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1 **Processes, applications and legislative framework for carbonized anaerobic**
2 **digestate: opportunities and bottlenecks. A critical review.**

3

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22

23 **Abstract**

24 Char is a valuable product obtained from thermochemical conversion processes of different biomass
25 feedstocks, mainly pyrolysis and hydrothermal carbonization (HTC). In this work, anaerobic digestion (AD)
26 integration with pyrolysis/HTC is critically reviewed, considering anaerobic digestates as feedstocks for char
27 production. This virtuous interconnection can boost sustainable digestate valorization in the circular economy
28 framework. Different substrates for AD are investigated, including sewage sludge, food waste, agricultural
29 residues, and animal manure. The available thermochemical technologies, including pyrolysis, HTC and other
30 processes, are considered, analyzing the effects of substrate characteristics and process parameters on char
31 quality. The possible fields of char application are successively presented, including agricultural application,
32 energy recovery, pollutants adsorption, catalysts production, and electrochemical technologies; the advantages
33 and drawbacks of each application are highlighted. Limitations still preventing the full-scale application of
34 digestate-derived char production and utilization include the variability in substrate characteristics and the
35 presence of undesired pollutants (especially in sewage sludge digestate), full-scale development of
36 thermochemical plants, lacking legislative frameworks, uncertain economic sustainability, limited eco-
37 toxicological studies, and stakeholders' acceptance. Future research needed on the topic is finally depicted,
38 with the aim of widening digestate reuse applications, as thermochemical processes may prevent safety
39 concerns linked to direct agricultural reuse, leading to sustainable biorefinery platforms.

40

41 **Keywords**

42 Char; hydrothermal carbonization; pyrolysis; energy recovery; soil application; legislation

43

44 **Abbreviations**

45	AD	Anaerobic digestion
46	AHL	Aqueous hydrothermal carbonization liquid
47	AOX	Adsorbable organic halogens
48	APC	Autogenic pressure carbonization
49	APL	Aqueous pyrolytic liquid
50	AW	Agricultural waste
51	BET	Brunauer-Emmett-Teller
52	BMP	Biochemical methane potential
53	BQM	Biochar quality mandate
54	CAP	Common agricultural policy
55	COD	Chemical oxygen demand

56	DIET	Direct interspecies electron transfer
57	DM	Dry matter
58	DSC	Differential scanning calorimetry
59	EBC	European Biochar Certificate
60	EC	Electrical conductivity
61	ED	Energy densification
62	EU	European Union
63	EY	Energy yield
64	FC	Fixed carbon
65	FW	Food waste
66	GHG	Green-house gas
67	GI	Germination index
68	HHV	Higher heating value
69	HTC	Hydrothermal carbonization
70	IBI	International biochar initiative
71	LAS	Linear alkylbenzene sulfonates
72	LCA	Life cycle assessment
73	LCC	Life cycle costing
74	MET	Microbial electrochemical technologies
75	MLHC	Microwave-assisted hydrothermal carbonization
76	MLHT	Microwave-assisted low-temperature hydrothermal treatment
77	MSW	Municipal solid waste
78	NP	Nanoparticles
79	PAH	Polycyclic aromatic hydrocarbons
80	PCB	Polychlorinated biphenyl
81	PCDD	Poly-chlorinated dibenzodioxins
82	PCDF	Poly-chlorinated dibenzofurans
83	PDS	Peroxydisulfate
84	PHA	Polyhydroxyalkanoates
85	PMS	Peroxymonosulfate
86	SBET	Surface area Brunauer-Emmett-Teller
87	SCWG	Supercritical water gasification
88	SS	Sewage sludge
89	TAN	Total ammoniacal nitrogen
90	TN	Total nitrogen
91	TP	Total phosphorus

92	TS	Total solids
93	VFA	Volatile fatty acid
94	WHC	Water holding capacity
95	WWTP	Wastewater treatment plant
96	ZVI	Zero valent iron

