Review

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Rafael Benjamin Evaristo , Romulo C Dutra , Paulo Anselmo Suarez , Grace Ferreira Ghesti * , Edgar Silveira *

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Biochar from Lignocellulosic Biomass: The Importance of Physicochemical Characterization and Multi-Criteria Decision Analysis for Its Applications

Rafael B. W. Evaristo [1], Romulo C. Dutra [2], Paulo A. Z. Suarez [2] and Edgar A. Silveira [3,*]
Grace F. Ghesti [1,*]

[1] University of Brasilia, Chemistry Institute, Laboratory of Brewing Bioprocesses and Catalysis to Renewable Energy, Brasilia DF 70910-900, Brazil
[2] University of Brasilia, Chemistry Institute, Laboratory of Materials and Fuels, Brasilia DF 70910-900, Brazil
[3] University of Brasília, Brasília, Mechanical Sciences Graduate Program, Laboratory of Energy and Environment, Brasilia DF 70910-900, Brazil
* Correspondence: edgar.silveira@unb.br (E.A.S.); grace@unb.br (G.F.G.)

Abstract: Biochar is a carbonaceous material derived from the thermochemical conversion of biomass under oxygen-lean conditions. Its properties render it many applications in agriculture, environmental remediation, and catalysis. Commonly produced by pyrolysis under a nitrogen atmosphere, the biochar composition is influenced mainly by residence time, heating rate, and process temperature. The existing literature primarily assesses biochar properties, such as ultimate, proximate, calorific, porosity, and combustibility, generated under various thermo-conversion conditions. However, there is a notable lack of sufficient investigation and attention given to the practical application of biochar. This article seeks to bridge that gap by enhancing the comprehension of the necessary experimental assessment for specific biochar applications and proposing process optimization methods using Multi-Criteria Decision Analysis (MCDA). By delving into these aspects, the study offers a concise overview of biochar production and presents a comprehensive panorama based on articles and patents. Additionally, the research explores the physicochemical characterization techniques associated with biochar and its various applications in conjunction with MCDA. This comprehensive approach aims to uncover valuable insights that could further advance the practical and sustainable utilization of biochar in a wide range of fields.

Keywords*:* biochar; pyrolysis; characterization; mcdm; fuel; wastewater treatment

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1. Introduction

Carbonaceous materials have played a significant role in human activities extensively. These materials, defined by their high carbon content (> 60% wt.), are produced through the thermal treatment of organic substances. The origins of these materials can be traced back to vegetal sources (primarily), as well as animal sources (such as agricultural residues), and even urban waste (including sludge and common domestic waste) [1,2].

Widely recognized as coal, carbonaceous materials have undergone extensive research and have attained a pivotal stage of development, serving as precursors to other commonly employed materials like activated carbon. Their remarkable adsorptive properties in both aqueous and gaseous mediums highlight the adaptability of carbonaceous materials, making it possible to modify and tailor their properties for specific purposes, similar to typical coal [3,4].

Biochar, a distinctive carbonaceous biomaterial, has garnered substantial attention in recent research. The escalating technology readiness level (TRL) of thermochemical conversion routes has significantly contributed to the increasing interest in biochar, primarily for its remarkable versatility

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across various applications [5]. The multifaceted potential of biochar in different domains underscores its significance in contemporary studies, and ongoing research continues to unveil more opportunities for its sustainable and effective utilization in various applications (soil amendment [6–8], biofuel [9–11], adsorbent material [12–14] and wastewater treatment [15–17]) and as a support for functionalized materials applicable in chemical synthesis.

Biochar can be produced by different thermochemical processes with controlled atmospheres (inert or oxygen-lean conditions) and a diversity of operational conditions (temperatures, heating rate and treatment time). Each process has a specific final product target, for example, torrefaction (200–300 °C, focused on biochar product [18–21]), pyrolysis (300–800 °C, whose process will also generate a gaseous and a liquid phase [22–24]) and gasification (600–1200 °C, where the main objective is producing synthesis gas [25–28]).

In addition, a crucial aspect of biochar production and related applications is its feedstock source, where its constituents will significantly influence the efficiency of the thermochemical process (given different degradation rates from each constituent) [29]. Therefore, different processes and related operation conditions will result in biochars with a large variety of physical-chemical characteristics, which must be assessed and assigned to a specific application.

The ongoing industrial focus has been integrating sustainable production processes, whether in conventional industrial environments (readapting parts of already established production lines) or in raw materials production, such as the agricultural sector (where the relationship with the food, materials and energy is intrinsic).

In this context, searching for new biomaterials designed around environmental impact mitigation issues attracts the most research development attention. Biochar is a clear example since it can be produced from renewable raw materials (biomass) and residues, for example, agricultural (straw, rusk, bark, bagasse, among others), and urban solids (municipal solid waste, pruning tree, sludge). Moreover, the obtained products are solid materials and other derivatives that can be used as liquid biofuels or syngas for energy and chemical synthesis [30].

In the agro-industrial context, integrating its residues into a new conversion route that can become economically viable is desirable. It aligns with biorefinery and circular thinking, pursuing minimizing the disposal of non-productive renewable residue and maximizing conversion process efficiency and product possibilities. An entire production chain can benefit from the 'relocation' of its residues. Figure 1 exemplifies such a concept, depicting possibilities and interactions between the correct application of recovered agro-industrial residues into new routes.

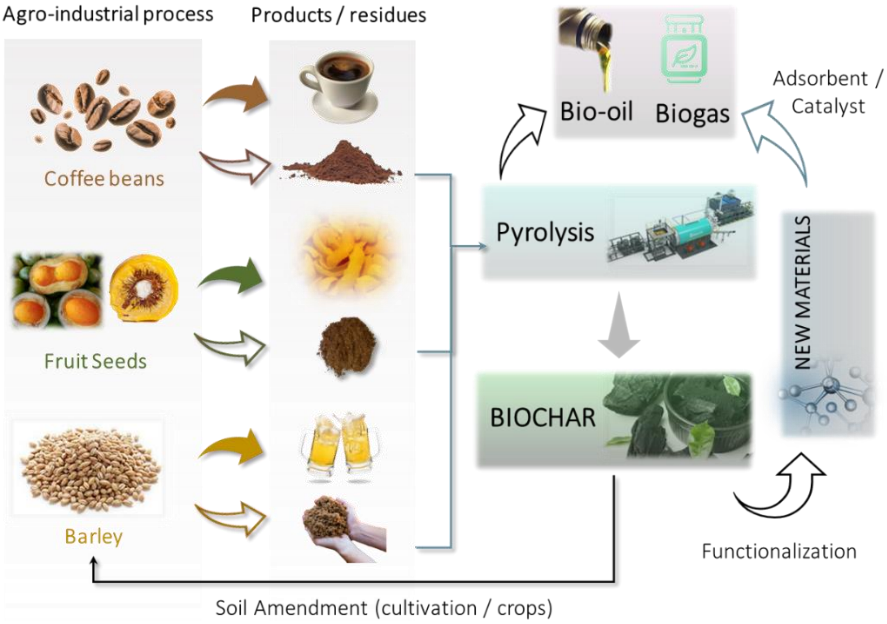

Figure 1. Schematic example of biomass residue recovery and application in producing biochar and new materials [26,28,31].

Figure 1 presents the coffee processing case. Its leading destination is the production of soluble coffee (food industry). Therefore, the spent coffee grounds are a by-product of this process (here, exemplifying the various other agricultural processes that generate residues). As lignocellulosic biomass has numerous possibilities, the pyrolysis process is highlighted as one of the possible conversion routes. Pyrolysis under suitable conditions will produce three fractions: gas (biogas), liquid (bio-oil) and solid (biochar). For the fractions, there is also a variety of possibilities. Gas and bio-oil can be used to produce direct energy as biofuels.

On the other hand, biochar can reintegrate sugarcane production as a soil enricher, or it can be functionalized and integrated into biofuel production through its acid functionalization and application as a catalyst, as described by Chin et al. [32]. Niju et al. [33] also addressed the production of biochar derived from sugarcane bagasse and its application in the transesterification of waste cooking oil to produce biodiesel. Thus, two integrated biofuel production chains can be contemplated, corroborating the feasibility of integrated biorefinery building and connecting different and more sustainable technologies.

Therefore, it is essential to acknowledge that biochar finds utility in various contexts and applications, making it crucial to assess production process conditions and the viability of specific biomass for this purpose. In light of this, specific questions arise concerning understanding the biochar formation process and its application. A fundamental aspect revolves around identifying the necessary criteria to evaluate the essential biochar properties. Additionally, one may wonder if standardized parameters apply to all biochar types. Another significant aspect to consider is the impact of biomass constituents on biochar formation and whether the properties of biochar undergo significant changes depending on the biomass origin. These questions raise a critical discussion intricately linked to investigating biochar properties, especially concerning its stability in the face of different processes to which it may be applied. Addressing these queries can significantly optimize biochar production and utilization while ensuring its efficacy and environmental benefits.

This work introduces the critical parameters for evaluating biochar production and explores how its destination/application can significantly influence these aspects. The study also discusses the evolution of biochar research over the past years through a prospective approach. Moreover, the study’s originality relies on discussing the linkage between experimental assessments and MCDA to optimize the pyrolysis process and/or set the desirable application based on process conditions and biochar properties.

2. Prospective Study on Biochar Research

The prospective study of a subject related to a specific technology helps understand the maturity and development level of a particular product or research segment [34,35]. Technological prospecting is usually carried out in three segments: a search for scientific articles/publications, patents, and/or products (focused on the technology already consolidated in the market). Therefore, the present study’s focus was to evaluate the tendency of the research related to biochar in the last 20 years. By analyzing the wealth of information gathered from scientific literature, patents, and existing biochar products, a comprehensive understanding of the advancements and potential future directions in this field was aimed. This investigation not only sheds light on the current state of biochar research but also provides valuable insights for future innovation and development in this promising area.

