



Innovative Pathways for the Valorization of Biomass Gasification Char: A Systematic Review

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Abstract: The thermochemical process of gasification is widely utilized for bioenergy production and is particularly attractive due to its high conversion efficiency. However, a gasification byproduct, known as char, is commonly treated as industrial waste despite its attractive qualities. Indeed, due to its high carbon content (up to 91%) and well-developed porosity (specific surface areas up to 1253 m² g⁻¹), gasification char could be considered a cost-effective substitute for activated carbon in various applications, such as catalysis and adsorption. However, its properties are highly dependent on the gasification parameters and the initial feedstock selected, and thus a careful characterization of the material is needed to find the most suitable applications. This review can act as a preliminary assessment of the gasification pathways. In particular, different application areas, their relation to the gasification process, and the char properties are extensively discussed.

Keywords: adsorption; biomass; catalysis; circular economy; gasification; char; waste management



Citation: Abdelaal, A.; Benedetti, V.; Villot, A.; Patuzzi, F.; Gerente, C.; Baratieri, M. Innovative Pathways for the Valorization of Biomass Gasification Char: A Systematic Review. *Energies* **2023**, *16*, 4175. https://doi.org/10.3390/en16104175

Academic Editor: Antonio Galvagno

Received: 25 April 2023 Revised: 14 May 2023 Accepted: 16 May 2023 Published: 18 May 2023



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1. Introduction

When biomass is sourced sustainably it can be a very attractive renewable energy source aiding in the transition towards climate neutrality. In 2017, Europe consumed 424 million m^3 of woody biomass for bioenergy production [1]. Among the different processes developed to harness the chemical energy stored in biomass, gasification offers the possibility to convert biomass not only into bioenergy but also into biofuels and other valuable materials. Biomass gasification results in a gas constituted of mainly carbon monoxide (CO) and hydrogen (H_2). This gas is called synthesis gas or syngas, which can be used directly in diesel engines, and for generating electricity and heat. H_2 can also be separated from the syngas to be burned or used in fuel cells. Moreover, liquid fuels can be produced from syngas by applying processes such as Fischer–Tropsch [2]. The conversion of biomass to syngas and then to biofuels could be a vital solution for renewable energy storage, which makes the gasification process more attractive [3]. Gasification plants can be classified based on their final output, expressed in megawatts of electrical energy (MW_e), to small-scale (70 kW_e–3 MW_e), medium-scale (3–10 MW_e), or large-scale (>100 MW_e) [4]. Typically, the small-scale decentralized system focuses on decentralized electricity generation and combined heat and power (CHP) applications [4]. At the moment, there are over 1700 CHP facilities in operation in Europe [5]. The production of gaseous or liquid biofuels or co-firing is more common at large-scale facilities. Currently, the downdraft gasifier is the most widespread gasification technology. However, also newer technologies such as updraft, double-fired, floating bed, and gasifiers with hot gas filtering are gaining momentum. The scale of operation also grew significantly, from around 180 kWel up to 1 MWel, which increased the total output volume of byproducts, such as tar and char [6].

In particular, char—the solid carbonaceous residue of the process accounting for nearly 10% of the original feedstock [7]—is still considered an industrial waste that requires proper disposal and handling, which can represent a non-negligible cost. However, depending on the feedstock and the technology of production, chars can exhibit unique features in terms of chemical composition (high carbon and mineral content), and textural properties (high porosity and surface area) leading to various potential uses. For instance, gasification char (GC) produced from woody biomass tends to have a larger surface area and higher carbon content compared to pyrolysis char [8]. Moreover, the highest specific surface area values were associated with dual-stage gasification technologies [9]. For example, GC from a dual-stage pilot scale gasifier had a surface area of 1253 m² g⁻¹ (Table 1). Other qualities, such as inorganic material content, also depend on the feedstock and process conditions. On average, GC could have 55 wt.% ash content for non-woody biomass or 18 wt.% for woody biomass (Table 1). At high process temperatures, some inorganics become volatile and have lower quantities in the final char (e.g., Zn, Cd, As, Se, K, and Na) [10]. The high process temperature typical of gasification also results in the loss of functional groups and a smaller fraction of aromatic C-H groups [11,12]. Nevertheless, GC has a high degree of aromaticity and environmental stability, which are both correlated with the low H/Cand O/C molar ratios. These ratios are essential parameters for measuring the degree of carbonization and stability, particularly for carbon sequestration and soil applications. The GC generally has these ratios well within the limits set by the European Biochar Certificate (EBC): 0.6 and 0.4, for H/C and O/C, respectively [13].

Hence, GC is a promising material, and its wise utilization could ultimately help enhance the environmental sustainability of the gasification process and drive the shift towards a circular economy, where the concept of "end-of-life" is replaced by reducing, reusing, recycling, and recovering materials during the production, distribution, and consumption phases [14]. Additionally, the Intergovernmental Panel on Climate Change (IPCC) has recently listed char as one of the mitigation options for achieving global emissions reduction targets [15]. Furthermore, combining biomass gasification with not only carbon dioxide capture and storage (BECCS) but also char valorization could lead to negative emissions [16,17]. Further, the economic viability of large-scale gasification processes could be improved through char valorization [18]. In 2020, the GC market experienced a 70% increase in growth rate [19], and recently, its utilization has been widely seen as an example of closing the loop in the field of sustainable energy [20].

This review aims to highlight the current applications of GC to guide future research in directions that are tailored to char characteristics in light of the circular economy principle. To the authors' knowledge, this is the first review carried out in the field of GC valorization. It lays the foundation for future GC research directions, especially as catalysts and adsorbents, which have grown rapidly in the last few years. It also highlights the differences between pyrolysis char, which is quite mature and has many applications, and GC, which is not at the same advancement in application. Briefly, char valorization pathways are mainly focused on adsorption (Figure 1), for instance, adsorption of pharmaceuticals (organic micropollutants), dyes, and removal of nutrients from aqueous solution. The next major application field is catalysis such as tar reforming and catalyst support. GC was also implemented in gas adsorption applications such as CO_2 , and H_2S adsorption. GC can also be found in other fields but with limited studies, such as in agricultural applications, polymers, electrochemical applications, and as an additive in anaerobic digestion and construction materials (roads, building blocks). These applications are explored in detail in the following sections. Furthermore, GC can be used as fuel, as recently reviewed by [13], but this does not fall under the circular economy principle (or it is the least favorable option).