97

98 **1. Introduction**

99 For a long time since, anaerobic digestion (AD) has been mostly investigated to maximize biogas production.
 100 Only in the last decade, when the implementation of circular economy principles became a priority, the number
 101 of research studies dealing with sustainable management strategies for anaerobic digestate valorization
 102 significantly increased. A survey in Scopus revealed that the number of research articles addressing digestate
 103 treatment (search within “Article title, Abstract, Keywords”; search tips: (digestate OR
 104 anaerobic digestate) AND (treatment OR valorization)) has more than tripled from 2016 to 2022, compared to
 105 the period 1960-2015.

106 Besides being a valuable product extracted from organic wastes or under-utilized resources, bioenergy
 107 produced by AD offers several advantages compared to other renewable energy sources (wind, solar, marine).
 108 Firstly, it can be stored, as the products are essentially chemical energy stores [1], and secondly, it is generated
 109 by highly flexible and scalable systems (digesters) [2]. The World Biogas Association [3] estimated that
 110 approximately 132,000 digesters were operating worldwide in 2018 (18,943 in Europe by the end of 2019 [4]),
 111 with an additional 50 million micro-scale digesters (reactor size: 0.2-100 m³) serving households and small
 112 communities. According to the International Energy Agency [5], biogas and biomethane production in 2018
 113 was around 35 million tons of oil equivalent (Mtoe), which is only a limited fraction of the overall potential
 114 (730 Mtoe) estimated considering the worldwide availability of sustainable feedstocks (i.e., not in competition
 115 with agricultural land for food). In view of the above, the implementation of AD processes is expected to
 116 further grow worldwide, together with the generation of anaerobic digestate. No affordable data on digestate
 117 production are available to date, but according to estimates for EU28, around 180 million tons of digestate are
 118 generated yearly, 68% being of agricultural origin [6]. Other estimates suggest that produced digestate amounts
 119 are 20 m³/yr per kW of the installed electric capacity of downstream combined heat and power units [7].

120 Digestate quality, which is primarily determined by feedstock’s composition and characteristics, defines its
 121 possible end-use applications. Agricultural digestate, as well as digestate from agroindustry by-products and
 122 source-separated biowaste from municipal solid waste (MSW), is typically used as fertilizer and soil improver
 123 in agriculture, horticulture and hobby gardening. Sewage sludge digestate and digestate from the organic
 124 fraction of mixed MSW, instead, is often incinerated or landfilled [6]. Overall, in Europe, 95% of digestate is
 125 applied in agriculture [8].

126 Despite the high potential for closing nutrient cycles in agriculture and reducing external inputs of mineral
 127 fertilizers, digestate application on agricultural lands poses some potential drawbacks [9]. In fact, its

128 uncontrolled disposal can cause nutrients runoff [10]: the anaerobic degradation of protein-rich biomasses
129 enriches total ammoniacal nitrogen (TAN) concentration in digestates, limiting its use in areas classified as
130 vulnerable for nutrient pollution of ground and surface waters. Likewise, phosphorus (P) content is of concern
131 in digestate management, being responsible for the eutrophication phenomenon (Water Framework Directive,
132 2000/60/EC). Traditional digestate application methods, such as spray irrigation, can cause ammonia, carbon
133 dioxide and nitrous oxide emissions [11]. In Europe, national legislations establish maximum nitrogen (N)
134 loads to be applied on the fields, minimum required digestate storing capacity and compulsory spreading
135 season to properly fertilize agricultural fields without posing environmental risks (Directive 91/676/EEC).
136 Depending on the specific feedstock, digestate may also contain heavy metals, antibiotics, organic pollutants
137 or pathogens [7]. Digestate from sewage sludge, in particular, tends to accumulate pollutants from wastewater,
138 and is often characterized by high heavy metal concentrations (0.5-2% on dry matter basis, but sometimes up
139 to 4%) [12] that may limit its direct agricultural reuse (according to current legislation standards) [13]. Despite
140 sewage sludge digestate did not show phytotoxic effects in tomato plants cultivation in poor alkaline sandy
141 soils [14], sewage sludge co-digestion with food or agricultural waste may improve its properties for
142 agricultural reuse, improving its fertilizing characteristics [15]. Manure-derived digestate, instead, may
143 include, beside heavy metals, antibiotics and pharmaceuticals (used in breeding activities) [16], while digestate
144 from organic waste (especially when coming from source-separated streams) typically shows more favorable
145 properties (reduced heavy metals and pathogens, presence of humic and fulvic acids, but also volatile fatty
146 acids having antimicrobial effects) [17].

