ($950 \text{ }^\circ\text{C}$ and several hours). Comparative studies of plasma activation and typical chemical process activation of biochar obtained from pine revealed the suitability of this method for char activation and provided a high electrical capacity and very favorable pore structure. A proposed mechanism of plasma activation and its suitability for the generation of activated carbons was shown. In order to organize the structure and increase the surface area of the biochar, it was subjected to partial graphitization. The procedure for the formation of mildly graphitized char includes pyrolysis, KOH activation, and graphitization at $900 \text{ }^\circ\text{C}$ catalyzed by cobalt nitrate. Thermal treatment resulted in carbon with a microporous structure and a specific surface area of $1775 \text{ m}^2/\text{g}$, and the electrical specific capacitance of the generated material was 178 F/g. Porous partially graphitized activated carbons based on biochar showed excellent stability of properties for more than 5000 charge/discharge cycles [8]. Catalyzed graphitization is an effective method for obtaining activated carbon as an electrode material for electrochemical capacitors (SCs).

The methods used to produce and modify biochar are presented in a previously published review [133]. Since biochar has been defined as a solid residue obtained by thermal conversion with limited oxygen, processes such as pyrolysis, gasification, and hydrolysis are distinguishable. The methods used for post-process modification to increase the specific surface area, change the pore structure, and for the recombination of surface functional groups were also discussed. This expands the applicability of biochar. Among the modification methods described, physical and chemical activation, and surface modification were highlighted. Unlike typical activated carbons and nanotubes, biochar contains many surface functional groups, especially oxygen-containing ones (carboxylic, phenolic, carbonyl). Hence, there are great possibilities to influence the configuration change of these groups, and produce materials with specific properties. Of the parameters determining suitability as SC electrode material, the most important is the specific surface area and electrical capacitance. Studies on the suitability of biochar as potential electrodes in supercapacitors have been extensively reported. The most attractive features of biocarbon are its easy availability, low price, and “green” origin compared to other carbon materials obtained by chemical processes. Another valuable advantage is its significant susceptibility to modification and, thus, alterations of important parameters.

To date, biocarbon-based materials have found applications in various fields, including environmental protection), catalysis manufacturing energy storage, etc. [129–131]. However, most of these applications are still in the early stages of development. Additionally, biochar has been employed in energy storage units. To adhere to specific requirements for SC electrode materials, various methods of biochar modification, such as activation, the introduction of heteroatoms, and obtaining composites with carbon nanostructures must be used. More expansive research is necessary for materials from biochar for the purpose of SC. The methodology program for this field is illustrated in Figure 5 [134].

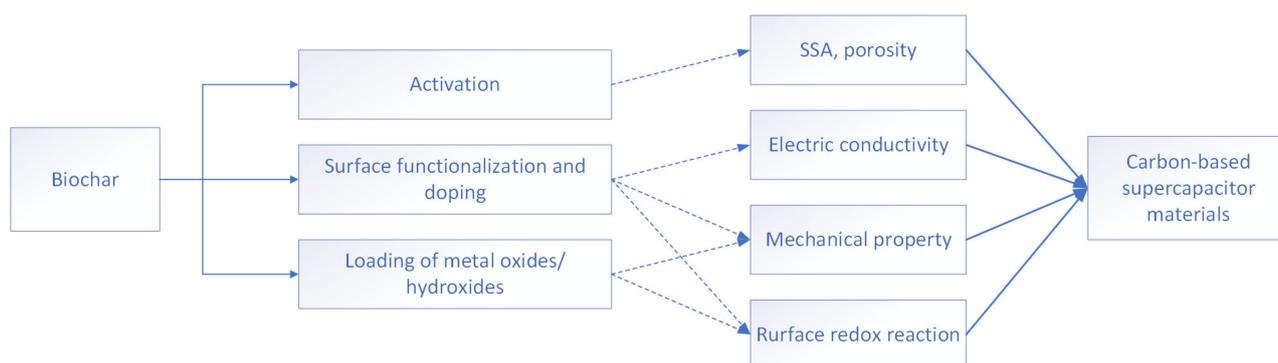


Figure 5. High-rate performance activated carbons prepared from ginkgo shells for electrochemical supercapacitors.