| Precursor | Technology | Gasifying Agent | Scale | С | Ash | S _{BET} * | Activation | Reference |
|--|---|--------------------|-----------------------------------|----------------------|----------------------|--------------------|-------------------------------------|----------------------|
| | | | | (%) | (%) | $(m^2 g^{-1})$ | | |
| Spruce Woodchips | Floating fixed-bed | Air | Commercial | 91.4 | 3.7 | 308 | | [21] |
| Woodchips | Downdraft | Air | Lab | 76.0 82.1 81.3 | 3.3 2.2 2.4 | 379 385 517 | | [22] |
| Spruce Woodchips | Dual-stage | Air | Pilot | 87.6 | | 1253 | | [23] |
| Spruce, Pine, and Fir Sawdust | Dual fluidized bed | Steam | Pilot | 91.1 | 13.2 | 458 | | [24] |
| Woodchips Wood Pellets | Dual-stage Rising co-current | | | 81.3 81.2 | 14.6 16.1 | 603 403 | | |
| Woodchips Woodchips | Downdraft Dual-stage | Air | Commercial | 80.6 75.9 | 15.8 15.1 | 427 774 | KOH | [25] |
| Woodchips Woodchips Woodchips | Dual-stage Dual-stage Downdraft | Air | Commercial | 78.1 79.0 68.6 | 15.0 22.2 27.8 | 739 587 352 | ZnCl ₂ | [26] |
| Wood Pellets Woodchips Woodchips | Rising co-current Downdraft Downdraft | Air | Commercial | 83.4 48.0 87.6 | 13.5 49.5 8.7 | 128 78 281 | | [27] |
| Woodchips Mesquite Woodchips | Dual-stage Downdraft | Air | Pilot | 91.4 84.5 84.5 | 4.2 9.8 9.8 | 272 777 737 | CO ₂ H ₂ O | [28] |
| Gliricidia Wood | | Air | Commercial | 50.0 | | 714 | | [29] |
| Woodchips | Downdraft | Air | Pilot | 52.1 | | 590 | CO ₂ | [30] |
| Woodchips | Fluidized bed | Air | Pilot | 72.0 | 23.0 | 1509 | K ₂ CO ₃ | [31] |
| Poplar Wood | Fluidized bed | CO ₂ | Lab Lab | | | 435 687 | | [32] |
| Rubber Tree Roots | Describert | A | Commercial | 68.0 | 5.5 | 478 | КОН | [33] |
| Almond Shells Corncob Char Switchgrass | Downdraft Downdraft Downdraft | Air Air Air | Commercial Commercial Pilot | 78.5 73.1 | 8.6 | 63 162 944 | КОН | [34] [35] [36] |
| Husks | | | | 56.8 | 21.7 | 5 | | |
| Poultry Litter Wood Pellets Wood Waste 1 | Fluidized bed | | Pilot | 12.6 29.1 39.6 | 74.9 53.6 45.2 | 12 5 2 | | [37] |
| Wood Waste 2 Paper and Plastic Waste 1 | | | | 39.4 34.4 | 48.9 45.1 | 2 65 | | |
| Paper and Plastic Waste 2 Paper and | | | | 26.2 | 55.1 | 42 | | |
| Plastic Waste 3 | | | | 15.8 | 75.4 | 20 | | |
| MSW | Fixed-bed downdraft | Air/Steam | Commercial | 48.3 29.7 | 50.4 54.5 | 3 11 | | [38] |
| MSW | Fluidized bed | | Commercial | 56.2 | 39.4 | 13 | | [39] |

Table 1. Total carbon content, ash content, and specific surface area of chars from selected studies on GC valorization.

 $^{\ast}\,S_{BET}$ values are referred to the activated char when activation is performed.



Figure 1. Summary of char applications referred to in the literature (relevant to this review).

2. Methods and Data Analysis

2.1. Literature Review Strategy

The different applications of char from commercial, pilot, and laboratory-scale biomass gasification plants were investigated in the literature. The investigation covered publications from four databases (Scopus, Web of Science, ProQuest, and Google Scholar) from 2012 to 2023. The following keywords: gasification AND char, char applications AND review, char AND gasification $-CO_2$ -coal, commercial AND gasifier AND char, etc., were used in searching the selected databases for relevant publications. The reference lists of relevant papers were further analyzed using the tool provided at https://www.connectedpapers.com/ (accessed on 4 March 2023) to identify related publications for the review.

2.2. Study Selection and Data Extraction

2.2.1. Pyrolysis and Gasification

At the beginning of this study, it was essential to classify the various types of chars and how they are produced to exclude nonrelevant publications from the review. A common trend in the literature is to use the terms pyrolysis (biochar) and GCs interchangeably despite being drastically different. Although both pyrolysis and gasification are thermochemical processes that convert biomass into solid, liquid, and gas fractions, pyrolysis can be distinguished from gasification by the absence of oxygen in the conversion process. Indeed, in the gasification processes, a partial oxidation of biomass takes place in the gasification chamber at elevated temperatures and atmospheric pressure or higher [40]. The pyrolysis process's main product is either the solid or liquid fraction [41]. The fraction of pyrolysis char depends on process temperature and holding time. It ranges from 35% to 50% in slow pyrolysis and as low as 10% in flash pyrolysis [42]. On the other hand, in gasification, the main product is synthetic gas with a limited amount of char (up to 10%) and liquids [40]. Figure 2 summarizes the process directions of the main thermochemical conversions of biomass. In addition to pyrolysis and gasification, char can be produced through other thermochemical pathways such as hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and torrefaction. The yield of char (also known as hydrochar) from HTC and HTL is 35–80% [43] and 3–55% [44], respectively, while char yield from torrefaction is in the range 60–80% [45]. Hydrochar is rich in oxygen functional groups and has a high cation exchange capacity. Nonetheless, it has a smaller surface area, less porosity, and lower carbon stability, compared to both pyrolysis and gasification chars [46]. For example, the surface area of hydrochar is usually below 200 m² g⁻¹ [43].



Figure 2. Key thermochemical process parameters, and C-H-O diagram of the gasification process, adapted from [47].

Comparing pyrolysis char produced at 400 and 600 °C using an auger reactor, and GC using two laboratory-scale fluidized bed systems operating at a relatively low temperature $(600-750 \degree C)$ revealed so many details about the difference between those two materials [48]. The most notable parameters are the process temperature and the presence or not of an oxidant. Gasification is usually conducted at a higher temperature range (600–1200 °C) than pyrolysis (300–800 °C) [42]. Increasing pyrolysis temperature decreases the molar ratios H/C and O/C as carbonization takes place. The GCs, produced at the same or higher temperatures, had lower H/C and O/C values, indicating a higher degree of carbonization of the original material. Higher temperatures and the presence of oxides also lead to larger pore volume and higher specific surface area beneficial for adsorption and catalytic applications [48,49]. The impact of process residence time had a larger effect at lower temperatures. Residence time comes second after process temperature [48,50]. Moreover, the impact of the gaseous environment was also found to vary with temperature. In fact, at 600 $^{\circ}$ C, the effect of the gaseous environment was negligible. However, increasing the temperature to 750 $^{\circ}$ C led to increased pore volume and specific surface area going from N₂ to air and then to steam. Aside, polycyclic aromatic hydrocarbons (PAHs) concentration was found to be related to the contact time of producer gas and char. In particular, separating the char and the produced gas at an early stage results in low PAHs content in GCs [48].

To avoid confusion between biochar and GC in this study, the former is called pyrolysis char, and the latter is called GC. The EBC clearly defines biochar as a porous material with a high carbon content produced through plant biomass pyrolysis. As stated by EBC, the applications of biochar must ensure that the carbon content remains stored as a long-term carbon sink or act as an alternative to fossil carbon in industrial manufacturing. Therefore, char made to be burned for energy generation does not fall under the EBC definition of biochar. Char from the gasification process can only fit to the EBC definition plants that are optimized for gas production. As a result, biochar is specific to the pyrolysis process and is characterized by its sustainable production, quality, and particular applications. A recent technical report by the European Commission has gone a further step by eliminating the use of the word biochar and replacing it with "pyrolysis and gasification materials" to clearly indicate the production technology and avoid confusion [52].

2.2.2. Subsequent Gasification of Pyrolysis Char

Another misleading terminology rises when subsequent gasification of pyrolytic char—usually carried out using steam or CO_2 —is referred to as GC. For instance, the process of biomass activation/gasification with CO_2 is divided into three global reaction steps. The steps involve: heating and drying the biomass; then, pyrolysis of the dried biomass to release volatile organic matter (CO_2 , CH_4 , CO, H_2 , tar) and create char; and, finally, the oxidation of the char by CO_2 to produce CO [53]. In a typical single-stage

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gasification process, all steps occur in the same chamber, making it difficult to control the temperature, gas environment, and holding time of each step separately. For this reason, the gasification of pyrolysis char results in different material characteristics compared to gasification char. The work of Zhai et al. and Yan et al. are some examples from the literature where subsequent gasification of pyrolysis char is referred to as GC [54,55]. In addition, pyrolysis char studies are commonly found in review articles that are focused on GC. For example, the work of You et al. refers to several studies on slow pyrolysis, fast pyrolysis, and hydrochar applications, in a review of sustainable biochar systems through gasification [13], as GC. Finally, in a dual-stage gasifier where the gasification process takes place in two steps, i.e., pyrolysis and gasification in series, there could be a similarity between the properties of GC and the subsequent gasification of pyrolysis char.