147 In Europe, the environmental regulations regarding pathogens (Commission Regulation EU No 142/2011) and
148 heavy metals (Directive 86/278/EEC) also apply to digestate quality. Some national legislations, such as
149 Austria's, Switzerland's, Denmark's, have imposed stricter quality parameters, including organic pollutants
150 such as polycyclic aromatic hydrocarbons (PAH), polychloro-dibenzodioxins (PCDD), polychlorinated
151 biphenyl (PCB), linear alkylbenzene sulfonates (LAS), adsorbable organic halogens (AOX) [18]. Besides, the
152 accumulation of emerging contaminants (antibiotics, anti-inflammatory drugs and antibiotic-resistant genes)
153 in digestate poses a significant issue for future sludge land application [19]. Finally, transport distances have
154 a crucial impact on the economic viability of using anaerobic digestate for land application [20], so the
155 matching between the localization of existing digesters and nearby agricultural lands should always be verified.
156 Considering this general framework, alternatives to direct agricultural reuse need to be investigated to ensure
157 environmental pollution minimization, and the implementation of the integrated biorefinery concept, in
158 accordance with the zero-waste strategy promoted by the EU [21]. Thermochemical conversion processes,
159 such as pyrolysis, hydrothermal carbonization (HTC), gasification, and torrefaction, are gaining interest due
160 to the wide variety of applications to valorize the generated gaseous, liquid and solid (char) end-products, not
161 only for energy but also for resource recovery. Furthermore, chars are considered as carbon sinks, capable to
162 remove carbon from the atmosphere and sequester it in the long term. However, char characteristics can
163 significantly differ depending on digestate feedstock and type of thermochemical process.

164 Due to a lack of standardized definitions, a vast number of different terms exist to indicate the solid products
 165 from thermochemical conversion processes [22]. The most frequent terms are reported in Table 1, including
 166 their common definition. It is essential to distinguish between terms such as charcoal, biochar and hydrochar,
 167 according to raw processed materials and field of application. Charcoal is a carbon-rich solid product obtained
 168 from the carbonization of natural organic materials, and is mostly used for energy production by combustion,
 169 whereas biochar is a synonym for charcoal when used in soil applications. On the other hand, the term
 170 hydrochar is similar to biochar, but is hydrothermally produced, resulting in a chemically and physically
 171 different product. Typically, biochar is produced as a solid product in dry carbonization processes like
 172 pyrolysis, while hydrochar is produced as a solid-liquid mixture. For the sake of clarity, throughout this
 173 manuscript, the words “biochar” and “hydrochar” are used to indicate the solid products obtained from
 174 pyrolysis and hydrothermal carbonization, respectively, regardless of their application.

175

176 **Table 1.** Common terms and definitions used to indicate thermal processes-derived solid products.