Web of Science, a platform with more than 20,000 indexed journals, was used for searches on the topic and associated with some related terms. The search period was defined between 2000 and 2019 with the terms shown in Table 1, searched in the title, abstract and keywords of these documents. The terms were associated with biochar, given its relation to the primary conversion processes (pyrolysis and gasification) and two possible applications (soils and catalysis) chosen as examples to be addressed herein.

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Table 1. Keywords used for prospective study based on publications.

Search	Keywords	Boolean Operator	Keywords	Boolean Operator	Keywords	Results
1	biochar	AND	-	-	-	29.645
2	biochar	AND	pyrolys*	-	-	11.417
3	biochar	AND	gasificat*	-	-	1.570
4	biochar	AND	Soil	-	-	13.954
5	biochar	AND	catalys*	-	-	2.504
6	biochar	AND	Water	-	-	12.264
7*	biochar	AND	Water	AND	treatment	4.783
8	biochar	AND	wastewater	-	-	3.486
9	#7	OR	#8	-	-	6.901

[a] Boolean operator: AND – restricts the searches to documents that necessarily have both terms; OR - searches for terms, but without the need to appear together (in this case, it was used to join searches 7 and 8, removing the repetitions). *biochar AND (water AND treatment).

Conte et al. [36] and Novotny et al. [37] have significantly contributed to the understanding and interest in studying biochar (also referred to as pyrogenic carbon) by providing valuable theoretical support. They conducted comprehensive searches based on the number of publications in recent years, covering the periods of 2000–2013 and 2007–2014, respectively. Both studies revealed a consistent and remarkable increase in the number of publications over the years, underscoring the growing interest of the scientific community in this subject. Our data update until 2022 demonstrates a substantial surge in published articles, reaching 27,138.

Figure 2 illustrates the number of publications per year to visualize this trend, clearly depicting the escalating interest and research activities surrounding biochar. These contributions have significantly enriched the knowledge landscape in this field and emphasize its importance for further scientific exploration.

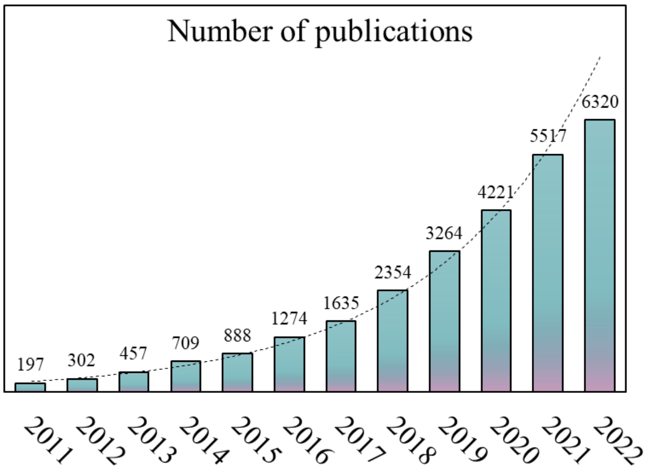

Figure 2. Number of articles published in the last 11 years for biochar research (data obtained from Web of Science based on keywords from Table 1).

In addition to the findings depicted in Figure 2, further refinement of the results can be accomplished through the Web of Science platform, enabling classification based on research fields and the countries with the highest publication rates, alongside various other classifications. The research field most closely associated with biochar is Environmental Sciences/Ecology, boasting 4,430 articles. It is closely followed by Agriculture, with 2,982 publications, and Engineering, which has contributed 2,746 articles to the corpus. Among the countries at the forefront of biochar research, China leads the way with a remarkable 4,470 articles, firmly establishing itself as a prominent contributor in this domain.

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The United States secures the second position with 2,264 publications, demonstrating its significant engagement in biochar-related studies. Australia also makes a substantial impact, with 807 articles showcasing its dedication to this area of research. Biochar is associated with research in environmental sciences, ecology, and agriculture precisely because of its widespread application and greater impact in current discussions on soil sustainability. China is emerging as one of the top publishing countries in the area, mainly due to its excellent agricultural capabilities (especially for rice, corn and wheat) and new technologies associated with reducing industrial environmental impacts [38].

The Chinese Biochar Network (CNB), created in 2010, strengthened the discussion of biochar in the country within the scientific academy and industries [38]. The CNB, as well as other organizations, were also crucial in consolidating parameters for the classification of its raw material and of the product as viable for agricultural applications, highlighting the International Biochar Initiative (IBI) and European Biochar Foundation (EBC) [39].

Similarly to the Chinese publications, the United States boasts substantial agricultural production and actively seeks innovative technologies to enhance productivity while mitigating the environmental impact, especially concerning greenhouse gas emissions. The US Biochar Initiative (USBI) has played a pivotal role in this regard by expanding its activities and effectively coordinating the efforts of the country’s biochar producers. Additionally, the US has attracted investments in pilot plants specialized in biochar production, encapsulating its objectives into three pillars: soil amendment, carbon sequestration, and greenhouse gas reduction. These concerted efforts mark a significant step towards sustainable agriculture and environmental conservation practices [40].

An analysis of the results presented in Table 1 reveals that when biochar is linked to the term “soil,” it yields a total of 6.319 articles, with nearly 56% of all articles solely focusing on biochar. This number reiterates the significance of academic production in the field of soil amendment while also shedding light on research opportunities and gaps for carbon materials of higher value when applied to fine chemistry. The utilization of these materials as supports and platforms for catalyst production is particularly noteworthy in this context [41].

When comparing the number of articles, it becomes evident that technology development remains under constant research owing to its extensive applications. This is primarily because ground applications are well-established and adhere to highly advanced European standards. At the national level in Brazil, there seems to be no promising outlook for innovation projects, as they generally exhibit low success rates, with biobased innovations showing no significant improvement. As for product development, the literature consistently indicates a broad spectrum of failure rates, ranging from 30% to 80% [42].

3. Lignocellulosic Biomass in Thermochemical Conversion

Biomasses, typically of vegetable origin, are materials formed essentially from cellulose (40–50 wt%), hemicellulose (25–35 wt%), lignin (15–25 wt%) [43], extractable components (organic acids and lipids; maximum 15–20 wt%) [44] and inorganic compounds (known as ash). Due to the wide variety of vegetable products, whether residues from agribusiness (bark, straw, shavings and stems), tree pruning, wood and grasses, their compositions may be decisive in the chosen conversion route [45]. This consideration becomes particularly crucial in thermochemical processes, especially in the most common production process of biochar, which is pyrolysis.

The complex plant structure means that the three main components of lignocellulosic biomass are not necessarily well distributed and well separated from each other, as well as depending on the part of the plant that gave rise to this biomass, the proportion between them will change. Analyzing this aspect may seem an indirect factor in evaluating and performing the conversion processes. The fact can be exemplified in a scenario in which biomasses have higher fractions of thermo-resistant compounds, as in lignin. With the increase in temperature, the probability of generating a greater quantity of solid product is more significant due to its greater amount of fixed carbon, which becomes aromatic compounds of greater molecular weight (without considering a comparison of the adjustments of the process parameters) [46].

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Several authors have been working on biomass constituents' degradation process within the thermochemical processes by comparing theoretical and experimental kinetic models [43,44,47]. The experimental conditions will determine the quantitative profile of the fractions derived from the conversion (greater or lesser quantity of a certain fraction). However, the qualitative profile of these derivatives will also be necessary, resulting from the characteristics of cellulose, hemicellulose and lignin in this matter -cousin. Knowing that the degradation process occurs first by hemicellulose (200–300 ºC), followed by cellulose (300–400 ºC) and finally lignin (600 ºC) [48,49], even if overlapping in some temperature ranges, monitoring its derivatives for each degradation zone helps to understand the composition of the final product. Understanding the behavior of each of its components in the conversion process allows us to make significant advances in optimizing these processes and the scale-up of these technologies [44].

EBC makes available a document referring to a set of biomasses classified in categories, primarily by their origin, appropriate for producing biochar [50]. Various raw materials can be observed, ranging from biomass from agricultural waste to waste from the food industry. The agro-industrial activities of each country will be decisive for the type of raw material available for biochar production. Thus, it is worth noting that the regional context will be an essential factor in the assessment for implementing the use of this material, in addition to the technology available for its production (essentially the reactors necessary for its production and the scale available).

4. Biochar Production

Biochar, also called pyrogenic carbon [37], black carbon [51] or charcoal, sometimes associated only as the carbonaceous material with specific application to the soil, is generally defined as the solid carbon-rich material obtained from the biomass thermoconversion into an environment with little or no oxygen [49,52]. Atmospheric conditions allow the formation of a material with unique characteristics due to incomplete combustion caused by the lack of an oxidizing agent that triggers the condensation of the biomass components.

The biochar is produced essentially by the pyrolysis process between temperatures that vary on average from 300–700 ºC (it may even be more depending on the type of reactor) [37]. In pyrolysis, three fractions are formed: a gas (non-condensable compounds), a liquid (bio-oil) and a solid (biochar). The proportion between these three fractions will depend on experimental conditions such as temperature, heating rate, residence time and type of pyrolysis. There are three main types of pyrolysis:

- Slow pyrolysis: happens at a temperature of 300–650 ºC, with residence time that can vary from 5 min to 12 h (longer duration) and a heating rate of 10–30 ºC min^{-1}; It produces a significant fraction of solids 20–40% (biochar) [37,49,53];
- Fast pyrolysis: occurs at higher temperatures (above 500 ºC) with a very short residence time (1–2 s) and heating ramp > 1000 ºC min^{-1}; This type of pyrolysis maximizes the production of bio-oil and can yield 50 to 70% and for the gaseous phase and 10–30% and 15–20% rinse, respectively [39,53];
- Flash pyrolysis: operates at high temperatures (above 800 ºC) with an even shorter residence time than fast pyrolysis (< 0.5 s) and heating ramp > 1000 ºC min^{-1}[39].