In addition to biomass, there are many other organic wastes that, might be applied to pyrolysis. To these group belongs chars with high carbon content, including plastics, car tires, sewage sludge, railroad sleepers, resins from ion exchangers, and textile waste [135–137]. Char from these wastes, obtained by pyrolysis, has been studied as a raw material for obtaining activated carbons to be used as adsorbents [133]. Char from waste plastics is being considered as a potential material for SC electrodes, which in the pyrolysis process is carried out under appropriate conditions, including in the presence of a catalyst, and the formation of carbon nanotube-like structures with parameters suitable for use as supercapacitors. Meeting the requirements needed for energy storage systems, various modifications are employed, such as activation of the specific surface area by enrichment of the surface via the addition of oxides/hydroxides of transition metals, including MnO_2 , CuO , AgO , NiO , Co_3O_4 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, and others, resulting in enhanced surface area and redox activity, as well as reduced agglomeration [120].

Current research studies aim to utilize biomass as a raw material for the production of supercapacitors. It has been confirmed that biomass can become a very interesting material after carbonization processes under suitable conditions, followed by appropriate modifications. Biomass-based materials can be modified to develop a specific surface area, or homogeneously saturated with various types of compounds. Additionally, biomass has been employed to prepare very uniform porous structures that are a good base for the production of more advanced materials.

2.5. The Use of Carbonisate in Pickering Emulsions and Energy Storage

Biochar, as demonstrated above, is a highly adaptable substance, and is primarily used on large scale, as a sorbent, soil additive, and in industrial and metallurgical operations. However, the application of biomass carbonate is not limited to the macro scale. At the micro scale, information regarding the usage of carbon nanomaterials, such as carbon nanotubes, graphite, graphene, and its derivatives, is readily available [138–142].

Pickering emulsions, which display unique features due to the utilization of nanoparticles, can be transformed into sufficiently fragmented biochar (down to nanometric size). Pickering emulsions are alternatives to the currently employed classical emulsions created by surfactant addition. The main benefits of polymerization utilizing Pickering emulsions are the reduction of changes to the coalescence in the presence of nanoparticles, which boosts the emulsion's stability (Figure 6).