Term	Definition	Source
Coal	Sedimentary rock, generally used as solid fuel	-
Char	Solid decomposition product from natural or synthetic organic materials	[23]
Coke	Elemental C-rich solid, with C structurally in the non-graphitic state. It is produced by pyrolysis of organic materials that have passed, at least in part, through a liquid or liquid-crystalline state during the carbonization process	[23]
Charcoal	Char obtained from wood, peat, coal or other related natural organic material; conventionally used for cooking purposes	[23,24]
Biochar	Term used in the fields of soil and agricultural sciences to indicate char, generally produced via pyrolysis, which is applied to the soil	[22,25]
Pyrochar	Char produced from pyrolysis or torrefaction (biochar)	[26]
Hydrochar	Char produced from hydrothermal carbonization	[22]

177

178 The integration between AD and thermochemical treatments may boost virtuous circular economies [27],
 179 reducing the aforementioned issues related to raw digested sludge disposal [28]. A standardized and flexible
 180 approach accounting for all these factors, including stakeholders’ acceptance, is required to properly select the
 181 best digestate management options for the specific local conditions [29,30]. However, at present, technical
 182 constraints, limited process efficiency and poorly developed legislative framework, together with uncertain
 183 economic sustainability of alternative treatment chains, are hindering commercial-scale applications. [29,30]
 184 To the best of our knowledge, limited review studies were focused on AD and thermochemical treatment
 185 integration, with a critical and holistic analysis of process conditions, char applications, economic and
 186 environmental aspects, and legislative framework. In this work, char production from digestates is introduced

187 considering industrial processes (Section 2), mainly focused on pyrolysis and HTC, and possible char
 188 applications (Section 3), with agricultural application and energy recovery as principal routes. The economic
 189 and environmental aspects related to char production and utilization are described in Section 4, while the
 190 current legislative framework is depicted in Section 5. Finally, emphasis is placed on the future research needed
 191 to boost AD-thermochemical treatments integration in the circular economy framework (Section 6). The
 192 novelty of the present study compared to recently published review papers is specifically detailed in Table 2.
 193

194 **Table 2.** Comparison between the main focus of the current review and previously published literature studies.

Main focus	Reference
Coupling AD with gasification, pyrolysis and gasification, with focus on char and aqueous products recycling to AD reactor	[31]
Integration of AD with thermochemical processes: focus on pyrochar applicability	[32]
Waste biomass valorization through thermochemical, biological and integrated technologies: analysis of process conditions, technology readiness level, economic/environmental aspects	[33]
Integration of hydrochar and pyrochar with AD to boost anaerobic processes and adsorb contaminants, including analysis of environmental and economic aspects	[34]
Holistic approach to integrated AD-thermochemical conversion, with detailed focus on process conditions linked to char applications, energy/environmental aspects, and legislation	This work

195

196 **1.1. Anaerobic digestate management framework**

197 Figure 1 shows an overview of existing digestate management technologies and related end-products: the
 198 integration of different solutions at a local scale is essential for closing the loop on AD energy and material
 199 flows. Depending on feedstock type (e.g., animal by-products, sewage sludge, organic fraction of MSW) and
 200 operating conditions (thermophilic/mesophilic temperature), a hygienization step may be required prior to
 201 digestate valorization to inactivate pathogens [35]. Digestate can be either utilized directly or separated into
 202 its solid and liquid fractions: solid-liquid separation requires high investment and operational costs but
 203 remarkably reduces storage and transportation fares [7], further increasing resource recovery potential through
 204 target-oriented technologies. Both fractions (or the whole digestate) can be applied to agricultural lands;
 205 however, the liquid fraction contains higher volatile TAN concentrations, with possible negative consequences
 206 on ammonia emissions [36].