Understanding the different types of pyrolysis systems affects the proportion of the products in the process, the general mechanisms of forming these components can be explored. Figure 3 shows the three possible fractions of biomass pyrolysis, a gas phase consisting of non-condensable gases (H_2, CO, CO_2, CH_4, in addition to other lighter hydrocarbons), the liquid phase comprising organic acids, water and the tar of lower molecular weight and the solid phase (biochar) [39]. During the evolution of the process and the thermal exchange carried out with biomass, understanding the mechanisms of formation of these fractions makes it possible to investigate the stability and viability of each one [46]. With an emphasis on biochar formation, this translates into the desire to form a stable carbonaceous material of known composition at the end of the process, established physicochemical properties and thus suitable for its application.

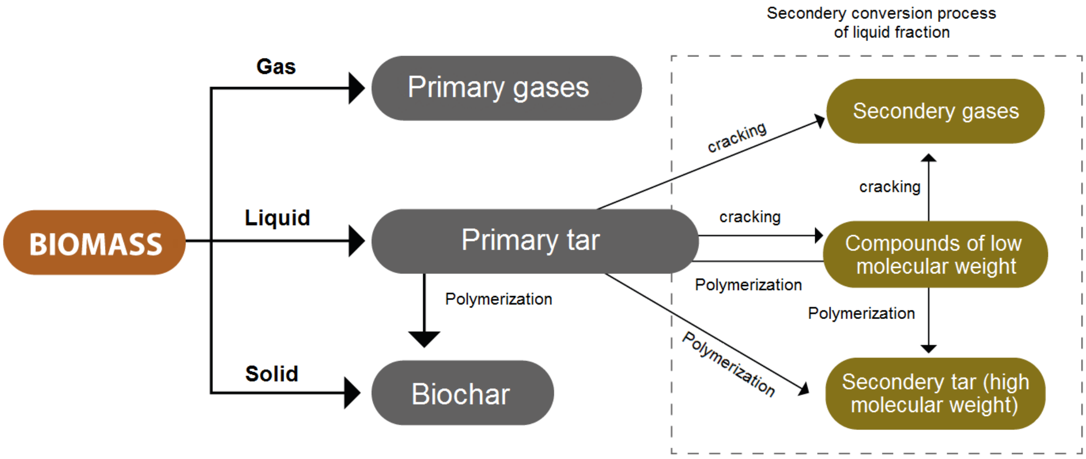

Figure 3. Pyrolysis process and production of its derivatives (adapted from [54]).

Figure 3 shows the mechanisms that guide the formation of each fraction and how they relate to the intrinsic composition of biomass reported by Collard and Blin [29]. During the thermal degradation process, the inter/intramolecular interactions of cellulose, hemicellulose and lignin begin to rearrange and break up, forming volatile compounds and changing the arrangement of their solid structure. This step concerns the primary mechanisms. Then, some volatile compounds and the primary products can recombine with each other, thus called a secondary mechanism.

In the primary mechanism, three main segments are highlighted during pyrolysis: char formation, depolymerization and fragmentation. It is worth pointing out and highlighting that, just as monomers of the polymeric structure can break (depolymerization), that chain fragmentation can occur, forming non-condensable gases (fragmentation). The resulting solid structure will be rearranged, favoring the formation of a more aromatic polycyclic structure stable with the concomitant release of low molecular weight compounds and water [29,46]. The reaction temperature will have a significant effect in this sense. Some authors suggest that the optimum temperature of the process is around 450 ºC, being flexible in an area that goes from 300–500 ºC to reach good biochar yields [39].

Steiner [55] points out that temperature plays a central role in the final characteristics of biochar. Although the residence time and the heating rate complement the aspects related to the process, several examples in the literature compare biochar’s stability and physical-chemical properties from different temperatures and standardize the same conditions as the other variables [56,57]. Keiluweit et al. [51] propose a diagram of how the transformation of biomass and its constituents occurs in the four types of char evidenced by the increase in temperature, illustrated in Figure 4. In addition, a gravimetric comparison of the fractions of char categorized in five different regions, which may summarize distinct characterization properties and possible applications.

The physicochemical properties relevant for the Region I (unaltered plant materials) include moisture content and functional groups, information relevant only for torrefaction products. Region II is associated with transition char and may include data similar to those obtained from Region I, applicable for material with desirable functional properties, such as adsorption unactivated char. The Regions III and IV char materials present properties relevant for surface and pore sizes, as well as fixed carbon contents, and may be relevant for applications related to physical or chemical adsorption. Region V char present material with unstable resistance and does not present interesting properties for char application [51].

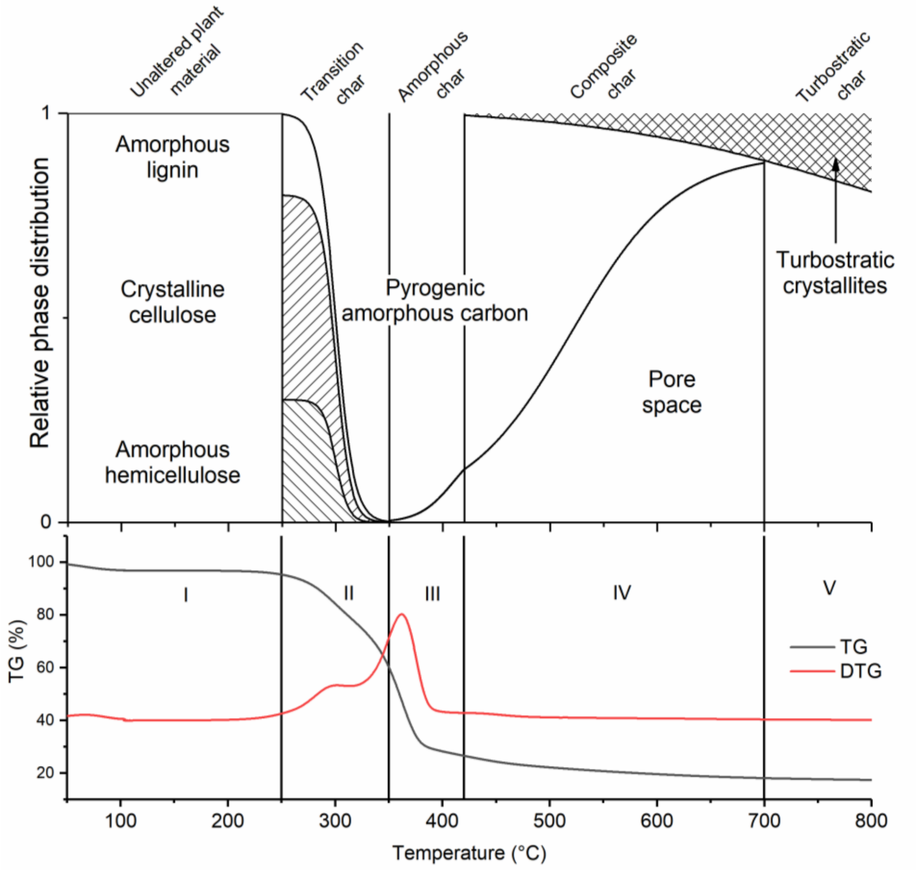

Figure 4. Schematic picture of the main phases of biochar along the thermochemical degradation of eucalyptus biomass, as well as the average yield of ash, volatile materials and fixed carbon throughout the process (adapted) [51].

5. Physicochemical Characterization of Biochar

The physicochemical characterization of a material is directly associated with investigating its fundamental properties related to its application or target destination. There are not always standard protocols for all types of materials; hence, there is a need to standardize them in some way to compare results and prove their effectiveness, whatever their application; this is the case of lignocellulosic biomasses. Although their primary constituents are known (cellulose, hemicellulose and lignin), their chemical composition is very variable since the proportion between these will change from species to species and depending on the part of the plant (leaves, branches, trunk, bark, bagasse, etc.) [58]. Groups like the National Renewable Energy Laboratory (NREL) [59] have established standard biomass analysis procedures that are a reference for several research groups, in addition to complementing some existing adapted procedures described by ASTM-certified institutions.

The same is valid with biochar; there are not necessarily uniform procedures in all countries for the analysis and application of the material. However, some organizations stand out and promote the centralization of these procedures. The International Biochar Initiative (IBI) [60] proposed the primary physicochemical analysis to be evaluated for producing biochar with application in soils. Several similar organizations are partners with IBI and share several analysis procedures [61]. Meanwhile, IBI is a signatory to the procedures described by organizations such as the International Standards Organization (ISO), ASTM International (ASTM) and the Institute of Electrical and Electronics Engineers (IEEE). Not all the characteristics of biochars are exploited by these procedures since they determine a specific application. Thus, to cover other studies that contemplate biochars destined to different areas, as in wastewater treatment, other characterization techniques will be described.

It is essential to highlight that the varied composition of biomasses, which depends on their type and origin, influence the composition of the derived biochar (logically if there is a comparison based on experimental conditions). It is, therefore, vital that the characterization process is conducted for any type of biochar due to the diversity of possible biomasses that have not yet been exploited for this purpose [58].

An adequate biochar characterization raises important considerations concerning essential characteristics when applying a thermochemical process to biomass. Among these considerations, the following questions stand out: Did the process conditions (including temperature, heating ramp, and residence time) adequately facilitate the degradation of biomass constituents and the formation of a stable solid? How can stability be measured? When utilized in soil applications, a pivotal characteristic becomes moisture retention and the material's porosity and hydrophilicity. These and other questions will be necessary to establish the properties that will be investigated for the applications already known and to explore new possibilities with these materials, showing again that the application will significantly affect the type of characteristics that will be analyzed.

5.1. Main Standard Biochar Characterization

The EBC described the leading techniques and requirements for biochar characterization in a document comparing its procedures with the points required by the IBI [61]. Both have a vision for application directed to use on the ground, as they define it in their design, while concisely discussed in Table 2.