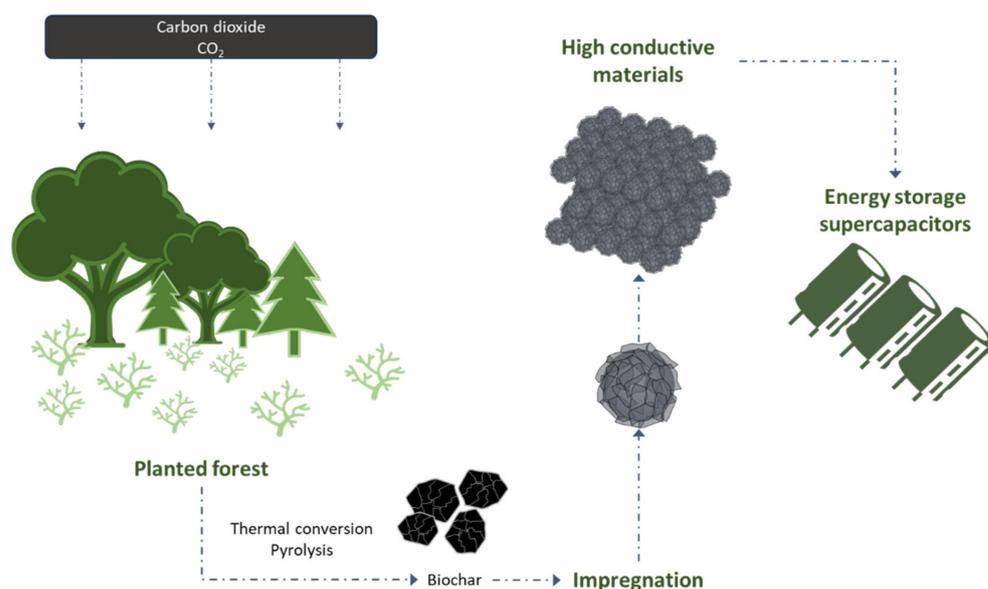


Figure 6. Utilization of biochar in Pickering emulsions and energy storage.

They are also less harmful to human health and the environment [141,142]. The formation of Pickering emulsion droplets involves the adsorption of a single monolayer of particles onto the droplet surface, resulting in core-shell structures [143,144]. Many types of inorganic nanoparticles, such as silica [43–45], organometallic framework nanoparticles [145,146], and carbon nanotubes [147], have been effectively utilized as a single emulsifier or co-emulsifier to stabilize Pickering emulsions [148].

Although the properties of Pickering emulsions are well defined, research is continuously ongoing to gain a greater understanding and explore new applications. The utilization of Pickering emulsions in energy storage devices has not received much attention. Phase-change materials (PCMs) [149,150], which store latent thermal energy during melting and release it after freezing, are regrettably characterized by chemical instability, which results in lower thermal conductivity. Pickering emulsions stabilized by nanoparticles, biomass carbonisate, or graphene materials generated from biomass sources [151], rather than organic surfactants, are being studied to enhance the stability of PCMs.

Usage of carbonisate derived from the pyrolysis of rice husks is an example of such a direction for the use of biomass carbonisate [152]. According to the report, before using carbonisate, it required milling to a size of approximately 576 nm, which had a negative surface charge of -45 mV and disperses in water with n-hexadecane to form a stable emulsion. Encapsulation was performed using an aqueous solution of poly(diallyldimethyl-ammonium chloride) (PDADMAC) at concentrations ranging from 2.0 to 5.0 wt% to generate a PCM. After 24 h, poly(sodium styrene sulphonate) was added to complete the encapsulation process, and the entire mixture was allowed to dry fully. Analyses were performed using thermogravimetric (TGA) and differential scanning calorimetry (DSC). This study demonstrated that the phase-change substance hexadecane was successfully encapsulated in capsules of the correct size by emulsification utilizing rice husk charcoal particles. Polymer chains adsorbed from layer-by-layer assembly adhered the rice husk charcoal particles to the surface of the microcapsules. DSC and TGA examination of the microcapsules generated revealed that the single- and double-layer polymer-coated microcapsules contained 41.0 and 35.6 wt% n-hexadecane, respectively, corresponding to phase transformation enthalpies of 93.2 and 80.9 kJ kg⁻¹ (120 MJ/m³).

Biochar can be successfully prepared using biomass of various origins and biomass wastes, including nutshell waste, which is employed globally in animal feed and building materials due to its novelty, low cost, and existence as a viable biological resource. Due to their high carbon concentration, nut shells first form biochar, which can then be easily transformed into graphene [55]. Bio-graphene, such as natural graphene, can be successfully

used in the creation of PCMs. Advincula et al. [153] investigated the usage of GO and rGO as material for the Pickering-stearic acid emulsion process for the manufacture of PCMs. The emulsion was created via the sonication of graphene oxide in water with sodium chloride. The mixture was then heated to 85 °C and emulsified at 4000 rpm with solid stearic acid. After cooling, ethylenediamine was added and then dried under reduced pressure for 24 h to produce PCM. The effect of various amounts of carbonaceous material utilized (0.5, 1.0, 1.5, 2.0, and 2.5 mg/mL) was investigated. The work demonstrated that stearic acid could be successfully encapsulated in rGO monolayer. The generated PCM material was heated beyond the melting point of stearic acid while remaining contained within the carbon framework. Furthermore, they exhibited larger melting and crystallization temperature ranges than stearic acid. When compared to pure stearic acid, the inclusion of rGO improved thermal conductivity. The quantity of latent heat that can be stored in such materials and the ease of heat movement inside this material, such material provides ideal properties for future optimization.