3. Char Applications

GC has gained widespread attention in recent years due to its unique properties and versatility in various applications. GC was found to be effective in adsorption applications, particularly in water treatment processes, gas adsorption, and soil remediation. In the field of catalysis, char is used as a support for catalysts to improve their efficiency and stability. It has also been used for tar reforming in the upgrading of producer gas. In agriculture, it has been used to improve soil fertility and crop yield. Char has also been used in the production of polymers, anaerobic digestion, composting, electrochemistry, construction, and other cutting-edge applications. In most of the studies reported in the following sections, GC was used without prior activation. Nonetheless, reports describing physical activation, mainly through H_2O (steam) and CO_2 or chemical activation of GC, can be found in the literature. In several studies, steam activation showed an improved adsorption capacity over unmodified GC due to the abundance of surface function groups [28]. Similarly, tar reforming with chemically activated GC demonstrated better performance than unmodified GC [36]. Moreover, from the studies covered in the following section, activated GC showed better or comparable performance to AC.

3.1. Adsorption

Adsorption is one of the most promising applications of GC, particularly in the areas of water treatment, gas adsorption, and soil remediation. Research has shown that GC can be successfully utilized in removing pollutants such as organic micropollutants, dyes, and heavy metals from wastewater. In the soil, it has also been found to effectively remove certain metals. In addition, GC has been explored in the adsorption of carbon dioxide and hydrogen sulfide.

3.1.1. Water Treatment

Commercial GC is a possible low-cost alternative to activated carbon (AC) in the field of water treatment. Indeed, the two materials show many similarities. Typically, the specific surface area of AC is in the range 500 to 1500 m² g⁻¹ [56]. The lower boundary of this range is commonly achieved in most wood-based GC. This material could be used without modification or with further upgrades through physical or chemical activation. GC with further activation can have a comparable specific surface area to that of the upper boundary of AC. For instance, char produced from pine wood gasification at 850 °C in a pilot-scale fluidized bed had a specific surface area of 1509 m² g⁻¹ after activation with K₂CO₃ [31]. It is worth noting that ACs are synthesized using a controlled process to carefully tune their properties for a specific group of adsorbates, unlike GC that is a process byproduct and not developed specifically to be adsorbents [9]. Moreover, char properties depend mainly on the gasification process conditions (temperature, gasifying agent, equivalence ratio) and biomass type [57]. Process scale also seems to influence the char properties. Additionally, it was observed that, in studies investigating certain pollutants such as dyes, the gasification feedstocks used were quite diverse. Moreover, char

activation was commonly implemented to chars from untypical feedstocks such as MSW due to its limited performance without activation.

Usually, woodchips are the preferred feedstocks for char production, but also MSW [38], palm shells [58], and almond shells [34] were used. The studied pollutants are rather organic ones (micropollutants, dyes, etc.) with limited studies found on nutrients and heavy metals removal. Table 2 gives a summary of gasification parameters, char properties, and the targeted pollutants covered in this section. It also elaborates on certain studies where more details are given about solution type (real or synthetic wastewater), initial pollutant concentration, and measured and predicted adsorption capacities. Overall, GC used in water treatment applications was produced from woodchips via downdraft gasifiers with specific surface areas ranging from 308 m² g⁻¹ [21] to 714 m² g⁻¹ [29]. When activated physically and chemically, this value can increase to 776 m² g⁻¹ [28] and 1509 m² g⁻¹ [31], respectively. Unconventional feedstocks typically result in lower specific surface area. For example, GC produced from almond shells had a surface area of 63 m² g⁻¹ [34].

Table 2. Summary of gasification parameters, char properties, and the targeted pollutants used in water treatment.

| Gasific | Char | | | Application | | | | | Reference | |
|---|------------|------|------|------------------|-------------------------------|--|-------------------------------|--|--|------|
| Biomass | Scale | С | Ash | S _{BET} | Pollutant | Matrix | Initial Concen- tration | Adsorption Capacity | Adsorption Capacity (AC or Similar) | |
| | | % | % | $m^2 g^{-1}$ | | | ${ m mg}~{ m L}^{-1}$ | ${ m mg~g^{-1}}$ | ${ m mg~g^{-1}}$ | |
| | | | | | Organic Micropol | lutants | | | | |
| Spruce | | | | 308 | Benzotriazole | Wastewater Treatment Plant Effluent | 5.60×10^{-3} | 166.9 ^a | 635.8 | [01] |
| Woodchips | Commercial | 91.4 | 3.7 | | Carbamazepine | | 0.28×10^{-3} | 9.3 ^a | 46.5 | [21] |
| | | | | | Diclofenac | Lindent | 1.6×10^{-3} | 20.9 ^a | 126.0 | |
| C_{1} | | | | | Metoprolol | | 10^{-3} | 58.7 ^a | 172.7 | |
| Woodchips | Commercial | | | 28 | Oxytetracycline | Deionized | 500 | 520.0 ^c | | [59] |
| Shell | Commercial | | | 712 * | Carbamazepine | Ultrapure | | 268.7 ^b | | [58] |
| Pine Woodchips | Pilot | 72.0 | 23.0 | 1509 ** | Acetaminophen Caffeine | Ultrapure | | 434.8 ^a 500.0 ^a | 267.7 296.3 | [31] |
| Pubbor Troo | | | | | Malachita | | | | | |
| Roots | Commercial | 68.0 | 5.5 | 478 ** | Green Roactivo Black | | 300 | 259.5 ^d | | [33] |
| Biomass Residues | Pilot | | | 404 | 5 Basic Blue 12 | Deionized | | 35.7 ^a 80 4 ^a | 128.2 86.2 | [60] |
| Wood Residue | | | | 350 | Black NF1200 | | 400 | 805.0 ^a | 00.2 | [61] |
| Mesquite Woodchips | | | | 776 * | Rhodamine B | | 30 | 189.8 ^a | | [28] |
| 1 | | | | | Heavy Meta | ls | | | | |
| Gliricidia Woodchips Rice Husk | Commercial | | | 28 | Cr (VĬ) Cd (II) | Deionized | | 7.5 ° 922.0 ° | | [59] |
| and Polyethy- | Pilot | 25.9 | 68.3 | 5 | Cr (III) | Industrial Wastewater | 100 | 14.9 | 14.0 | [62] |
| lene Pine and Spruce Woodchips | Pilot | 61.8 | | 259 ** | Fe (II) Cu (II) Ni (II) | Milli-Q | 25–125 | 21 23 18 | 13.9 5.1 2.9 | [63] |
| A 1 1 | | | | | Other Polluta | ints | | | | |
| Shells | Commercial | | | 63 | Phenol | Deionized | 5×10^3 | 65.0 ^a | 270.0 | [34] |
| Woodchips | Commercial | | | 28 | Glyphosate | | 250 | 83.0 ^c | | [59] |
| Gliricidía Woodchips | Commercial | 50.0 | 19.7 | 714 | Glyphosate | D' ('11 1 | 100 | 44.0 ^a | 48.0 | [29] |
| Woodchips | Pilot | 52.1 | | 590 * | Phosphates Nitrates | Distilled | 140 | 30.2 ^a 11.2 ^a | 8.7 14.6 | [30] |

* physical activation, ** chemical activation, ^a Lang, ^b Redlich–Peterson, ^c Hill, ^d n-BET.