Table 2. Main properties for biochar (modified from Xie et al. [4]).

Properties	
Specific surface area (SSA)	High values of SSA are indicators of adsorption capabilities
Porosity	High values of porosity are indicators of adsorption capabilities
Pore volume/distribution	Pore volume and distribution are significant criteria for the adsorption/desorption capability and selectivity
Surface functional Group	The superficial composition of biochar delimitates the application and adsorption capabilities
Water holding capability	High water holding capability values indicate water retention and delimitate the applications on plant stress remediation
Ion exchange capability	Indicative of efficiency on remediation of soil nutrient leaching
Elemental composition	The elemental composition is an indicator of stability and possible remediation applications
High heating value (HHV)	Indication of combustion energy production. The greater the value, the better

The characterizations for biochar are also commonly required for their original raw materials. As with the immediate analyzes where moisture, volatiles, ash and fixed carbon are evaluated [62], these will be essential parameters in the processing of pyrolysis (also associated with the issue of forecasts regarding yield and process efficiency) and are also present among the analyzes performed with the biochar.

Biochar parameters include pH, organic carbon (OC) content, volatile compound content, ash content, elemental composition, nutrient content, plant-available nutrients, bulk density, pore volume, porosity, specific surface area, water holding capacity, cation exchange capacity (CEC), iodine number, surface functional groups, sorption properties, nutrient release dynamics, and stability. Some of these parameters are challenging to assess.

Some characteristics, such as surface area, are mainly influenced by production conditions. The density and initial pore-size distribution of feedstock are also critical. Huge surface areas characterize activated carbon, and the pore-size distribution depends on the lignin or cellulose content of the feedstock. A superior lignin content is generally responsible for a macroporous structure, whereas a higher cellulose content yields a microporous structure [55].

5.2. Atomic H/C and O/C Ratios

According to the IBI and EBF, H/C and O/C can classify biochar samples. The classification based on H/C is preferable due to the H direct experimental determination, whereas O is indirectly determined. IBI classifies biochar samples based on organic carbon contents, being Class 1 OC ≥ 60%, Class 2 30% ≤ OC < 60%, Class 3 10% ≤ OC < 30%, and non-biochars OC < 10%. [63] The atomic H/C ratios might be used to predict pyrolytic temperatures, aromatic cluster sizes and sorption properties. [64] However, O/C can be used to estimate carbon stability in biochar samples. Spokas [65] stated that the half-life of an O/C < 0.2 biochar would be >1000 years, for an O/C 0.2–0.6 biochar sample, the half-life would be 100-1000 years and for O/C > 0.6 the half-life would be < 100 years. Table 3 shows the % C, H and O, the H/C and O/C.

Table 3. Pyrolytic CHN elementary data for different biomass sources from 300 °C to 800°C.

Feedstock / Biochar	**%C**	**%H**	**%O**	**H/C***	**O/C***	
Pinewood						[66]
PW	48.90	6.20	42.50	1.51	0.65	
PW450	75.50	3.70	17.00	0.58	0.17	
Timothy grass						
TG	43.40	6.10	45.40	1.68	0.79	
TG450	63.70	3.60	23.10	0.67	0.27	
Wheat straw						
WS	44.10	6.00	45.00	1.62	0.77	
WS450	64.80	3.10	23.00	0.57	0.27	
Pinewood-2						[67]
PW-2	48.50	5.92	45.16	1.45	0.70	
PW450-2	71.80	3.94	22.66	0.65	0.24	
PW600-2	84.66	2.81	10.25	0.40	0.09	
PW800-2	89.7	1.24	3.61	0.16	0.03	
Switchgrass						
SW	45.58	5.45	45.65	1.43	0.75	
SW450	66.54	3.43	15.31	0.61	0.17	
SW600	71.52	2.53	5.39	0.42	0.06	
SW800	71.62	1.16	4.85	0.19	0.05	
Wheat straw-2						[57]
WS-2	45.53	3.56	42.53	0.93	0.70	
WS300-2	61.48	2.73	19.61	0.53	0.24	
WS400-2	64.18	1.78	13.93	0.33	0.16	
WS500-2	67.39	1.01	7.35	0.18	0.08	
WS600-2	65.34	0.52	10.77	0.09	0.12	
Corn straw						
CS	44.53	5.31	41.18	1.42	0.69	

CS300	61.2	3.68	17.39	0.72	0.21	
CS400	63.36	1.96	16.46	0.37	0.20	
CS500	65.08	0.77	11.36	0.14	0.13	
CS600	67.48	0.18	8.98	0.03	0.10	
Rape straw	44.63	4.89	42.34	1.31	0.71	
RP						
RP300	61.80	3.54	17.95	0.68	0.22	
RP400	63.74	1.91	13.48	0.36	0.16	
RP500	66.96	0.87	9.46	0.15	0.11	
RP600	67.85	0.18	7.89	0.03	0.09	
Rice straw						
RS	42.12	4.16	41.22	1.18	0.73	
RS300	56.49	2.95	17.73	0.62	0.24	
RS400	56.42	1.35	13.71	0.29	0.18	
RS500	59.59	0.47	8.27	0.09	0.10	
RS600	61.30	0.12	5.71	0.02	0.07	
Brewers' spent grain						
BSG	44.72	6.86	44.66	1.83	0.75	
BSG300	63.28	5.03	31.20	0.95	0.37	[31]
BSG500	71.67	4.11	23.84	0.68	0.25	
BSG700	83.17	3.66	12.62	0.52	0.11	

* The ratios were recalculated from the CHN values of the references using the following molar mass values: C - 12.0107 g mol^{-1}; H - 1.0078 g mol^{-1}; O – 15.999 g mol^{-1}.

Figure 5 presents the Van Krevelen diagram illustrating the standard regions of biomass and derived biochars based in Table 3. This diagram proves valuable in assessing the coalification and reaction pathways of the modified products [68]. It offers valuable insights into the reduction of polarity (O/C) and aromaticity (H/C), as well as the extent of reactivity (degradation of carboxyl and hydroxyl groups) [69,70].

The conversion of hemicelluloses (at temperatures ranging from 200 to 350 °C) involves a process of dehydration combined with the cleavage of weak linkages between small substituents and the leading polymer chains [71]. In the case of cellulose, dehydration reactions start at approximately 200 °C, releasing water as the primary product. As the temperature increases to around 280 °C, the reactions release CO, CO_2, and small organic compounds [72]. On the other hand, lignin undergoes a gradual and partial degradation during torrefaction, commencing from around 200 °C. Its dehydration reactions involving the hydroxyl substituents of the phenolic rings take place at lower temperatures [73]. Understanding these thermal conversion processes and their corresponding temperature ranges is crucial for optimizing pyrolysis and tailoring the properties of the resulting biochar.

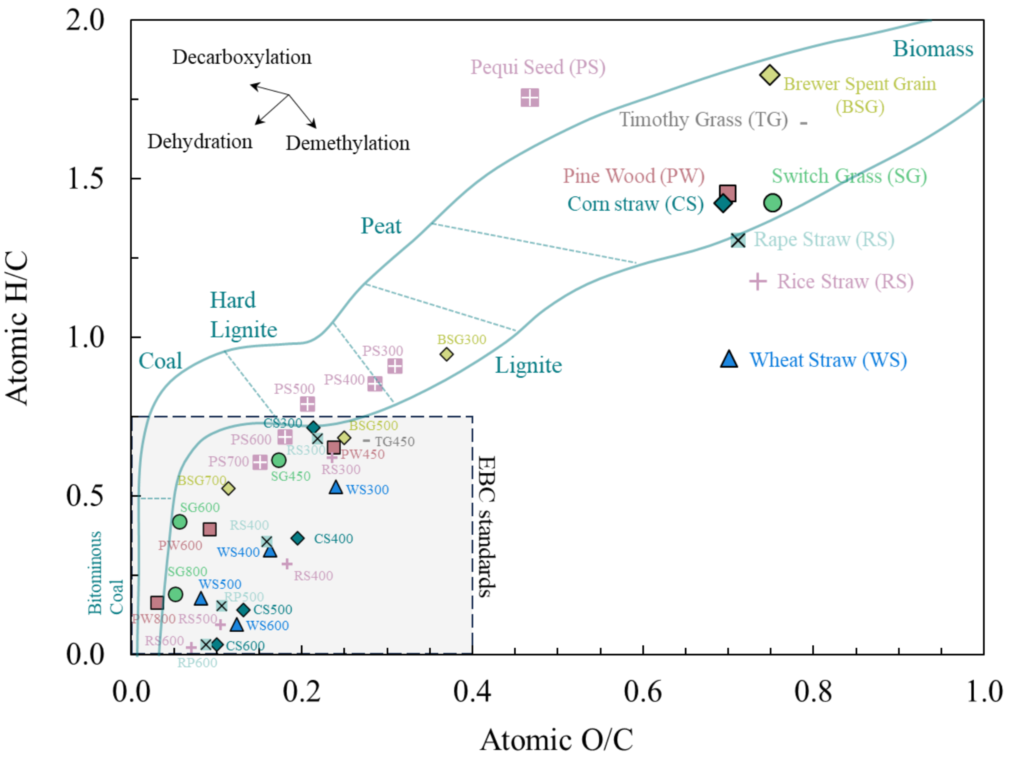

Figure 5. Van Krevelen's diagram of the H/C to O/C ratio (Table 3). The gray area represents the EBC standards.