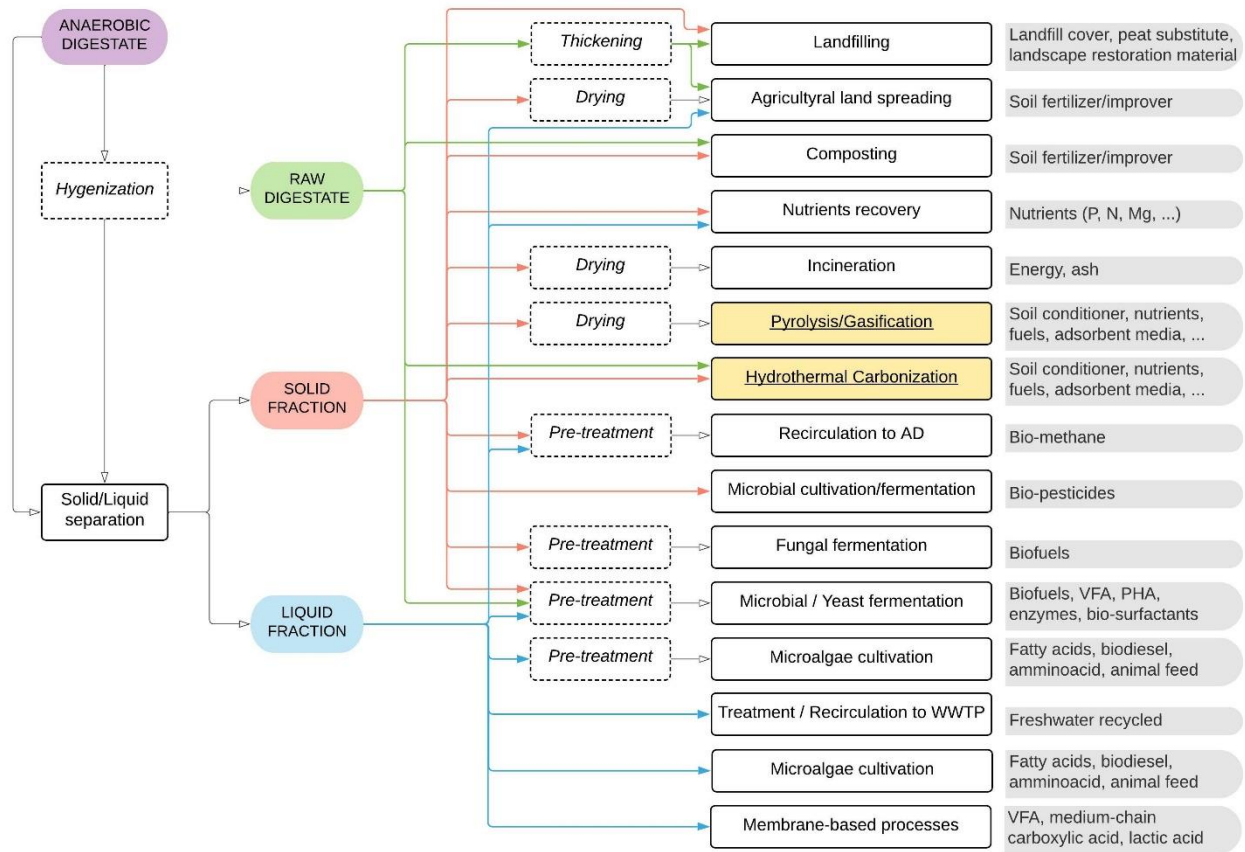
207 After solid-liquid separation, the digestate liquid fraction contains soluble N, P, K, organics and mineral salts
 208 that can be recovered by using proper extraction techniques. Conversely, nutrients in the solid fraction (Ca,
 209 Mg, P) are largely organically bound, offering limited recovery possibilities [9,37]. Nutrient recovery
 210 technologies, including phosphorus crystallization or extraction, ammonia stripping, acid air scrubber,

211 membrane filtration, ammonia/phosphorus sorption, macrophytes or microalgae production and evaporation,
212 have been extensively discussed in previously published reviews [37,38].

213 Since digestate is rich in active anaerobic microbes, nutrients and undegraded organic matter with a residual
214 biomethane potential, recirculating to AD reactors part of its solid or liquid fractions may improve process
215 performance and stability [39]; however, the potential accumulation of TAN and other metabolic products may
216 lead to microorganism inhibition [40].