Organic Micropollutants

GC utilized in organic micropollutants removal was mainly produced from woody biomass such as spruce woodchips, pine woodchips, or wood residues. Limited studies examined other waste streams such as pharmaceutical residues [64] or MSW [38], as they tend to be very heterogeneous with poor surface properties. Back et al. investigated the removal of benzotriazole, carbamazepine, diclofenac, metoprolol, and sulfamethoxazole from wastewater treatment plant effluent using GC produced from a commercial gasification plant [21]. The char was characterized by high carbon content (91%) and surface area $(308 \text{ m}^2 \text{ g}^{-1})$ leading to a high removal rate of >90% [21]. Depending on the tested compound, GC performed on average 65-80% less than AC. Testing char in real wastewater showed that dissolved organic matter had a strong impact on adsorption due to the competition for active site and pore blockage, as this is generally observed with adsorption on AC. Similarly, To et al. examined char from a commercial biomass gasification power plant in Indonesia in the removal of carbamazepine from ultrapure water [58]. The char was activated to increase the surface area using CO₂ at different conditions, and the highest BET surface area achieved was 711.5 m² g⁻¹. The maximum modeled adsorption capacity (q_m) was 268.7 mg g⁻¹, which was much higher in comparison to other adsorbents such as granular carbon nanotubes–alumina composite (37 mg g^{-1}). By using K₂CO₃, Galhetas et al. activated char from a pilot scale gasifier to adsorb acetaminophen and caffeine from ultrapure water [31]. The study found that activated chars were very effective and their removal rate for the given experimental conditions was superior to commercial AC. For activated char, the q_m of acetaminophen and caffeine was 434.8 and 500.0 mg g⁻¹, respectively, while for commercial AC 169.5 and 303.0 mg g^{-1} [31]. Ramanayaka et al. developed nanochar based on char from a commercial biomass gasification power plant [59]. The aim was to study the removal capacity of oxytetracycline from DI water. The nanochar had a flakelike structure with length and diameter of >1 μ m and 50–150 nm, respectively. The authors report a high q_m of 520 mg g⁻¹ that was attributed to the structural modification of char resulting in a material similar to graphite and with an improved adsorption performance [59]. Carnimeo et al. explored the potential of poplar wood GC for the adsorption of xenoestrogens 4-tert-octylphenol and bisphenol A and the herbicide metribuzin from water [65]. The char was characterized by 74.5 and 8.8 %, carbon and ash content. The authors reported a very rapid sorption with a prominent role of hydrophobicity in the sorption process [65].

Dyes

Unlike pyrolysis char, which has been extensively studied as an adsorbent for dye removal with over one hundred papers published according to a recent review [66], testing of GC is still in its infancy. Removal of malachite green dye (cationic dye) using tree roots GC showed a modeled q_m of 259 mg g^{-1} [33]. Char activated with KOH and CO₂ in microwave irradiation had a surface area and a total pore volume of 478 m² g⁻¹ and 0.273 cm³, respectively. For comparison, Parthasarathy et al. reported for pyrolysis char used as adsorbent for dye removal, surface areas ranging from 3 to 640 m² g⁻¹ and pore volumes ranging from 0.03 to 0.271 cm³ [66].

In a similar study, the impact of biomass GC size on malachite green dye removal was explored. The results showed a higher removal percentage for fine (150–300 μ m) char from woodchips in comparison to wood pellets [67].

Mesquite woodchips GC was used to investigate its adsorption capability for rhodamine B (RhB, cationic dye). Char was activated using CO₂ and steam [28]. Less than 10% of RhB was removed using raw char while 100% removal was achieved within the initial 50 min using steam-activated char, and the modeled q_m was 190 mg g⁻¹. Despite having a similar surface area (~736 m² g⁻¹), steam-activated char outperformed CO₂-activated char mainly due to the abundance of hydroxyl (–OH) and carboxyl (–COOH) groups on the char surface [28]. Kelm et al. explored the potential of wood waste GC in azo dye (Indosol Black NF1200, anionic dye, pH at point of zero charge: pH_{PZC} = 9.8) removal. The char resulted in 99% removal of dye at an initial concentration of 50 mgL⁻¹ and pH 2. At pH = 12, the adsorption equilibrium was reached after 3 h and the Langmuir q_m was around 14 mg g⁻¹. On the contrary, at pH = 2, the equilibrium was reached after 5 min and the experimental q_m value was 185 mg g⁻¹ [61]. Thus, the adsorption of anionic dyes is favored at a pH below pH_{PZC}. Wood waste GC was also utilized in the removal of anionic reactive black 5 (RB5) and cationic basic blue 12 (BB12). The char with a surface area equivalent to 403 m² g⁻¹ had a satisfactory q_m of 35.67 mg g⁻¹ (RB5), and 80.41 mg g⁻¹ (BB12) [60].

Heavy Metals

GCs from pine and spruce woodchips were utilized for the removal of iron (II), copper (II), and nickel (II) cations from an aqueous solution. The highest experimental q_m reported for iron, copper, and nickel by activated carbon residue were 21, 23, and 18 mg g⁻¹, respectively [63]. Nanochar produced by Ramanayaka et al. that was developed for micropollutants removal was used in the removal of chromium anions Cr (VI), and cadmium cation Cd (II) from DI water [59]. The reported q_m for Cr (VI) and Cd (II) was 7.46 and 922 mg g⁻¹, respectively. In aqueous media, cadmium exists as a cation (Cd²⁺) that can bind to the negatively charged nanochar surface at pH > 7.4 (pH_{pzc}), while dichromate ions—negatively charged—are repelled from the nanochar surface and physisorption does not take place [59]. Char from the co-gasification of 80% rice husk and 20% polyethylene was tested for the removal of Cr (III) cations from industrial wastewater. Column tests showed a q_m of 3.25 and 7.83 mg g⁻¹ for GC and commercial AC, respectively [68], while 8 mg g⁻¹ was observed for batch tests and GC [62]. In short, removal is generally favored on a basic char surface for cations rather than anions.

Other Pollutants

Char was also investigated as an adsorbent for nutrients such as phosphates and nitrates (anions) in aqueous solutions. In particular, Kiplimaa et al. used char produced from a pilot woodchips downdraft gasifier in Finland [30]. The results showed enhanced phosphate removal using activated char over commercial AC for an initial phosphate concentration range 20–140 mg L⁻¹ at optimum solution pH 6. For the same range, activated char achieved a removal rate of 50–60%, while AC achieved a 20–50% removal rate. On the other hand, the nitrate removal rate was higher for AC. The Langmuir q_m for phosphate and nitrate was 30.2 and 11.2 mg g⁻¹ for activated char, and 8.7 and 14.6 mg g⁻¹ for commercial AC [30].

In terms of herbicides, Mayakaduwa et al. used char from a commercial biomass gasification power plant operating on gliricidia woodchips to remove glyphosate from DI water [29]. It is a type of organophosphorus herbicide widely used to control annual and perennial weeds. The char had a large surface area equivalent to 714 m² g⁻¹. The q_m of 21.6 mg g⁻¹ was reached at the pH range 5–6 [29]. The nanochar studied by Ramanayaka et al. was also tested for glyphosate removal from DI water [59]. The authors report a moderate q_m of 83 mg g⁻¹ and the interaction of glyphosate with nanochar can be suggested as a physisorption process through electrostatic and van der Waals attractions [59].

With the main objective of treating gasifiers' scrubber wastewater, Catizzone et al. compared phenol adsorption performance using chars produced from biomass pyrolysis and gasification with commercial AC [34]. The GC was produced in a commercial downdraft gasifier operating on almond shells. The modeled q_m was 65 mg g⁻¹ for GC, compared to 270 mg g⁻¹ for AC. This is also within the range for micropollutants removal relative to AC. Furthermore, the authors explored the adsorption performance using actual wastewater and concluded that the char usage rate was 1.5 times higher than modeled adsorption [34].

GC (surface area: 491.9 m² g⁻¹; pore volume: 0.315 cm³ g⁻¹) produced from açaí endocarp was chemically activated and then used to adsorb fermentation inhibitors, such

as furfural. The modeled q_m was 48.02 mg g⁻¹ for furfural with 100%, 52%, and 40.4% removal of 5-Hidroximetilfurfural, furfural, and acetic acid, respectively [69].