5.3. Calorific Value

The increase in temperature in biochar production decreases the H/C ratio due to the condensation of carbonaceous structures and increases the calorific value of this material. The High Heating Value (HHV) indicates an upper limit for the available thermal energy produced on a given combustion and stands as the main comparison parameter for the combustion of biochar samples [4]. Padilla et al. [48] characterized the biochar produced from eucalyptus bark at temperatures of 300–500 ºC. Their study reported increased calorific value from 20.88–22.94 MJ kg^{-1}, respectively. The use of coal as a source of increasing the energy density of a product is a resource that has also been explored for biochar. Since the material has a calorific value greater than its original biomass, its use for energy will be much more profitable with the concomitant possibility of generating other derivatives that may also integrate the fuel chain, as is the case of bio-oil production. Miranda et al. [74] used Brazilian residual biomass studying its pyrolysis process and consecutively applying biochar in gasification since the increase in carbon content would significantly influence the syngas profile using biochar instead of crude biomass.

5.4. Spectroscopic Analysis

Spectroscopic analyses are commonly used to analyze the profile of the molecular bonding/interaction types in each compound. For the biochar, this analysis is combined with the comparison with its original biomass since, in the degradation process, some functional groups are disrupted, and chemical bonds of the C-C type associated with the formation of the carbonaceous material are formed more intensely. Such a principle will also be essential to corroborate a process temperature gradient (if addressed) since there is an increasingly intense degradation of the original compounds with increasing temperature.

5.4.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is an absorption and vibrational technique in which biochar surface functional groups absorb the energy of a beam and emit the energy at a different frequency. After data processing (Fourier transformation) is possible to identify characteristic bands for different functional groups, such as hydroxyl, carbonyl, esters, aromatic rings and others, allowing the direct study of the biochar decomposition degree [75,76]. Table 4 shows the leading characteristic of stretching.

Table 4. Main stretches for biochar FTIR.

Band position (cm^{-1})	Component	Ref.
480, 592, 652	Aromatic deforming rings, C-C stretching	[66]
782, 840, 885	C-H, aromatic hydrogen	
1097	C-O-C symmetric stretching	
1618	Aromatic C-C ring stretching	
1709	Phenyl ring substitution overtones	
2950	Alkyl/aliphatic C-H stretching	
3544	-OH stretching	
3642	-OH stretching, alcohols, phenols	

The most classical biochar FTIR method consists of preparing KBr pastilles and analysis on standard FTIR equipment. Biochar samples may also be prepared in KBr pellets for Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), placed over a crystal for Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR), disposed on photoacoustic cells with the Fourier Transform Infrared Photoacoustic Spectroscopy (FTIR-PAS), or even treated with synchrotron radiation for Synchrotron-based Fourier Transform Infrared (SR-FTIR) [77–81].

5.4.2. Raman Spectroscopy

Raman Spectroscopy is a scattering and vibrational technique on which a beam is applied over a sample and dispersed in frequencies related to the photon’s vibrational states post-exposition. The scattering is elastic (input and output frequencies are the same – Rayleigh scattering) and inelastic (output frequencies are higher or lower than input – Stokes and Anti-Stokes Lines). The Stokes and Anti-Stokes lines (given in cm^{-1}) compose a quantifiable fingerprint pattern for the molecule, or in the case of biochar materials, the fingerprint of a specific point on the surface [81,82].

Therefore, Raman Spectroscopy (Figure 7) might be used to identify functional groups and carbonaceous structure aspects, such as amorphous and crystalline, as described by Wu et al. [83]. Although FTIR and Raman’s analysis are complementary techniques for biochar study, Raman has higher sensitivity, suffers less interference from water, and requires minimal sample preparation, although at a higher cost, limiting its adoption [81,82,84].

The Raman spectroscopy as a characterization technique for crystalline and amorphous carbon materials is directly dependent on two modes, band D and band G, as represented in Figure 7. The D band over 1350 cm^{-1} is commonly assigned to K-point phonons with A_{1g} symmetry. At the same time, the G band between 1580 and 1600 cm^{-1} is usually attributed to E_{2g} symmetry zone center phonons. Amorphous carbon material comparisons using fix values of λ and integrated D (I_d) and G (I_g) bands allow ordering identification. Consequently, for amorphous carbonaceous samples, I_d/I_g increases with increasing ordering or crystallinity [84,85].

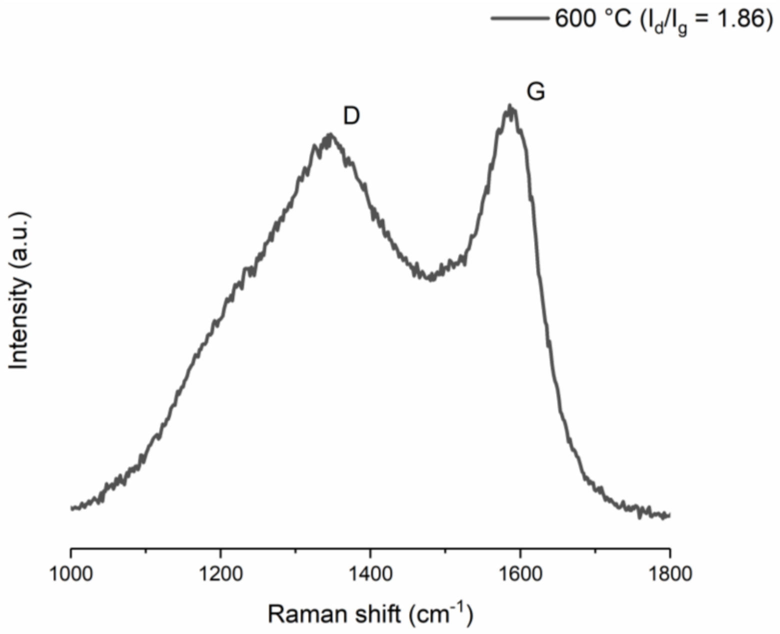

Figure 7. Raman spectra of barley biochar, at 633 nm, prepared by pyrolysis over 600 °C. Source: The authors.

5.5. Thermogravimetric Analysis (TGA)

TGA is a technique where a sample is heated from room temperature until 1000 °C at a steady flow of nitrogen, helium or air, and a weight loss pattern is registered. The interpretation of the final TGA pattern allows the assessment of structural stability, moisture content, inorganic content (ashes content), and loss of characteristic functional groups and may also be used for kinetic studies and feedstock pyrolytic temperature assessment. Biochar materials prepared below 400 °C are less stable than those prepared above 400 °C due to the greater stability of cyclic carbon chains formed at higher temperatures. Degradation temperatures vary based on the material stability, but commonly, degradations between 100 and 200 °C are assigned to loss of water, between 200–600 °C to volatile matter, and the residue past 600 °C to inorganic materials, if under air flow, or inorganic materials and graphite, if under He or N_2 flow [81,86]. Figure 8 presents the weight loss patterns for residual brewer spent grains biomass and biochar samples [31].

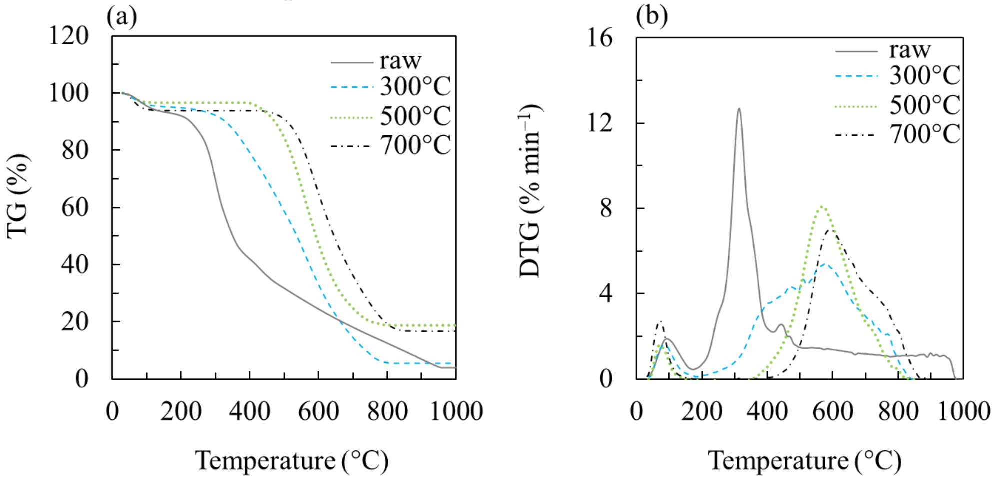

Figure 8. TGA analysis of residual biomass: a) Brewer spent grains thermogravimetry and b) Brewer spent grains derivative thermogravimetry. Adapted from Evaristo et al. [31].

5.6. Scanning Electron Microscopy (SEM)

SEM is a morphological technique for the characterization of surfaces. When applied to biochar, it is possible to identify pore arrangement and distribution. In direct contrast, SEM coupled with Energy Dispersive X-Ray spectroscopy (EDX) allows the localized estimation of surface elemental composition and, therefore, can be used for elemental mapping post-adsorption, as shown in Figure 9 [87–89].