217 Biochemical processes for digestate post-treatment, instead, exploit biochemical reactions catalyzed by
218 microorganisms and/or enzymes to produce biofuels or other high-value products. Digestate composting or
219 co-composting with carbon-rich and/or dry bulking agents can be applied to reduce AD effluent volumes and
220 improve its quality for fertilizer use (nutrient availability, trace elements release) [41,42]. Microalgae
221 cultivation is a promising solution for nutrient recovery from digestate liquid fraction, while promoting
222 sustainable production of micro-algae derived biofuels [43,44]. Furthermore, fermentative processes are
223 getting increased interest due to the possibility to produce bio-based fuels and valuable materials for the
224 chemical industry [35], including bioethanol [45], biodiesel [46], bio-pesticides [47], bio-surfactants [48],
225 enzymes [49], volatile fatty acids (VFA) [50] and polyhydroxyalkanoates (PHA) [51].

226 A common solution for WWTPs (but also for agricultural digesters) [52], is using the dried digestate as a solid
227 biofuel through incineration. Since during incineration, thermal decomposition happens by oxidation at
228 temperatures above 800°C [53], and under a more than stoichiometric amount of oxygen [54] only thermal
229 energy is obtained. Thermochemical conversion processes, instead, are carried out at rather lower temperatures
230 and mainly in an inert atmosphere [53], producing both energy and valuable materials. Thermochemical
231 conversion technologies rely on the thermal breakdown of biomasses into gaseous, liquid and solid products
232 [55], characterized by a pool of applications (e.g., agricultural reuse [56], energy recovery [57], pollutant
233 adsorption [58], AD amelioration [59], nutrients recovery [60], catalysts production [29]). In contrast to
234 biochemical conversion, thermochemical technologies have two main advantages: they can potentially convert
235 the whole feedstock's organic fraction; they are more efficient, taking only seconds or hours (in contrast to the
236 days required for biochemical conversion) [53]. Nevertheless, they are multi-phase processes and require high
237 temperatures with negative consequences when moving to full-scale applications. Feedstock quality, type of
238 generated products, local emission standards and economic aspects push for the selection of a specific
239 thermochemical process. A comparison of challenges and bottlenecks for thermochemical conversion
240 processes is provided in Section 6.



241
 242 **Figure 1.** Anaerobic digestate management: conventional solutions and emerging technologies. Black
 243 bordered boxes depict processes, while dotted lines indicate optional processes; grey boxes show end-
 244 products.

245

246 1.2. Research methodology

247 The following criteria were considered to retrieve indexed literature related to thermochemical processes
 248 applied to anaerobic digestate:

- 249 i. *Bibliometric sources:* Web of Science, Scopus and Google Scholar.
- 250 ii. *Keywords (in different combinations):* “anaerobic digestate”, “pyrolysis”, “hydrothermal
 251 carbonization”, “gasification”, “torrefaction”, “thermochemical processes”, “char”, “biochar”,
 252 “hydrochar”.
- 253 iii. *Publishing date:* between 2016-2022.

254 The survey resulted in 115 research articles summarized in Table A1-A3 and reviewed in Sections 2 and 3.
 255 Review articles, book chapters and reports published without constraints of date were used to depict the
 256 theoretical framework.

257

258 **2. Processes for char production from anaerobic digestate**

259 Carbonization processes yield different products, including char, bio-oil and gas. A summary of the latest
260 studies (2016-2022) focused on digestate-based char production and characterization is provided in the
261 paragraphs below.

262 About half (48%) of the existing literature reviewed is focused on pyrolysis processes, including co-pyrolysis
263 and pyrolysis coupled with other processes or with chemical modification. HTC processes (including
264 combined processes and chemical modification) account for 43% of the studies, while gasification is less
265 common (8%). Gasification is uncommon for char production, being typically used to produce syngas, rather
266 than biochar; it requires high temperatures (above 700 °C), a sub-stoichiometric oxygen environment, and the
267 addition of gasification agents (e.g., air, oxygen, steam) [61]. Tar, a mixture of condensable hydrocarbons (1-
268 5 aromatic rings) and PAH, is also generated during pyrolysis/gasification, implying serious operational issues
269 [31].