3.1.2. Gas Adsorption and Soil Remediation

GC utilization can be also found in gas adsorption applications such as carbon capture and storage. These applications are summarized in Tables 3 and 4. For instance, the CO₂ adsorption capacity of five commercial GCs was analyzed and compared to two commercial ACs. The highest uptake (3.7%) was observed for KOH-activated char, which was comparable (3.01%) to the commercial AC that was tested [25]. A more recent study utilized two GCs (woodchips and a 70:30 mixture of woodchips and chicken manure) [70]. Char produced from woodchips and chicken manure mixture then activated with KOH had the largest surface area (1408 m² g⁻¹) and demonstrated the highest CO₂ adsorption capacity of 12.85% [70].

Table 3. Summary of gasification parameters, char properties, and the targeted hazards used in gas adsorption.

| Gasification | | | Char | | | | Reference | | | |
|-------------------------------|------------|----|------|------------------|-----------------|---------------------------------------|-------------|------------------|------------------------------|------|
| Biomass | Scale | С | Ash | S _{BET} | Hazard | Matrix (Flow) | Temperature | Uptake | Uptake (AC or Similar) | |
| | | % | % | $m^2 g^{-1}$ | | mL min ⁻¹ | °C | ${ m mg~g^{-1}}$ | ${ m mg}{ m g}^{-1}$ | |
| Woodchips Woodchips | Commercial | 76 | 15 | 774 | CO ₂ | CO ₂ :N ₂ (40) | 50 | 3.7 (%) | 3.0 (%) | [25] |
| and Chicken Manure | Pilot | 72 | | 1409 | | CO ₂ (100) | 25 | 128.5 | 95.8 | [70] |
| Woodchips | Commercial | 78 | 15 | 587 | | H ₂ S:N ₂ (100) | 25 | 6.9 | 2.6 | [71] |
| Pinus Patula | Lab | 76 | 3 | 379 | H_2S | Synthetic Syngas * | 25 | 18.0 | 20.3 | [22] |
| Grandis | | 82 | 2 | 385 | | (20) | | 15.5 | | |
| Paper and Plastic Waste | Pilot | 34 | 45 | 65 | Hg | Synthetic Gas ** (500) | 150 | 0.17 | 0.23 | [37] |

* H₂, CO, CO₂, CH₄. ** O₂, SO₂, NO₂, HCl.

Table 4. Summary of gasification parameters, char properties, and the targeted hazards used in soil remediation.

| Gasification | | | Char | | | Reference | | | |
|----------------------|------------------------------|----|--------|--------|---------------------------------|---|-------------------------------------|--------------------------|------|
| Biomass | Scale C Ash S _{BET} | | Hazard | Matrix | Reduced Dissolution Rates | Immobilized Bioavailability | | | |
| Gliricidia Sepium | Commercial | | | | Pb Cu | 17 g Pb/kg soil and 10 wt.% char 1.1 g Cu/kg soil and 10 wt % char | Pb: 10.0 to 99.5% Cu: 15.6 to | | [72] |
| | | 49 | 21 | 714 | Ni Mn | 6.5 g Ni/kg soil and 5 wt.% char 2.6 g Mn/kg soil and 5 wt.% char | <i></i> | Ni: 68–92% Mn: 76–93% | [73] |

Moreover, the adsorptive removal of H_2S using GC was investigated in some recent studies. Marchelli et al. compared the performances of five chars from different small-scale gasification plants and two commercial AC [71]. The highest H_2S adsorption capacity (6.88 mg g⁻¹) was obtained using a char produced from a dual-stage gasifier operating at 900 °C and characterized by the highest surface area (586.72 m² g⁻¹). The authors also attributed this behavior to the abundance of metal and oxygen content in the best-

performing char [71]. Similarly, char from a downdraft laboratory-scale gasifier operating on debarked fresh logs of Pinus Patula (PP) and Eucalyptus Grandis (EG), was tested for H₂S adsorption from synthetic gas containing H₂S (composition: 65.0% CH₄, 34.8% CO₂, 2000 ppm H₂S). The scrubbing test resulted in adsorption capacities of 18.0, and 15.5 mg g⁻¹ for PP and EG chars, respectively. In comparison, commercial AC achieved a removal rate of 20.3 mg g⁻¹ [22]. Mercury removal was explored using eight biomass GCs from agricultural sources, poultry litter and wood, and one AC. The chars were obtained from a pilot fluidized bed gasification plant (500 kW) with a circulated fluidized bed in the Netherlands. The mercury concentration during the test was approximately 100 µg m⁻³. Char derived from the paper and plastic waste mixture showed the highest capacity of 172 µg g⁻¹ [37]. The impact of char on the release rate of certain trace metals in soils contaminated with organic and inorganic acids was assessed in two studies [72,73]. The addition of woodchips GC to the contaminated soil reduced the bioavailability of Ni and Mn, and reduced the Pb and Cu release rate to the soil.

3.1.3. Removal Mechanisms

Based on the previous discussion, the adsorption mechanisms are found to be highly dependent on the char properties (i.e., surface area, functional groups, pH_{pzc}), adsorbate properties (i.e., pKa, speciation, species size) and the solution pH. For water treatment applications, the predominant adsorption mechanisms reported are hydrophobic interaction, electrostatic interaction, π - π interactions, pore diffusion, and H-bonding. Unmodified GCs are relatively hydrophobic due to their highly aromatic structure, despite containing limited nitrogen and oxygen surface functional groups. On the other hand, steam-activated GC tends to have an abundance of hydroxyl (-OH) groups and carboxylic (-COOH) groups, which impact the electrostatic interaction between the char and adsorbate [28,74]. Depending on the working solution pH, the char pH_{pzc} , and the pollutant pKa, the hydroxyl and carboxyl functional groups can be deprotonated or protonated leading to either strong electrostatic repulsion or attraction. For electrostatic attraction to take place, the following inequality should be true: $pKa < solution pH < pH_{pzc}$ [75,76]. For metal removal, metal precipitation as hydroxides can take place in addition to adsorption [77]. In the case of metal ions, adsorption could be the dominant removal mechanism. However, precipitation can still occur depending on the pH and the concentration of the metal ions present in the solution [78].

3.1.4. Challenges

From the studies covered in this section, it can be seen that raw GC has good removal capacity that can be further enhanced through char activation. Moreover, testing in real wastewater effluent has shown an impact on adsorption capacity. Often, decreased performance is observed due to competition for active sites. The same is true for gas adsorption where competition for active sites can be observed. Another challenge for utilizing char in wastewater or contaminated soil treatment is the leaching of secondary pollutants. This issue remains a significant concern that is often less investigated [79]. In one study, commercial wood waste GC was explored as an alternative to AC in potable water filtration. While it met the limit of leachable PAHs ($10 \ \mu g \ L^{-1}$) and metals, it did not meet the limit on ash content (15%) set by the EN 12915-1 standard [80]. Thus, future studies considering char for water treatment applications should investigate leachable compounds to avoid introducing secondary pollutants.

3.2. Catalysis

GC used in the field of catalysis is a relatively broad area of research. In tar reforming for syngas production, char has been found to effectively reduce tar levels. As catalyst support, char improves the efficiency and stability of catalysts in chemical reactions.