Many applications, such as its use as a bio-adsorber, metal ion removal, and wastewater treatment, stimulate the recycling of this low-cost graphene resource [154]. Another intriguing application is graphene quantum dots (GQDs), which are produced using electrochemical methods, transforming biomass carbonate into nano- and one-dimensional sheets. When the charcoal graphene sheets were chopped into very small particles, they were termed E-GQDs by electrochemical oxidation [155], and possessed homogeneous size, and optical and structural qualities of 5 nm. In the synthesis of E-GQDs, charcoal is a cheap and widely available material [156], which provides a gateway for new possibilities, and the materials produced have the potential to display varied and interesting features.

2.6. Hydrothermal Carbonization (HTC) as a Biomass Upgrade Method

Hydrothermal carbonization (HTC) is a thermochemical process used to increase biomass carbonization, and a liquid, rich in organic acids (acetic, formic, levulinic, or lactic acid) in subcritical water. Compared to a more traditional dry torrefaction (DT) i.e., low-temperature pyrolysis, HTC process produces a more carbonized, high-energy-density solid. Additionally, HTC processing provides advantages over DT, e.g., the ability to convert highly moisture content biomass, lower devolatilization at comparable temperatures, enhanced ash removability, or relatively shorter reaction times due to higher reactivity of liquid phase [157].

The process occurs in hot compressed water at a residence time varying from 1 to 12 h and temperatures corresponding to autohydrolysis (150–260 °C). Sub-critical water plays a crucial role during the process, and acts as both the reaction catalyst and solvent, owing to a significant shift in water polarity at subcritical parameters due to a dramatic decrease in dielectric constant, compared to standard conditions [158–160]. Water under standard conditions (25 °C and 0.1 MPa) has a dielectric constant of 78, and its polarity is unsuitable for non-polar organic compounds. However, in the region near 200 °C up to a critical point (374 °C, 22.1 MPa), water acts as a non-polar solvent, making it an extremely effective reaction medium for organics. This change in the density correlates with other properties of water such as solvation power, degree of hydrogen bonding, polarity, dielectric strength, molecular diffusivity, and viscosity [161].

Over the years numerous studies investigated HTC biomass processing, providing insight into product quality, yields, and the influence of various experimental conditions [162]. Hydrochar is commonly employed as an alternative to fossil coal for combustion purposes [163], produced by HTC of wet biomass and wet residues, e.g., sewage sludge, waste straw, and spent coffee grain [164]. Additionally, the unique ability of HTC to remove the mineral ash has resulted in increased interest in the chicken breeding industry, to upgrade the properties of raw chicken manure and poultry litter in order to create a sustainable solid fuel for combustion and gasification [165].

Table 2 presents the results of the latest HTC studies of the most dominant biomass types in the literature i.e., waste straw, sewage sludge, spent coffee grain, and poultry