270 In the first sub-section, a brief description of pyrolysis and HTC processes is included; in sub-section 2.2, the
271 influence of process conditions on biochar and hydrochar properties is critically discussed by linking it with
272 positive or negative effects considering different possible applications. The last sub-section includes other
273 processes for char generation, such as gasification, co-carbonization of different substrates, processes
274 combination, and physical/chemical char activation.

275

276 **2.1. Pyrolysis and HTC process description**

277 Recent literature on digestate-derived char generated from pyrolysis and HTC is summarized in Tables A1 and
278 A2 respectively, where a brief description of each study (objective, process conditions, digestate type). [62]
279 Overall, a wide variety of investigated substrates arises: food waste digestates [62–72], sewage sludge digestate
280 [28,59,73–82], animal manure digestate [67,73,83–88], lignocellulosic biomass digestate [68,88–93] are
281 widely investigated for char production. In addition, a remarkable number of studies analyzed anaerobic
282 digestates from co-digestion of different organic wastes [27,94–96]. Almost all the investigated studies refer
283 to lab-scale tests, while very few are conducted at pilot [66,89,97–99] or industrial-scale conditions [74,100].

284

285 *2.1.1. Pyrolysis*

286 The pyrolysis process consists of decomposing reactions occurring in series at increasing temperatures and in
287 an inert atmosphere. Depending on the heating rate (°C/min), a basic distinction between slow (heating rate <
288 100 °C/min) and fast (heating rate > 100 °C/min) pyrolysis is made [101,102]. Most of the studies can be
289 considered as slow pyrolysis, while only a few papers refer to heating rate conditions typical of intermediate
290 pyrolysis [62]. In general, pyrolysis processes are applied on dried substrates (solid content > 90%), thus, a
291 preliminary dehydration phase (air drying and/or oven drying at 60-105 °C) to minimize carbonization energy
292 requirements is required [65,74,96]. Then, the raw biomass (initial biosolids particle size of biosolids in the

293 range of 5-50 mm [103]) is decomposed in the absence of oxygen at temperatures of 300-900 °C [104]
294 obtaining higher biochar yields (15-35%) compared to other thermal processes, such as gasification (5-15%)
295 [105]. Char yield is defined as the ratio between char mass and initial feedstock mass, both on dry basis. Slow
296 pyrolysis usually shows higher biochar yields (25-40%), compared to fast pyrolysis (15–20%) [106]. A
297 downstream condenser is required to separate the gaseous combustible stream (syngas) from a liquid fraction
298 that can be further separated into pyro-oil and aqueous pyrolytic liquid (APL).

299 Pyrolysis process generates gaseous emissions that must be properly treated: carbon-containing substances,
300 especially volatile organic carbons, carbon monoxide and aerosols are emitted [107]. Heavy metals and PAH
301 may be produced as well. Modern pyrolysis reactors have introduced post-combustion of gaseous products,
302 substantially reducing overall emissions; it was shown that it is possible to meet CO, NO_x, SO₂ standards
303 required by US Environmental Protection Agency (EPA) without implementing advanced air pollution control
304 systems [108]. Emission factors, normally expressed as g/kg biochar, can be useful to estimate the total
305 emissions generated by pyrolysis processes; nonetheless, specific emission data for pyrolysis are still limited
306 [107]. Recently, mathematical simulations were proposed to better estimate hydrocarbons, dioxins and furans
307 emitted by pyrolysis and combustion systems, considering as input parameters waste composition (elemental
308 analysis) and gas flowrate [109].