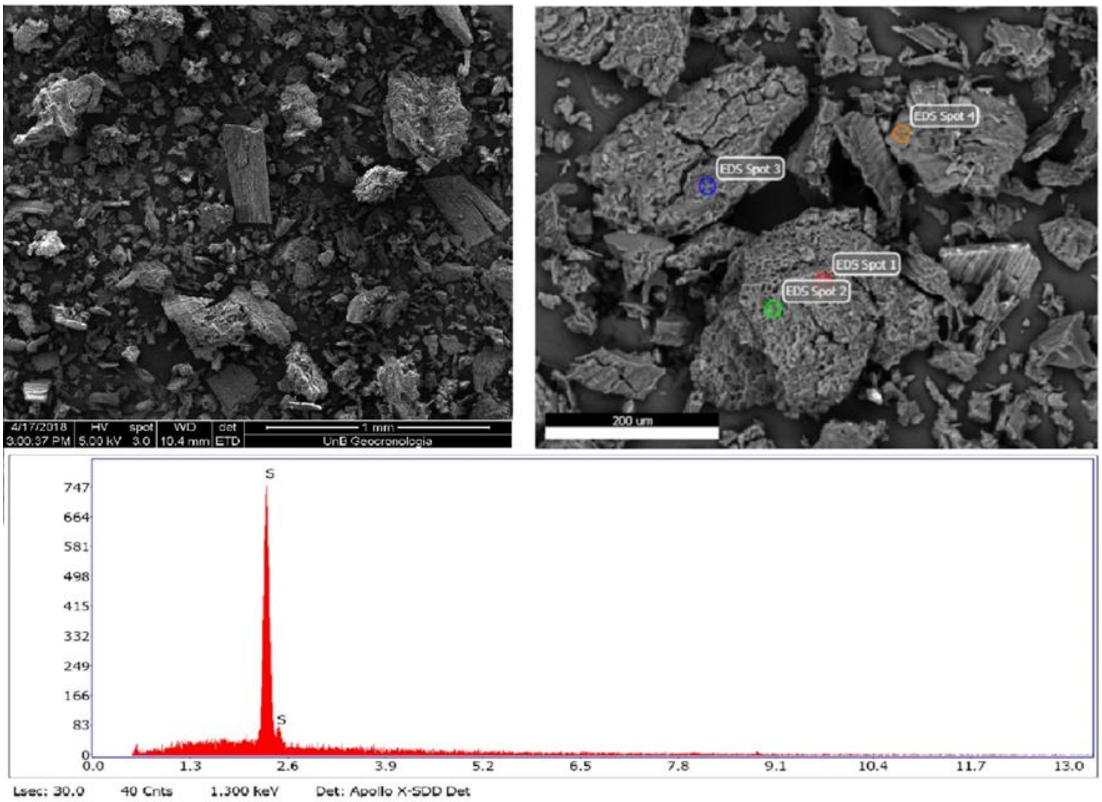

Figure 9. SEM-EDS analysis from biochar sulfonated catalyst. Source: The authors.

5.7. Böehm Titration—Functional Group Identification and Acidity Analysis

The Böehm titration technique, first proposed by Böehm in 1994 [90], is a characterization method for the quantification and identification of oxygenated groups on the surface of carbonaceous materials, such as biochar. The method is based on the acidity difference between oxygenated groups. Carboxylic acids, phenols and lactic groups are neutralized by sodium hydroxide, carboxylic acids and lactic groups are neutralized by sodium carbonate and carboxylic acid groups are neutralized by sodium bicarbonate. The biochar samples undergo a pre-treatment by washing to remove superficial inorganic compounds to avoid interferences, while the system itself is degassed with Ar or N_2, reducing the effect of dissolved CO_2 [91].

5.8. Solid-State Nuclear Magnetic Resonance (ssNMR)

The ssNMR of ^{13}C is a spectroscopic technique used to study the structural compositions of carbonaceous materials. On biochar, C^{13} ssNMR allows the determination of carbon-containing compounds and groups, such as aliphatic and aromatic hydrocarbons, phenolic and methoxyl groups and others. Moreover, ssNMR and FTIR are commonly and simultaneously used to identity structure and functional biochar groups [92,93].

5.9. X-ray Photoelectron Spectroscopy (XPS)

XPS analysis allows the identification of compounds and bonds on a particular point of the biochar surface at a depth of up to 10 nm. It is an essential technique for determining heavy metals and may also be used to determinate elements on the surface of biochar, such as Fe, Mn, Si, Al, Na, N, O and others [94–96].

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6. Biochar Application

6.1. Soil Amendment

Soil amendments must possess properties such as high binding capacity and environmental safety and should have no adverse effect on the soil structure, soil fertility, or the ecosystem on the whole [36]. By definition, biochar consists of relatively labile aliphatic carbon, stable aromatic carbon, and mineral ash. Because of that, the use has been accepted as a sustainable approach and a promising way to improve soil quality and remove heavy-metal pollutants from the soil. Moreover, it has been used to promote improvements in soil properties, which is particularly important. It may be argued that it is necessary for regions where naturally poor soils predominate, whose fertility and structure maintenance depend almost exclusively on the conservation of soil organic matter [97].

A high surface area and abundant functional groups are favorable if high sorption potential (e.g., nutrient retention and adsorption of pesticides or toxic compounds) is needed. If used as a bulking agent during organic waste composting, larger particle size is advantageous, whereas powdery biochar might be better for other applications, such as the remediation of contaminated soils. Additionally, ash-rich biochars may increase soil pH and EC and provide nutrients, whereas biochars rich in volatile matter may reduce nitrogen availability. Biochars with a high OC content and relatively low ash and volatile matter content (clean biochars) are versatile, ranging from potting media to bulking agents and soil amendment [37].

6.2. Catalysis

Applying biochar as catalysts (catalyst support or heterogenic catalyst) is directly dependent on the mass transport phenomena. Functional sites must be accessible for subtracts while successfully diffusing the products out of the catalytic interface. The control of access and diffusion is accomplished by the pore size/volume control, surface activation/functionalization and distribution of active sites. Thus, information about pore structure, pore volume, superficial area and distribution of active sites are the most important properties related to biochar as a catalyst [41,98].

Biochar supports heterogeneous catalysts based on noble, non-noble, and bimetallic metals. In addition, it applies to biorefinery processes: esterification, transesterification, hydrogenation, catalytic reform, catalytic pyrolysis, hydrolysis, Fisher-Tropsch reactions, isomerization, electrocatalysis and others [98,99]. Yan and coworkers [100] showed the effectivity of iron nanoparticles, supported over biochar, for converting syngas into liquid hydrocarbons by Fisher-Tropsch synthesis. Biochar was demonstrated to be effective as a solid acid catalyst for the transesterification of oils and esterification of oleic acid due to its density of sulfonic acid groups, hydrophobicity and site strength [101,102].

Biochar was also demonstrated to be an efficient and low-cost catalyst for removing tar in the catalytic reform process of pyrolytic biomass volatiles [103]. Biochar catalysts presented great catalytic activity in producing phenols and hydrogen-rich gas from catalytic pyrolysis of Sargassum brown macroalgae [104]. Biochar was studied by Zhao and coworkers [105] as an activator for peroxymonosulfate and applied to the degradation of organic contaminants in water. Therefore, biochar-based catalysts represent a cost-effective and catalytic active possibility for a broad range of applications [98].

The characterization techniques of biochar as catalysts and their application are directly related. The results of the direct comparison are often limited due to non-standard methodologies. For instance, in biodiesel production using sulfonated biochar, Cao and collaborators demonstrated the application of sulfonated corncob biochar to the esterification of oleic acid [106]. The biochar catalyst was characterized by elemental composition, BET, XRD, FT-IR, XPS, TGA and SEM+EDS, while the $–SO_3H$ content was determined by Boehm tritation. Corrêa et al. demonstrated the activity of murumuru kernel shell sulfonated biochar catalyst on the esterification of oleic acid [107]. The catalyst was characterized by SEM, EDS, CHN, FT-IR, Raman, TGA and XPS. The $–SO_3H$ content was determined by NaOH tritation.

Azman and collaborators showed the application of activated woodchip biochar on waste oil esterification/transesterification [108]. The biochar catalyst was characterized by XRD, TGA and FESEM (Field Emission Scanning Electron Microscopy). Daimary and co-workers presented the application of potato peel alkaline biochar on the cooking waste oil esterification/transesterification [109]. The catalyst characterization methods included XRD, FTIR, TEM, EDX and FESEM, while the catalyst basicity was determined by Hammet indicator test.

6.3. Biofuel

The biomass pyrolytic process, fast or slow, produces tree main portions with the energetic application. The gas phase might be used as a hydrogen source, the liquid phase as a fossil fuel substitute, and the solid phase (biochar) can be used as a substitute for coal [110,111]. Therefore, solid fuel sources for bioenergetics applications must be energetically dense, with proper fuel ratio, combustibility index and high heating values (HHV) [4,18,112,113].

Table 5. Biochar applications as fuel along source biomass and preparation conditions.

Source Biomass	Biochar Preparation Conditions	Optimum Biochar Characteristics and Combustibility Properties	Ref.
Orange peel	Pyrolysis Atmosphere: N_2 Temp.: 500 °C HR: 5 °C min^{-1} Time: 60 min	Biochar O/C – 0.12; Biochar H/C – 0.66; HHV–25.73 MJ kg^{-1}; Energy yield – 47.52%; Fuel Ratio – 5.87; Thermal stability – 0.85.	[114]
Sugarcane bagasse	Pyrolysis Atmosphere: N_2 Temp.: 600 °C HR: 10 °C min^{-1} Time: 30 min	Biochar O/C – 0.3; H/C – 0.2; HHV–29.99 MJ kg^{-1}; Biochar yield – 21.75%; Fuel Ratio – 3.21; Energy yield – 36.32%.	[115]
Palm fiber	Pyrolysis Atmosphere: N_2 Temp.: 700 °C HR: 5 °C min^{-1} Time: 120 min	Biochar O/C – 0.23; Biochar SSA – 0.272 m^2 g^{-1}; HHV – 26.77 MJ kg^{-1}; Biochar yield – 28.37%; Energy yield – 45.72%.	[116]
Spent coffee grounds	Torrefaction Atmosphere: N_2 Temp.: 300 °C Time: 30min	Biochar O/C – 0.39; Biochar H/C – 0.10; Biochar SSA – 0.524 m^2 g^{-1}; HHV- 30.32 MJ kg^{-1}; Biochar yield – 62%.	[117]
Poplar wood	Pyrolysis Atmosphere: N_2 Temp.: 600 °C HR: 5–20 °C min^{-1}	Biochar O/C – 0.06; Biochar H/C – 0.025; HHV-32.73 MJ kg^{-1}; Biochar yield – 24.3 %; Fuel Ratio – 6.86; Combustibility Index – 1.9 s^{-1} °C^{-2}; Comprehensive combustion characteristic index – 3.3 s^{-2} °C^{-3}.	[118]
Sewage sludge	Pyrolysis Atmosphere: N_2 Temp.: 450 °C HR: 10 °C min^{-1} Time: 30min	Biochar O/C – 0.19; Biochar H/C – 0.74; HHV–13.58 MJ kg^{-1}; Biochar yield – 57.90%; Fuel Ratio – 0.86; Energy yield – 42.04%; Combustion index – 0.59 10^6 %$^{-2}$ s^{-2} °C^{-3}.	[2]
Sesame stalks	Torrefaction Atmosphere: N_2 Temp.: 275 °C	Biochar O/C – 0.64; Biochar H/C – 1.25; HHV–20.5 MJ kg^{-1}; Biochar yield – 76.25%; Fuel Ratio – 0.52;	[119]