manure/chicken litter. The types of biomass selective for this review were based on the global availability of the resource, problems with direct utilization of the raw biomass for combustion, and favorable feedstock properties such as high moisture, such as spent coffee grain, wet waste straw, poultry litter, and high ash content, including sewage sludge or chicken manure. The discussed and compared parameters include HTC conditions (temperature, and residence time) and corresponding solid product quality expressed by mass yields (MY, %), energy yields (EY, %), and hydrochars higher heating value (HHV, MJ/kg) [166]. In all reviewed reports, HTC temperature had a greater impact on the solid fuel quality compared to time; thus, all results were evaluated relying on the process temperature. Waste straw is the first type of lignocellulosic biomass, and it is a widely utilized feedstock for HTC processing. Low bulk energy density and high content of alkali metals in ash set are required for its removal before large-scale utilization in industrial boilers [163]. HTC processing of waste straw generates highly-carbonized solid fuels with HHV as high as 25.00 ± 1.34 MJ/kg at temperatures of 275 °C, however, at reduced EY of approximately $62.69 \pm 3.65\%$. As shown by Reza et al., waste straw hydrochars, apart from solid fuel, were implemented as an alternative adsorbent [167], where the pH of the feedwater significantly influenced the hydrochars pore volumes and pore size, generating a solid product with higher porosity HTC in an acid environment. Vega et al. [168] reported that the lower initial pH strongly influenced the ash chemistry of the hydrochars, promoting the removal of alkali and alkaline earth metals from the biomass.

Hu et al. studied HTC of spent coffee grounds for solid fuel production [169]. The results showed that high EY 83.93% and HHV 23.54 MJ/kg of spent coffee hydrochar was obtained under moderate conditions, 150 °C, 30 min, and feedstock to water weight ratio of 1:5 compared to traditional DT. According to the literature, spent coffee grounds and grains are a perfect feedstock for HTC due to their high content of lignocelluloses and moisture, which is especially interesting in the Circular Economy business models as an alternative for fossil coal and source of phenolics [170]. In another study HTC of spent coffee grains, it was found that the highest hydrochar HHV, 33.5 MJ/kg, resembled that of anthracite and dry steam coal (Table 2). At optimal conditions of 216 °C and 60 min residence time resulted in maximal HY of ~64% with HHV of 31.6 MJ/kg.

One of the most intensively studied feedstock in recent years is chicken manure and poultry litter, as the by-product of poultry breeding and farming industry, this waste biomass is rich in N and S-containing compounds [171]. Ghanim et al. [172] indicated that HTC at temperatures of 150–300 °C, at residence times 30, 120, and 480 min of the poultry litter improved HHV by 25.17% up to 25.17 MJ/kg. The overall ash content was significantly reduced compared to poultry litter; however, this coincided with lower HY. Huang et al. [165] proposed that the process water produced from hydrothermal carbonization of N-rich poultry litter can be a renewable resource utilized as a liquid N fertilizer. The results showed that the addition of PW relative to pure urea decreased organic N mineralization due to low bio-accessibility, increased N loss due to high soil pH, and decreased NO_3^- -N due to low nitrification substrate. The best fertilizer was found to be 50:50 mixture of urea and post water that provided optimal seeding growth and seed germination, only mildly affecting the microbial activity.

The most promising feedstock to be utilized and managed in the Circular Economy is sewage sludge [173]. Different fractions of sewage sludges at any stage of municipal wastewater treatment plant (MWWTP) allow efficient HTC processing without the requirement of external water [174]. High-temperature processing allows for the destruction of microbial activity in the sludge, promoting the reduction of bio toxicity, deactivation of antibiotics and hormones, and partial removal of alkali ash from the solid fuel, or production of phenol-rich liquid [175].

Danso-Boateng et al. [176] investigated sewage sludge HTC using a batch reactor, where the amount of carbon retained in hydrochars decreased with increasing temperature and time, obtained carbon retentions of 64–77% at 140 and 160 °C, and 50–62% at 180 and 200 °C. An increase in temperature and treatment time resulted in increased energy

content of the hydrochars from 17 to 19 MJ/kg but reduced their energy yield from 88% to 68%. Hämäläinen et al. [177] studied sewage sludge HTC by assessing the role of HTC in digestate processing in centralized biogas plants receiving dewatered sludge from regional wastewater treatment plants and producing biomethane and fertilizers. Apart from enhancing the sewage sludge fuel properties in the obtained hydrochars (Table 2), the integration of HTC to a centralized biogas plant was extrapolated to enhance annual biogas production by 5% and NH_4^+ recovery by 25%. The hydrochars were estimated to produce 83 GJ in combustion or to direct 350,000 kg P to agriculture annually.