3.2.1. Tar Reforming

Tar is a byproduct of the gasification process characterized by its black or brown color and liquid or viscous semisolid nature. It consists of complex mixtures of PAHs, phenolic compounds, and heterocyclic compounds [81]. Condensation of this material at relatively lower temperatures can lead to blockage and fouling of downstream pipelines or process equipment. Reducing the tar content can be achieved in several ways, one of them being reforming. Tar reforming is the conversion of condensable hydrocarbon derivatives (tars) into noncondensable lower molecular weight products such as H₂ and CO. Tar reforming can be achieved thermally, catalytically, or both, either in the presence or absence of steam [81]. In catalytic applications, char with high specific surface area, well-developed porosity, various surface functional groups, and good thermal stability has drawn great attention among the scientific community [82–85]. Figure 3 shows the adsorption/catalytic mechanisms of tar reforming over the char surface.



Figure 3. Tar-reforming mechanism pathways on char surface. Reprinted with permission from [86] © Elsevier.

Char was tested in tar-reforming applications by several research groups. However, char is usually collected from gasification plants of different scales, technology readiness levels (commercial, pilot, and laboratory scales) and configurations (e.g., downdraft, fluidized bed, dual-stage), making the comparison among them more challenging. Properties such as metal content, surface area, and pore size distribution always showed the greatest impact on tar reforming.

The presence of Ca, Mg, Na, and Fe silicates, aluminates, and oxides in char was found to enhance tar reforming significantly [26,39,87]. Assima et al. measured tar (synthetic) conversion over an alumina/char bed and observed a conversion rate of 85% at 871 °C compared to 56% obtained during thermal cracking, while the remaining tars after reforming were xylene and naphthalene [87]. The same authors further investigated the impact of the metal oxide content on the catalytic conversion of tar from municipal solid waste (MSW) gasification, testing both char and char-derived ash, richer in metals. Tar concentration was reduced from 65 g Nm⁻³ to 173.3 and 90.2 mg Nm⁻³ when char-derived ash and char bed were used with steam, respectively, demonstrating the beneficial effects of the presence of metals [39]. Conventional, single-stage, tar-reforming processes often fail to capture lighter tar compounds that might otherwise be captured, as shown earlier. A solution to this issue was proposed by Singh et al., who studied tar (synthetic) removal using two consecutive char beds, at 750 and 220 °C, respectively [86]. The removal efficiency was enhanced in the

two-stage process where 40% of the improved performance was attributed to the second stage [86].

Cordioli et al. found that using a char bed at 900 °C increased the toluene (synthetic) removal rate from 39.9% (thermal cracking) to 60.3% (with char) [26]. Additionally, in this case, the high content of alkali and alkaline earth metals (AAEM) in char promoted catalytic tar cracking reactions and resulted in enhanced tar reforming. However, a more detailed study on toluene (synthetic) conversion using GC showed that the presence of AAEM increased the char gasification rate significantly, but it did not impact toluene conversion directly [88]. The abundance of unsaturated carbons in char structure, which attract volatile compounds, makes the char surface area available for toluene adsorption (i.e., pores with a size greater than the kinetic diameter of toluene) the determining factor for the toluene removal efficiency. Nevertheless, inorganics present in the char could indirectly enhance toluene conversion by catalyzing the gasification, thus activating the char [88].

The relevance of a well-developed porosity and large surface area was confirmed by the work of Ravenni et al., where char produced from a two-stage demonstration plant using spruce woodchips as a feedstock was used [23]. In this case, char showed a very large surface area (1253 m² g⁻¹), one of the highest values reported in the literature for commercial chars. Moreover, Ravenni et al. found that the wide range in pore size distribution of GC in comparison to the mostly microporous activated pyrolysis char resulted in a prolonged tar (from a pilot scale gasifier) reforming activity time [89]. In addition, coke deposition is more pronounced in chars with higher microporosity leading to limited access to active sites and lowered catalytic reaction rates [85,90].

The beneficial effect of both high surface area and high content of AAEM was also proved by Cheng et al., who analyzed the decomposition of naphthalene (synthetic) using a catalyst derived from bauxite residue and GC (7:3) in the presence of steam [24]. The study concluded that GC was more effective than pyrolysis char in reducing iron oxides, possibly due to its higher surface area and higher content of AAEM. Bauxite residue and char mixture showed much higher and more stable activity in terms of naphthalene conversion compared to using each catalyst separately [24]. Moreover, the production of char-based catalysts was found to be more sustainable (less greenhouse gas emissions and fewer impacts on human health) than conventional metal catalysts [91].

Performances of activated char, with a better-developed porosity than untreated char, were also investigated. Bhandari et al. examined the toluene (synthetic) removal capacity of as-received char, activated char (with KOH at 700 °C), and activated char coated with dilute ascorbic acid [36]. At 700 °C, toluene removal was 82%, 79%, and 69%, for activated char, coated activated char, and as-received char, respectively. Activated char was characterized by a high surface area (about 900 m² g⁻¹), pore volume (about 0.4 cm³ g⁻¹), and prolonged catalyst activity time compared to the other two samples [36]. Qian and Kumar also activated GC with KOH at 800 °C, followed by impregnation with nickel nitrate solution and, finally, reduction in H₂ at 350 °C, before testing it [92]. At 700 °C and in the presence of steam, the average removal of phenolics (from pyrolysis tars) was about 50%, while at 900 °C, 90% of phenolics and 60% of monoaromatic hydrocarbons were removed [92].

The surface properties and activity of GC catalysts in tar reforming can be impacted by coke deposition inside the pores [88]. Coke consists mainly of small aromatic ring with the size 2–5 nm, which makes microporous materials more prone to blockage and deactivation than mesopores [82]. In the presence of steam, gasification of the coke takes place and the pore structure is reserved [88]. However, introducing steam to tar-reforming reactions should be performed with caution, as it could lead to a declined catalytic performance due to the oxidation of active metallic phase on the catalyst surface [24].

In addition to the impact of inorganic content and surface properties, char particle size can also play a role in tar removal efficiency, as explored in a recent study. When the catalyst size was reduced from pellets (D: 3 mm, L: 5–7 mm) to powders (0.3–0.4 mm), the removal of naphthalene increased from 79% to 97%, at 750 $^{\circ}$ C [93]. At a high temperature

(900 °C) the char size had no impact on naphthalene (synthetic) removal, which approached 99% for all sizes [93].

Tars were not the only compounds used to demonstrate char catalytic performance. Klinghoffer et al. explored the impact of GC on the catalytic decomposition of methane (CH_4) and propane (C_3H_8) to produce H_2 and solid carbon [32]. The authors found that higher char surface area resulted in increased performance and diffusion limitations due to the presence of micropores [32]. Finally, GC was found to be very effective in tar-reforming applications due to multiple factors, namely its high surface area, high AAEM content, abundance of unsaturated carbons, and wide range in pore size distribution.

3.2.2. Catalyst Support

In addition to its catalytic properties, char can act as an economical and environmentally friendly alternative to conventional catalyst support materials such as Al₂O₃ or SiO₂. Usually, catalyst support materials demonstrate high surface area, chemical stability, and the ability to highly disperse catalyst particles over their surface.

Char generated from a dual-stage gasifier and woodchips as feedstock was used in the dry reforming of CH_4 . The study examined the conversion rate of CO_2 and CH_4 as well as the yield of H_2 and CO [94]₂. Different treatments were compared to untreated char. The study concludes that loading the char just with cobalt was not effective. However, adding 2 wt.% MgO resulted in a boost to the conversion rates (95 and 94% for CO_2 and CH_4) and yields (44 and 53% for H_2 and CO). These values were comparable to conventional catalyst supports [94].

Similarly, char was tested as catalyst support for Fischer–Tropsch synthesis, a process used to convert syngas to biofuels. The study analyzed two different metal loadings: 10% Fe and 10% Co, with acid washing of char produced from woodchips before metal impregnation [95]. The results showed better performance for iron-loaded char compared to cobalt, which achieved a 26% CO conversion rate. Moreover, only hydrocarbons in the range C_1 – C_{22} and C_1 – C_{24} have been detected for 10% Fe and 10% Co, respectively [95].