	Time: 30min	Energy yield – 86.16%; Bulk density – 290.01 kg m^{-3}.	
Microalgae - *Chlorella pyrenoidosa*	Pyrolysis Atmosphere: N_2 Temp.: 400–600 °C HR: 10 °C min^{-1} Time: 30min	Biochar O/C – 0.23; Biochar H/C – 0.055; HHV–17.15 MJ kg^{-1}; Biochar yield – 51.23%; Fuel Ratio – 1.72.	[120]
Camellia shell	Steam-torrefaction Atmosphere: N_2 Temp.: 280 °C Time: 30min	Biochar O/C – 0.36; Biochar H/C – 0.07; Biochar SSA – 28.66 m^2 g^{-1}; HHV–24.76 MJ kg^{-1}; Biochar yield – 50.45%; Fuel Ratio – 1.04.	[121]

Thermo-chemical processes might enhance the quality of biochar as an energetic source. The main objective of such is to increase density while decreasing O/C and H/C ratios [110,122,123]. Some applications for biochar as solid fuel are shown in Table 5, where it is possible to identify the correlation between biochar preparation conditions and HHV. In other fuels-related applications, biochar as an electrode has been studied in the composition of solid oxide fuel cells with exciting results [124,125]. One such is using the composition of anodes for lithium-ion batteries, where extensive surface area, porosity and ion storage capabilities are desired [126].

6.4. Wastewater Treatment

Wastewater treatment solutions based on biochar adsorption depend on the material's adsorption capabilities. On the other hand, the biochar adsorption capabilities depend on parameters such as superficial area, pore volume, activation and functionalization processes, among others [127,128]. Therefore, a functionalized high surface area is desirable for higher adsorption values, while the pore volume can be tuned to assign selectivity to the process [128,129].

Different contaminants require different biochar parameters for efficient adsorption and possible desorption for biochar recycling/reuse [130,131]. The publications on wastewater treatment with biochar present adsorptions with synthetic solutions of contaminants, varying between antibiotics, dyes and toxic metals [132–134]. Some studies with possible water contaminants, such as tetracycline (antibiotic), methylene blue (dye) and Cr (III)/Cr(IV) (toxic metals), are compiled in Table 6, which identifies the direct relation between adsorption capabilities, superficial area, pore volume and temperature/activation conditions.

Table 6. Biochar applications as adsorbent along source biomass and preparation conditions.

Biomass	**Process**	**Contam.**	**Biochar Properties and Adsorption Data**	**Ref.**
Microalgae (*Spirulina sp.)*	Pyrolysis Atmosphere: N_2 Temp.: 750 °C Time: 120min	Tetracycline (TC)	O/C–0.138; H/C–1.38; SSA–2.63 m^2 g^{-1}; Desorption efficiency–61 %; Highest TG adsorption at 147.9 mg g^{-1} (TC 100 mg L^{-1}; dosage 0,1 g L^{-1}; pH 6).	[135]
Wheat Straw	Pyrolysis Atmosphere: N_2 Temp.: 500 °C Time: 120 min Activation: $KMnO_4$/KOH		O/C–0.225; H/C–0.007; SSA–1524.6 m^2 g^{-1}; Pore volume–0.85 cm^3 g^{-1}; Raman I_D/I_G before adsorption–2.58; Desorption efficiency (NaOH solution)–7%; Highest TG adsorption at 584.19 mg g^{-1} at 318 K (TC 10–200 mg L^{-1}; pH 3–10); No co-existing ions effect	[136]
Sunflower Seed Husk	Pyrolysis Atmosphere: N_2 Temp.: 700 °C Time: 120 min		O/C–0.1; H/C–0.014; SSA–1578.3 m^2 g^{-1}; Pore volume–1.138 cm^3 g^{-1}; Raman I_D/I_G before adsorption–0.585; Desorption efficiency–97.61%; Highest TG adsorption at	[137]

	Activation: $KMnO_4$/KOH/$ZnCl_2$		673.0 mg g^{-1} at 298 K for 24h (TC 1–20 mg L^{-1}; pH 3.0–11.0); Highest TG adsorption with ions at 583.1 (K^+), 539.8 (Mg^{2+}) and 555.9 (Ca^{2+}).	
Microalgae - *Chlorella sp.* GD	Wet Torrefaction (Water vapor) and Microwave Torref. (2450MHz, 800W) Temp.: 160–170 °C Time: 5–10min	Methylene Blue (MB)	O/C between (0.462–0.506); SSA–2.66 $m^2\ g^{-1}$; Pore volume 0.00043 $cm^3\ g^{-1}$; Maximum removal of 85.47% MB; Highest MB adsorption at 113 mg g^{-1} (optimum pH 2–8).	[138,139]
Penicillin mycelial residues	Torrefaction Atmosphere: N_2 Temp.: 260 °C HR.: 5 °C min^{-1} Time: 45 min Impregnation: KOH		O/C–0.08; H/C–0.021; SSA – 1809.74 $m^2\ g^{-1}$; Pore volume 1.02 $cm^3\ g^{-1}$; Raman I_D/I_G before adsorption – 1.21; Highest MB adsorption at 620 mg g^{-1}.	[140]
Bamboo particles	Pyrolysis Atmosphere: N_2 Temp.: 700 °C HR.: 10 °C min^{-1} Time: 120 min Impregnation: $KHCO_3$/ Urea		O/C–0.081; SSA–1693 $m^2\ g^{-1}$; Biochar total pore volume 0.90 $cm^3\ g^{-1}$; Raman I_D/I_G before adsorption – 1.10; Highest MB adsorption at 499 mg g^{-1}.	[141]
Orange peel	Pyrolysis Atmosphere: N_2 Temp.: 400 °C HR.: 5 °C min^{-1} Time: 180 min Activation: KOH	Cr(III)/Cr(IV)	Cr(IV) synthetic solution; O/C–0.100; SSA–998 $m^2\ g^{-1}$; Biochar total pore volume–1.24 $cm^3\ g^{-1}$; Raman I_D/I_G before adsorption–1.03; Highest Cr(IV) adsorption at 285.5 mg g^{-1} (pH – 2, Dosage 0,2 g L^{-1}, C_0 100 mg L^{-1}, T = 25 °C, contact time = 40 h).	[142]
Vegetal waste – Rice Husk/ Polyethylene	Co-pyrolysis Atmosphere: N_2 Temp.: 390 °C Time: 35 min		Cr(III) synthetic solution; O/C 0.089; Biochar SSA <5.0 $m^2\ g^{-1}$; Adsorption capacity–9.23 mg g^{-1} (final pH 4–5).	[143]
Algae - *Potamogeton crispus*	Pyrolysis Atmosphere: N_2 Temp.: 300 °C HR.: 5 °C min^{-1} Time: 120 min		Cr(IV) synthetic solution; O/– 0.53; H/C–0.09; SSA–0.42 $m^2\ g^{-1}$; Pore volume–0.002 $cm^3\ g^{-1}$; Raman I_D/I_G before adsorption–1.83; Highest Cr(IV) adsorption at 34.37 mg g^{-1} (pH–2, Dosage 2 g L^{-1}, C_0 100 mg L^{-1} and T = 25 °C.).	[144]
Paper sludge waste	Pyrolysis Atmosphere: N_2 Temp.: 350–550 °C HR.: 5 °C min^{-1} Time: 120 min Activation (KOH) Temp.: 105 °C Time: 150 min / Pyrolysis Atmosphere: N_2 Temp.: 800 °C		Cr(IV) synthetic solution; O/C–0.383; H/C–0.059; SSA–3336.7 $m^2\ g^{-1}$; Pore volume–2.10 $cm^3\ g^{-1}$; Raman I_D/I_G before adsorption–0.95; Highest Cr(IV) adsorption at 356.25 mg g^{-1} (99% removal under 30 min.).	[145]

	Time: 120 min Impregnation: NH_4Cl

5. Multi-Criteria Decision Analysis

Different technologies characterize the thermochemical conversion route, which refers to various biomass feedstock and operational conditions, reflecting different applications that often conflict with each other, thus requiring multidisciplinary decision support. Therefore, for an optimized and comprehensive decision-making process, it is critical to include multiple criteria, allowing the selection of feedstocks, technologies, and operational conditions for a specific biochar application. Multi-Criteria Decision Analysis (MCDA) is a tool that can effectively contribute to answering that challenge.

Previous literature reviewed the way, the scope, and the multi-criteria techniques that have been applied up-to-now to waste to energy management, considering anaerobic digestion, incineration, gasification, landfill to gas and pyrolysis routes [146]. The study reported the application of different MCDM techniques, mainly focusing on selecting WtE generation technologies based on environmental, economic, technical, and socio-political [147]. The reviewed literature evaluates the technologies that could efficiently convert biomass by applying technologies WTE to produce different energy carriers [147–151]. However, few studies in the literature applied MCDM, focusing on evaluating and optimizing specific WTE technologies based on the produced biochar properties and their applications.