Figure 7 presents the drift of the hydrochar HHV with increasing HTC temperature for all investigated feedstock types presented in Table 3. The most improved HHV, with moderate EY loss, was obtained for the spent coffee grain hydrochars, presented with green markers. Afolabi et al. [178] reported that HHV of the spent coffee grain was as high as 31.15 MJ/kg, with EY of almost 84%. Additionally, similar reports described the utilization of poultry manure and waste straw, in which it was determined that poultry manure contained all of the bedding material from the chicken farm, including biomass laying, and usually straw [171]. However, chicken litter was classified as a fraction of poultry farm waste containing much more inorganic content with Ca, N, and S, and significantly lower shares of biomass additives [179]. Only sewage sludge exhibited a lowering trend of HHV with increasing HTC temperature. This phenomenon was also observed in the pyrolysis process, where the devolatilization of the feedstock reduced the calorific value of the solid product, containing mostly ash, with only minimal carbonization [180]. However, for such crucial waste as sewage sludge, each method for its utilization and management, even with minimal energy recovery, can be considered from a waste management perspective.

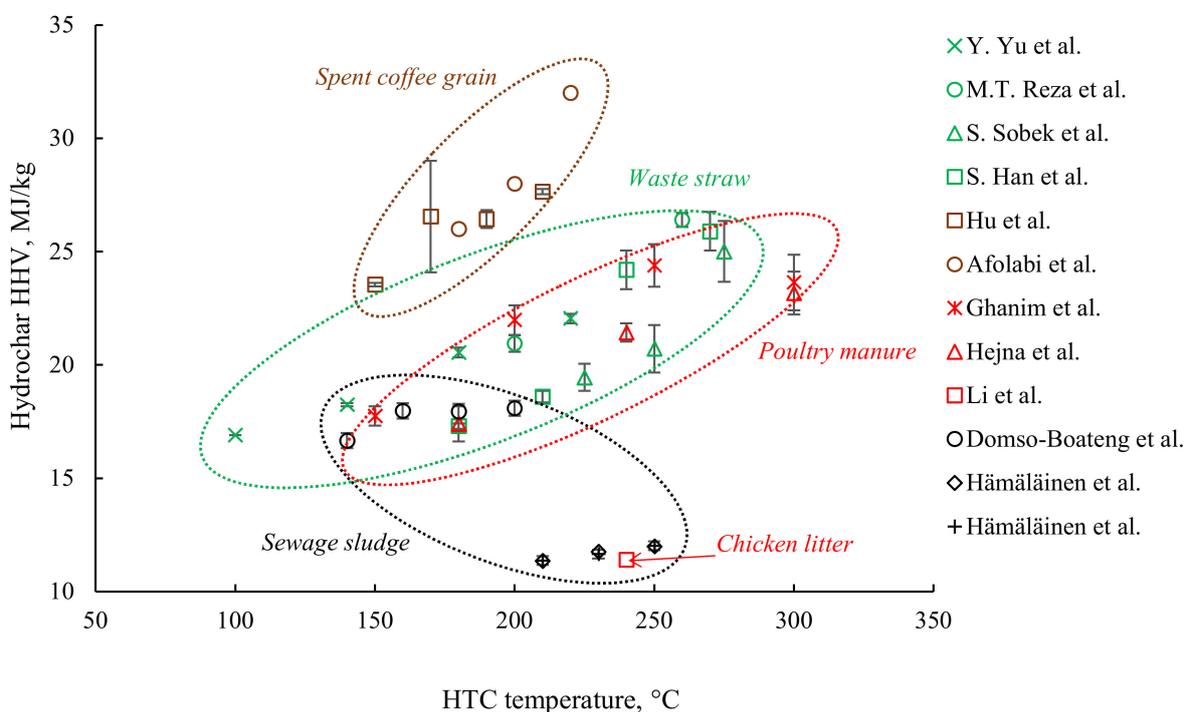


Figure 7. Impact of HTC temperature on straw hydrochars higher heating value and energy yields [163,167,169,172,177,178,181–185].