In a recent study, char from palm kernel shells gasification was used to produce a CaO-rich catalyst for biodiesel synthesis [96]. The char high calcium content, mainly in the form of CaCO₃, offered a low-cost alternative for CaO catalyst preparation. It was also advantageous in terms of low synthesis temperatures and showed an adequate catalytic effect. Moreover, increasing the loading of the catalyst led to an accelerated reaction [96]. This application pathway is a great example of a circular economy as oil-palm trees waste is used to produce catalysis that enhances the production of biodiesel, which can be done from oil-palm trees.

Overall, the surface of char obtained starting from woody biomass used in catalysis applications was found to be rich in calcium oxides (CaCO, CaCO₃, Ca(OH)₂) and silica oxide [23,36,89]. When other feedstocks are used to produce char, additional mineral phases emerge. For instance, char produced from MSW was rich in silicates (NaAlSiO₄, Ca₃Mg(SiO₄)₂, Mg₂(SiO₄)₂, CaSO₄) and aluminates (Ca₃Al₂O₆, Al₂O₃) [39]. Figure 4 shows the metal composition of char produced from a range in biomass sources and through different gasification technologies.

It is worth mentioning that none of these studies investigated the possibility to regenerate the catalysts supported on GC after the process. Therefore, further research on this topic would be beneficial to fill this gap.





3.3. Other Applications

In this section of the review, we examine the use of GC in several cutting-edge fields, including polymers, electrochemistry, construction, and phase-changing materials. Some other fields that are commonly investigated using pyrolysis char were less examined, such as using GC in soil, anaerobic digestion, and composting applications. These applications are also explored in this section.

3.3.1. Agriculture

Unlike pyrolysis char, which was thoroughly studied as a soil amendment, GC is still being explored. To prove char's beneficial effects on plant growth, Pedrazzi et al. investigated the effect of char from agricultural and forestry waste gasification on basil growth [98]. The results showed that fresh basil biomass production in the 30% char substrate was significantly higher (p < 0.05) than in standard soil and compost [98]. Similarly, a 30% application rate of GC from water hyacinth resulted in a harvested sunflower seed weight of 7 g compared to 5 g for the control [99]. Moreover, applying GC to coarse sandy soil at a rate of 1 wt.% increased average barley root density from 33% (control) to 54%, and increased grain yield by 22% [100]. This study was followed by a long-term study in which spring barley and winter wheat were grown during a three year period in GC-amended soil. An application rate of 1 wt.% increased the in situ field capacity of the subsoil by 3.5% and led to a higher total dry matter yield (18%); however, no positive impact on grain yield was observed [101].

Char application to the soil does not always positively affect plant growth. Martos et al. demonstrated that at an application rate of 30 t ha^{-1} , char was able to increase water retention in loamy soil and decrease the need for N fertilizers, while not impacting crop yield [102]. Yang et al. produced char at a pilot scale downdraft gasifier from various feedstocks (woody, wood and chicken manure biochar, wood and food waste, wood and anaerobic digestion residue) and pyrolysis char from sorghum, concluding that char can drive a reduction in bioavailable trace metals in soil without an improvement in the microbial activity [103]. Application of 20 wt.% cedar wood GC to dry soil resulted in increased water holding capacity (25%), available phosphorus, and reduction in ammonium content [104]. Although average soybean seed yield was improved for the first cropping cycle, in the second cycle the char no longer had a significant impact on water holding

capacity due to compaction and warming weather [104]. Moreover, Tonon et al. tested chars from different commercial gasifiers to study their suitability for corn growth [105]. The study found that plants grown in char–soil mixtures exhibited 40% lower chlorophyll content, and a decrease in Mg, Ca, and P content in the plant leaves and a reduction in the germination index, suggesting a presence of phytotoxic substances [105].

Considering compliance with international and national soil applications regulations, Fryda et al. tested char from a small and a large laboratory-scale fluidized bed gasifier utilizing agricultural and forest residues and operating at a low temperature (600–750 °C) [48]. The char produced demonstrated compliance with the International Biochar Initiative (IBI) definition and the concentration of 16 PAHs and trace heavy metals were within the standards [48]. Additionally, in the study by Hansen et al., who tested chars from the precommercial fluidized bed and dual-stage gasification plants, the total PAHs content of both chars was well below the threshold limit of 12 mg kg⁻¹ for soil application set by the Danish Ministry of the Environment [8]. However, Tonne et al. found that among eight chars collected and characterized from different commercial gasifiers, not one completely satisfied the Italian law's requirements on fertilizers, thus untreated char cannot be added directly to the soil [105].

3.3.2. Polymers

GC was tested as a carbon source in polyacrylonitrile (PAN) nanofiber fabrication via electrospinning [106]. The char from vine pruning pellets gasification was mixed at different ratios (10, 25, 50%) with PAN. Char grains were well dispersed among the fiber mat with 97 wt.% carbon content. At a high carbonization temperature (1700 °C), the char inorganic content disappeared, resulting in a nearly pure carbon fiber matrix [106]. GC can also act as a polymer filler, improving the thermal stability and electric conductivity of the final polymer. In a recent study, char from a dual-stage commercial gasifier was compared to carbon black (CB) [107]. The two filler materials were used with styrene–ethylene–butylene–styrene (SEBS) matrix. The results showed that a matrix with 44 wt.% char increased the electrical conductivity up to 2×10^{-3} S cm⁻¹ without impacting the structural and mechanical properties. Moreover, CB and char addition enhanced the polymer's thermal stability [107].

3.3.3. Anaerobic Digestion and Composting

Using char as an additive in anaerobic digestion is one of the areas similar to the agricultural application where no consistent positive performance has been reported. Char addition could alleviate volatile fatty acids inhibition and related acid stress, affecting methanogens negatively. Pinewood and white oak char from steam gasification at a pilot scale were used as additives for anaerobic digestion of sludge from a municipal wastewater treatment plant [108]. Two char dosages were tested, 2.49 and 4.97 g g^{-1} dry matter of sludge, and the CH₄ content reached 92.3 and 79.0 vol.% for mesophilic and thermophilic anaerobic digestion, respectively [108]. A more recent study on the use of char with an organic fraction of MSW was also able to achieve increased methane yield (up to 36.6%) when the char ratio was in the range 0-45 mg/L [109]. In another study, char from woodchips gasification was tested in anaerobic digestion of organic fraction of MSW [110]. The addition of 6% char did not increase methane yield significantly but led to a more stable digestate with less heavy metal content and decreased toxicity due to the dilution effect [110]. However, a higher PAH content (8.9 mg kgTS⁻¹) was observed, which could lead to noncompliance with soil application limit regulations. Poor methanation performance was attributed to the low surface area of the char (272 m² g⁻¹), inappropriate char particle size, or digester configuration (dry instead of wet) [110]. The digester configuration is a more likely reason, as other studies highlighted in this section utilized char with a similar or even lower surface area. GC was found to have a positive impact on the compositing of the organic fraction of MSW in a recent study. Mixing 3 wt.% of fine and coarse GC led to composters running 4 °C more than the control [111]. Fine

char had a slightly improved thermal energy production mainly due to the compaction effect and less accessibility to air convection through the pores [111].

3.3.4. Electrochemistry

The potential of using GC as an electrode material was investigated in a few studies. Char generated from forest residue (428.6 m² g⁻¹) was compared to granular AC (1247.8 cm² g⁻¹) in a microbial fuel cell [112]. The char showed a similar power output (457 mWm⁻²) to granular AC (674 mWm⁻²) at a reduced energy and carbon footprint associated with electrode manufacturing [112]. In a related study, char–MnO₂ composite was used as an electrocatalyst support for oxygen reduction in a microbial fuel cell [113]. The composite showed a satisfactory maximum power density of 187.8 Wm⁻² at a much lower cost [113]. A similar microbial fuel cell was used for wastewater nutrient recovery. Studies on actual industrial wastewater showed 95% removal of chemical oxygen demand and a reduction in ammonia and phosphorus by 73% and 88%, respectively [114]. The char from a mixture of biomass and polymeric waste gasification was upgraded into carbon nanotubes, which were characterized by high electronic conductivities and specific surface areas [115]. This indicates its capacity to absorb oxygen species, and tendency towards oxygen reduction reaction in the alkaline environment, making it a good candidate for electrocatalyst support in fuel cells and electrode materials of lithium-ion batteries [115].