The previous study has applied MCDM (Dominance analysis and metric distance based on the approach of compromise programming) to select optimum operational parameters for pyrolysis grape pomace [152]. The MCDM evaluated the pyrolysis operational parameters (temperature and heating rate) considering the criteria that most favor biochar for biofuel application (solid yield, carbon content, HHV, and Activation energies from pyrolysis kinetics) [152]. In addition, soil amendment application was assessed considering the criteria: solid yield, carbon content, H/C, O/C N, P, Mg and K biochar contents. The results demonstrated that multi-criteria decision methods could help determine the biochar's advantages for each application, depending on the associated production process characteristics [152].

Regarding wastes from food industries, the valuation route of pequi seed and its extractives was investigated using MCDM and considering pyrolysis, gasification and transesterification WTE routes [26]. The obtained biochar at different temperatures was investigated for biofuel and soil amendment applications. Results provided insights into the energetic supply and demand in local/rural communities, showing that the decision support method helped identify and compare the optimal conversion parameters.

Past work assessed spent coffee grounds and brewers' spent grains considering biochar production via pyrolysis for biofuel (biochar criteria: H/C, O/C, HHV, EF and EY) application [31]. The MCDM results recommended optimum operational conditions to valorize low-cost feedstock more economically through pyrolysis and gasification.

MCDM was applied to investigate and define optimum biomass blends from urban forest wastes (pruning waste) for biochar production as biofuel via mild pyrolysis (torrefaction) [68,153]. As indicated, the MCDM allowed identifying the optimum conditions for each application and the definition of an optimized blend.

In a recent and complete study, Petrova et al. [154] performed a multi-objective decision analysis of produced biochars (grape pomace, cherry, peach, colza, sunflower husks, and softwood). Utilizing the experimentally obtained physical and chemical characteristics of the produced biochar (500 °C), a decision-support tool was employed, concentrating on its potential functions as a biofuel, catalyst, CO_2 sequestration method, soil enhancement, and even as a supercapacitor [154]. The evaluation aimed at aiding decision-making revealed that biochar derived from peach stones, cherry stones, and grape pomace exhibited the most advantageous results for various applications, encompassing biofuel. Furthermore, the CO_2 adsorption potential of biochar suggests its utility could go beyond just energy conversion techniques.

In this context, the scientific challenge of the topic under consideration can be categorized into three main categories: (i) knowing which MCDM provides a multifaceted analysis with less effort for a specific application, (ii) knowing which properties (criteria) must be assessed for each specific application, (iii) the applied analytical technique evolved to characterize the obtained biochar and obtain those properties, and (iv) conducting the process optimization for a specific thermochemical route.

7.1. MCDM Criteria Selection, Analytical Technique, and Optimization

Due to its versatile physicochemical properties, biochar is indicated to have various potential applications [152]. For example, biochar can be used as biofuel, fertilizer, catalyst and absorbent depending on its different properties derived from the process operational conditions. In addition, specific biochar properties are benefic for some applications. Therefore, the step of criteria selection is essential and depends mainly on biochar criteria that have the most influence for a determined application and less complex/expensive analytical technique. Table 8 summarizes the MCDM studies indicating the investigated lignocellulosic biomass, evolved criteria, required analytical techniques and decision methodology for each biochar application. In addition, studies related to wastewater treatment were selected to allow insight for future research.

Table 8. Summary of biochar studies indicating the assessed feedstock (lignocellulosic biomass), biochar properties for each application, required analytical techniques and the MCDM (if applied).

App.	Biomass	Properties/Criteria	Analytical Technique	MCDM	Ref.
Biofuel	Grape pomace	Biochar yield, Carbon (%), HHV, Kinetics Combustion parameters (E_a)	Proximate analysis Calorific analysis Ultimate analysis TG/DTG	Pareto Dominance Analysis / Metric distance based on compromise programming	[152]
	Grape pomace, cherry stones, peach stones, colza, sunflower husks, and softwood	Moisture%, Ash, HHV, Kinetics Combustion parameters (E_a)	Proximate analysis Calorific analysis TG/DTG	Pareto Dominance Analysis / Metric distance based on compromise programming	[154]
	Fruit seeds	Carbon enhancement index (CEI), HHV and its enhancement factor (EF) and energy-mass coefficient index (EMCI)	Calorific analysis Ultimate analysis	Pareto Dominance Analysis / Metric distance based on compromise programming	[26]
	Spent coffee ground Brew spent grains	O/C and H/C, HHV and its enhancement factor (EF), energy yield (EY)	Calorific analysis Ultimate analysis	Pareto Dominance Analysis / Metric distance based on	[31]

				compromise programming	
	Pruning trees	FC, ash, HHV, O/C and H/C	Proximate analysis Calorific analysis Ultimate analysis	Pareto Dominance Analysis / Metric distance based on compromise programming	[68]
Catalyst	Grape pomace, cherry stones, peach stones, colza, sunflower husks, and softwood	K, Ca, P (%), Carbon (%), Specific surface area (m^2 g^{-1})	EDS Ultimate analysis Brunauer–Emmett–Teller (BET) method	Pareto Dominance Analysis / Metric distance based on compromise programming	[154]
Soil Amendment	Fruit seeds	O/C and H/C, Carbon enhancement index (CEI), K, N, P(%)	EDS Ultimate analysis	Pareto Dominance Analysis / Metric distance based on compromise programming	[26]
	Grape pomace	Biochar yield, Carbon content, O/C and H/C, N, P, Mg, K	EDS Ultimate analysis	Pareto Dominance Analysis / Metric distance based on compromise programming	[152]
Soil Amendment / CO_2 sequestration / Supercapacitor development	Grape pomace, cherry stones, peach stones, colza, sunflower husks, and softwood	K, Ca, P (%) / Carbon (%) / Specific surface area, Bulk density, electric conductivity, pH	EDS Ultimate analysis Brunauer–Emmett–Teller (BET) method Biochar pH, Electrical Conductivity and Liming Potential	Pareto Dominance Analysis / Metric distance based on compromise programming	[154]
Wastewater treatment	*Spirulina sp.* Wheat straw Sunflower seed husk *Chlorella sp.*	O/C SSA Pore volume Raman I_D/I_G Surface composition Adsorption capability	Ultimate analysis Physicochemical analysis Surface analysis Molecular/structural analysis	-	[81,135–138,140–145]

	Penicillin mycelia
	Bamboo particles
	Orange peel
	Rice husk
	Paper sludge

Table 8 identifies the criteria for each application. Biofuel: Biochar may be suitable as an alternative solid biofuel compared to raw biomass and has a lower CO_2 emission than coal. Even though the concerns with yield capacity may not yet be settled for large-scale (industrial) applications, advantageous biochar characteristics show promise in management and energy recovery. As can be seen in Table 8, previous studies focussed on proximate, ultimate and calorific analysis and TG/DTG for assessing combustion behavior. Therefore, MCDM criteria selection must focus on lower moisture content, higher fixed carbon, lower volatile matter and ash content, lower H/C and O/C and higher HHV for biofuel applications. The activation energy (mainly in the devolatilization stage) should be evaluated considering combustion behavior.

Catalyst: Catalyst processes are known to use carbon-based materials, where biochar can have its role. As depicted by Table 8, only one study applied MCDM to evaluate six biochar produced at 500 °C for catalysis application. For instance, a higher specific surface area (SSA) and K, Ca, P and C contents indicate a better biochar for this application.

Soil amendment: Biochar possesses considerable benefits for soil enhancement. Considering the three studies that assessed biochar for soil amendment application, the explored criteria contemplated a higher biochar yield with more excellent carbon content and lower O/C and H/C. Moreover, a biochar with superior SSA and K, N, P, Ca and Mg (%) is beneficial. In addition, higher bulk density, electric conductivity, and pH are also aimed. As stated by [154], the comparable characteristics of biochar have potential applications in other processes, such as carbon dioxide (CO_2) capture and the advancement of supercapacitors, owing to its significant specific surface area, porous framework, surface functional groups, and substantial mineral content.

Wastewater treatment: Biochar as an adsorbent for water treatment is considerably more efficient than non-treated biomass. The adsorption capabilities, and therefore application, of such materials are directly linked to the pyrolytic conditions, activation and superficial characteristics. From the literature review (Table 8), no study has applied MCDM to evaluate produced biochar aim to apply to wastewater treatment. Based on the assessed properties of the previous research [81,135–138,140–145], MCDM criteria selection must include higher SSA, higher pore volume, higher Raman I_D/I_G and higher adsorption capability.

7. Conclusions and Perspectives

Biochar production is one of the most efficient possibilities for using agro-forests-industrial residues. Therefore, it is directly linked to the circular economy concepts, mainly on the WtE, while also aligning with the 17 goals for sustainable development established by the United Nations [155].

Biochar, at its most simple definition, is a carbon-based material used in soil remediation processes. This review gives a broader contextualization for its different definitions, source lignocellulosic biomass, production techniques, characterization methods, applications and multi-criteria analysis.

The versatile physicochemical properties of biochar highlight its potential for diverse applications, ranging from biofuel production and catalysis to soil enhancement and wastewater treatment. The selection of criteria is a crucial step in determining the suitability of biochar for specific applications, and this choice is influenced by the dominant factors governing each use case. While primary studies have provided insights into biochar's potential as biofuel, there remains a need for comprehensive multi-criteria decision-making (MCDM) assessments in several areas, including catalysis and wastewater treatment. Moreover, due to its unique physical attributes, biochar's exceptional properties also extend to emerging fields like carbon capture and supercapacitor development.

To further the knolowdge, future investigations could ally economic and environmetal aspects such as energy expenditures for biochar production and impact categories (such as Global Warming Potential) from life cycle assessment. These assessments would guide the selection of biochar properties that hold significance for each application, ultimately contributing to informed decision-making in the sustainable utilization of biochar's capabilities.

The amount of studies related to biochar preparation, characterization and usage is expected to increase in the following years, along with implementing more efficient processes and green energy plants. This prospect indicates a bright future for countries with abundant biomass and that more studies must be conducted to implement biochar materials in more complex applications, effectively promoting sustainable development.

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