Table 3. Impact of process parameters on higher heating value and energy yields of the hydrochars from hydrothermal carbonization of different biomass types.

Feedstock Type and Raw Biomass HHV	T, °C	Time	MY, %	HHV, MJ/kg	EY, %	Ref.
Wheat straw (HHV = 20.0 MJ/kg)	200	6 h	53.1 ± 2.24	20.95 ± 0.37	55.61 ± 2.27	Reza et al. [167]
	260		34.3 ± 2.54	26.4 ± 0.31	45.28 ± 2.26	
Waste straw (HHV = 17.04 MJ/kg)	225	10–40 min	64.18 ± 3.19	19.45 ± 0.59	73.19 ± 1.65	Sobek et al. [163]
	250		60.74 ± 3.19	20.71 ± 1.05	73.79 ± 3.19	
	275		42.9 ± 3.19	25.00 ± 1.34	62.69 ± 3.65	
Waste corn straw, no acid washing (HHV = 16.3 MJ/kg)	180	60 min	74.5 ± 0.2	17.30	77.3	Han et al. [181]
	210		67.9 ± 0.4	18.60	77.1	
	240		42.6 ± 1.1	24.20	63.1	
	270		38.5 ± 1.3	25.90	60.8	
Wheat straw (HHV = 16.1 ± 0.1 MJ/kg) *	100	15–30 min	99 ± 1.0	16.90	105 ± 2.5	Yu et al. [182]
	140		90 ± 2.1	18.25	106 ± 2.0	
	180		70 ± 2.0	20.55	90 ± 2.0	
	220		63 ± 2.3	22.05	82 ± 2.0	
Spent coffee grains (HHV = 22.83 MJ/kg)	150	30 min	80.5 ± 2.0	23.54 ± 0.08	83.93	Hu et al. [169]
	170		68 ± 5.0	26.55 ± 2.46	79.95	
	190		63.0 ± 0.5	26.44 ± 0.40	73.88	
	210		62.0 ± 0.5	27.65 ± 0.11	77.05	
Spent coffee grounds (HHV n.a.) *	180	1–5 h	n.a.	26.00	81.16 ± 1.75	Afolabi et al. [178]
	200		n.a.	28.00	85.14 ± 0.64	
	220		n.a.	32.00	83.69 ± 4.09	
Poultry litter (HHV = 17.18 ± 0.02 MJ/kg)	150	30–480 min	79.67 ± 7.93	17.75 ± 0.43	82.27 ± 8.06	Ghanim et al. [172]
	200		42.48 ± 2.99	21.98 ± 0.65	54.42 ± 5.17	
	250		32.35 ± 0.01	24.39 ± 0.94	46.50 ± 1.81	
	300		26.13 ± 3.20	23.64 ± 1.23	36.10 ± 6.33	
Poultry litter (HHV = 15.55 ± 0.052 MJ/kg)	180	30–180 min	66.08 ± 5.43	17.40 ± 0.78	74.05 ± 8.46	Hejna et al. [183]
	240		62.00 ± 5.56	21.43 ± 0.40	85.36 ± 6.03	
	300		42.12 ± 2.51	23.17 ± 0.95	62.66 ± 1.50	
Chicken manure (HHV = 11.95 MJ/kg)	240	10 h	46.6	11.4 ± 0.25	42.55 ± 1.56	Li et al. [184]
Sewage sludge (HHV = n.a.)	140	15–240 min	74.64	16.66	76.14	Danso-Boateng et al. [185]
	160		73.11 ± 7.23	17.97 ± 0.25	81.35 ± 9.60	
	180		66.03 ± 3.82	17.95 ± 0.44	72.80 ± 5.11	
	200		64.40 ± 3.71	18.085 ± 0.80	70.74 ± 5.13	
Sewage sludge, digestate (HHV = 11.49 MJ/kg)	210	30–120 min	87.02 ± 0.79	11.35 ± 0.04	86.00 ± 1.05	Hämäläinen et al. [177]
	230		81.80 ± 0.25	11.76 ± 0.18	83.72 ± 1.06	
	250		73.74 ± 2.12	11.98 ± 0.19	76.93 ± 3.44	
Sewage sludge, dilluted digestate (HHV = 11.9 MJ/kg)	210	30–120 min	83.47 ± 6.82	11.37 ± 0.02	79.72 ± 6.66	Hämäläinen et al. [177]
	230		77.53 ± 0.18	11.65 ± 0.24	75.89 ± 1.39	
	250		74.79 ± 3.95	12.03 ± 0.23	75.54 ± 2.52	