3.3.5. Construction

He et al. applied GC from water hyacinth for augmented concrete generation at a rate of 2%, which resulted in 19.1% and 13.7% enhancement in compressive and flexural strength, respectively [99]. Similarly, Restuccia et al. mixed char from wood waste gasification with ordinary Portland cement (OPC) at different ratios ranging from 0 to 2.5% [116]. Tests with 2 and 2.5 wt.% char resulted in enhanced or comparable flexural strength and toughness to plain specimens [116]. In another study, Sirico et al. explored char application up to 10 wt.%. After 28 days of curing, 2.5% and 5% char addition resulted in an increase in compressive strength by 5% and 3% for water curing, respectively [117]. Increasing the char ratio to 7.5 wt.% and 10 wt.% led to a decrease in strength by 19% and 33% for the case of water curing, respectively [117]. Consequently, increasing the char ratio in concrete beyond 5 wt.% was not recommended. Additionally, multiple authors reported no improvement in concrete mechanical strength when mixed with GC at 0–2.5 wt.% [118,119].

Additionally, GC was employed to improve insulation materials production. Gasification of biomass from riparian vegetation maintenance in a region in Italy was mixed with polyurethane at a ratio of 0-2 wt.%. The results showed reduced thermal conductivity from 0.044 to 0.037 W mK⁻¹ for the cases of no char and 0.5 wt.% char [120]. Moreover, char from a pilot-scale fluidized bed gasifier utilizing olive mill cake as a feedstock was tested as an additive in brick manufacturing [121]. Bricks were manufactured using char percentages of up to 20 wt.%. The results showed that the bricks can be used as low-density clay masonry units with good thermal insulating capacity [121]. Even if it showed neutral performance in certain cases, GC application to construction materials still could offer long-term carbon storage in buildings and reduce buildings' embodied carbon. Pioneering applications include char as a precursor in phase-changing materials (PCMs), which can store thermal energy as they change phase from solid to liquid. For instance, Atinafu et al. developed shape-stable composite PCMs based on dodecane and a renewable precursor, activated GC with a high surface area equivalent to 882.2 m² g⁻¹ [122]. The new material was characterized by latent heat storage of 102.2 J g^{-1} and thermal conductivity of 0.416 W m^{-1} K⁻¹, which is within the range for other dodecane PCMs (52–127.4 J g^{-1}) [122].

4. Outlook

In the shadow of increasing bioenergy demand, more CHP gasification plants are put into operation. These plants are usually classified as small-scale (70 kW_e–3 MW_e) plants with a large diversity in operation conditions and feedstock. Limited data can be found on

the amount of GC produced globally. However, in the region of South Tyrol (Italy), where 42 CHP plants are operational, it is estimated that 1180 t of GC are generated annually [6]. Another example comes from Japan, where Syncraft[®] recently commissioned a wood power plant that is generating 1600 t of GC annually [123]. In almost all cases these operational conditions are optimized for increased heat and power generation. Consequently, a large variation in GC properties is observed. Moreover, there are significantly more studies on pyrolysis char applications that at first glance can be used to draw correlations between the two materials. However, as explained earlier, the difference between the properties of pyrolysis char and GC makes this a challenging task. Therefore, it is essential to conduct more studies with the same test conditions that compare the performance of pyrolysis char, gasification char, and similar commercial material currently in use.

Currently, regulations only exist for the soil application of char, which, as observed, is not the largest area of application for GC. Thus, more regulations should be introduced for other applications, particularly, water treatment. For example, researchers tend to focus on adsorption performance while overlooking the leaching of secondary pollutants from char. In addition, the disposal of used adsorbents or catalysts is rarely discussed in the literature. Inappropriate disposal of spent char defeats the main goal of pollutant removal from water, gas, or soil. More recent work has considered this issue. For instance, Wurzer et al. have examined the hydrothermal treatment of spent char used as an adsorbent of emerging micropollutants, which is otherwise sent to landfills or incinerated [124].

Owing to its versatile properties, GC can be used in multiple applications either in series or in parallel. The concept of cascade use of char was observed in two studies for GC [23,99] and for pyrolysis char [125]. More studies should consider this cascade approach in which the waste originating from a process becomes the feedstock for a further process. In multiple studies, the final valorization pathway was soil application for carbon sequestration purposes [101]. The continued use of the recycled chars in subsequent applications without regeneration was also driven by the high cost of regeneration [126]. In other words, the focus should be on degrading the contaminants from char used in catalysis or adsorption instead of restoring the original char properties [126].

Despite these research gaps, our review shows that GC is a promising material for a wide range of applications and has the potential to effectively contribute to sustainable and environmentally friendly solutions in many areas. Further research is needed to fully realize the potential of char and to optimize its use in the reviewed applications and future applications.

5. Conclusions

In this article, GC applications reported in the literature were extensively reviewed. A line was first drawn to distinguish between pyrolysis char and GC, which are often referred to as biochar despite their differences. It was also shown that governing bodies such as the European Commission are currently differentiating the two materials in official reports to avoid confusion. The number of studies on GC is far less than other types of char (mainly pyrolysis char), which creates a false impression of its limited application. GC often does not require further activation, which makes it a more environmentally and economically sustainable alternative to pyrolysis char for many industrial applications. The main challenge for GC utilization stems from the variability of the gasification process conditions, i.e., temperature and residence time, and feedstocks. This results in a variation in char properties that will require continuous monitoring to be diverted to optimum utilization.

Commercial downdraft gasifiers operating at around 800 °C on woody biomass can produce char with a specific surface area comparable to the lower end of the AC range (500 m² g⁻¹). On the other hand, dual-stage commercial gasifiers are able to produce char with an even higher surface area that is in the middle range for AC surface area (1000 m² g⁻¹). The reason for this is the controlled process that mimics AC production. Activating the char either physically or chemically further enhances the surface properties. The high process temperature at which char is produced comes at the cost of losing various functional groups and certain minerals. This might limit GC applications in specific areas such as agricultural applications. Moreover, char coming into contact with the syngas might lead to a higher PAH content in the char. However, multiple studies showed that PAH content in char can be below the limits set by regulatory bodies for soil application.

Char applications were found to be dominant in two areas: adsorption and catalysis. The utilization of GC in tar reforming serves as a great example of a circular economy where a process byproduct is converted into a useful material that enhances the process outcomes. In addition to the environmental benefit of diverting this material away from landfills, economic gains can be made in terms of improved process outcomes (higher quality syngas) and waived disposal costs.

Several cutting-edge applications were also reported in the literature, such as polymers and electrochemical applications. If the features of the GC permit, it can be used as fuel, as recently reviewed by [13], but this does not fall under the circular economy principle (or it is the least favorable option). The various applications of GC help to achieve a zero-waste process and work towards promoting a circular economy. Finding the optimum use for this waste material could be challenging. So, instead of following a bottom-up approach and engineering the char for one application, a top-down approach would be more applicable. Consequently, the same GC material could be evaluated for multiple valorization pathways and decided based on its performance. Finally, if these challenges are overcome, many benefits could be harnessed from GC utilization.

Author Contributions: Conceptualization, all authors; methodology, A.A., V.B., F.P. and A.V.; formal analysis, A.A.; investigation, A.A. and V.B.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, V.B., A.V., F.P., C.G. and M.B.; visualization, A.A.; supervision, M.B., C.G., F.P. and A.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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