* Values decrypted from the graph. n.a.—not available

3. Discussion

Due to its properties, the use of biochar is a technological challenge. Due to its origin, its use is a current and desirable direction in all sectors where reducing greenhouse gas emissions is necessary. For this purpose, a discussion was held on the use of biochar for CO₂ sequestration and improving the quality of agricultural soils. The analysis showed that in both directions, biochar can be a tool for CO₂ sequestration and an important component that enriches the stimulating potential of the soil solution. On the other hand, biochar is also increasingly used as a component of coke, where it is incorporated into a carbon matrix, and its non-fossil origin is able to make this material more environmentally friendly. Improvement of the effects of biomass carbonization to produce biochar can also be achieved by the use of hydrothermal carbonization (HTC). Compared to other thermal methods, as mentioned earlier, this process is characterized by higher efficiency at lower temperatures, which is a significant advantage when it comes to the technological optimization of the production of this material. This means that the approach to producing

biochar suitable for use in a variety of applications is critical and should be used to optimize technical solutions in accordance with sustainable development.

4. Conclusions

The review that was presented concentrated on the specific applications and utilizations of biochar. Biochar usage was considered in a selective yet interrelated manner. The key components for soil improvement and CO₂ sequestration were examined. It is concluded that because biochar is a time-stable form of carbon, it is generally resistant to degradation, and aids in the stabilization of organic matter in the soil. It is estimated that by 2050, the amount of carbon that can be sequestered in soils worldwide may grow by two to five billion Mg of CO₂. Biochar can help to create a more sustainable agricultural system, owing to its ability to repair damaged soil while producing excellent yields with minimal environmental impact. The pH of biochar influences various factors, such as feedstock type, production temperature, and production length, among others. Many soil restrictions can be altered by applying biochar to the soil, including high Al availability, soil structure, and nutrient availability. Pesticides, fertilizers, and minerals in the soil are absorbed by biochar, hindering their ability to leach into the surface and groundwater.

In support of the European Commission's Green Deal concept, an increasing number of heavy industry businesses are aiming to reduce carbon emissions in Europe by 30% by 2030. Biochar is one of the potential allies in this regard. Carbon is utilized in numerous stages of steel manufacturing, including carbon reduction, where it acts as a carbon source in iron oxide reduction reactions. As a result, the application of biochar may be an appealing alternative to coal and coke. This article provides an overview of activated carbons generated specifically from biomass for use as electrodes in electrochemical energy devices due to their wide range of potential applications in current energy storage technologies. Biochar is abundant, cheap, and "green", and can be created with a very homogenous porous structure, making it a good foundation for the production of more advanced materials. Biochar is a versatile material and has various applications, such as a sorbent, a soil additive, and in industry and metallurgy on a large scale. Pickering emulsions, which have unique features due to the presence of nanoparticles, can be made with biochar. Additionally, biochar has been used to successfully prepare PCMs for energy storage. According to our literature review, the usage of biochar is a fairly broad area of interest and shows how it can be successfully employed in many environmentally essential areas.

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