309 In [110] a model using data from anaerobic digestate pyrolysis was proposed and validated, assuming three
310 independent stages of decomposition, respectively corresponding to biodegradable organic matter, dead
311 bacteria and non-biodegradable compounds. The decomposition occurs in three stages centered on three
312 different temperatures: 250, 350, and 550 °C. In the first stage, the main products are methane, carbon dioxide,
313 water, and acetic acid; in the second step, hydrocarbons and alcohols are generated, while the third process
314 produces hydrogen, methane, carbon dioxide, hydrocarbons, and alcohols. Since the non-biodegradable
315 component is the preponderant char-forming fraction, anaerobic digestate is a convenient substrate for char
316 production, given its relatively high amount of poorly biodegradable or unbiodegradable organics [111]. At
317 higher process temperatures (550-900 °C), cracking of large molecules converts biosolids into biochar, gases
318 (mainly CO, CH₄, CO₂) and condensable volatiles (pyrolysis-oil). Depending on the possibility of using a
319 catalyst, this last step is either called thermal cracking or catalytic cracking [103,112].

320 *2.1.2. Hydrothermal carbonization*

321 During HTC, the biomass is usually heated up to lower temperatures than pyrolysis (160-250 °C) [113–117]
322 in sealed confined systems, in the presence of water under saturation pressure (2-10 MPa) [102]. The pressure
323 is autogenous, rising proportionally with temperature [86], while biomass-included water acts as a reaction
324 medium. Temperature is the main process parameter controlling HTC reactions mechanism, which is not fully
325 understood yet [118]. Feedstocks with high moisture content (75-90%) can be directly fed to HTC [22], then
326 resulting particularly suitable for digestates, whose total solids (TS) content is normally low (<20% w/w).
327 Reaction time ranges from several minutes to a few days (30 min-72 h) [119], with most frequent values of 1-
328 8 h.

329 During HTC process, slurry and gases (mainly CO₂ with small traces of CH₄, H₂ and CO) are generated. The
330 slurry is then separated into a solid product, namely hydrochar, and a liquid phase (a mixture of bio-oil and
331 water) called aqueous HTC liquid (AHL) or process water. These fractions typically account for 45-70% and
332 5-30% of product mass, respectively, with small amount of gases produced (5-25%) [120]. The atmospheric
333 emissions are much lower than in pyrolysis and are mainly composed of CO₂ and ammonia [86]. HTC
334 commonly results in chars with higher carbon content than that produced by pyrolysis and gasification [121].
335 The main advantage of HTC, when compared to pyrolysis or gasification, is that the wet biomass does not
336 require a preliminary drying step (as the process takes place in water), thus saving high amounts of energy and
337 allowing direct processing of wet waste streams such as digestates [122]. Besides, HTC improves sludge
338 mechanical dewatering, enhances feedstock stabilization and sanitization, and reduces digestate volume [123].
339 The main involved reactions in HTC process include hydrolysis, dehydration, decarboxylation, condensation,
340 polymerization, and aromatization, occurring both in sequence and parallel [76]. Organic feedstock
341 characteristics strongly affect the specific reactions pathway. However, hydrolysis is likely to be the first
342 reaction, due to its lower activation energy [124]. Biomass is degraded to monomers and oligomers. Then,
343 dehydration occurs, and water is released in the reaction medium. Hydroxyl (-OH) groups reduction causes
344 O/C and H/C ratios decrease. During decarboxylation reactions, carboxyl (COOH) and carbonyl groups (C=O)
345 degradation causes CO₂ and CO release. Thus, decarboxylation is the main reaction responsible for gas
346 formation [114]. Through condensation and polymerization reactions, small molecules combine to form larger
347 molecules, leading to water release. When aromatization takes place, aromatic polymeric structures are formed,
348 which are hydrochar building blocks [125].

349

350 **2.2. Biochar and hydrochar properties**

351 Figures 2 and 3 report the main physicochemical properties of pyrolysis and HTC derived chars (respectively)
352 collected from literature, as a function of main process conditions (temperature for pyrolysis, temperature and
353 residence time for HTC) and digestate type (grouped into three main categories: sewage sludge -SS-, food
354 waste -FW- and agricultural waste -AW-, the latter including both manure and crop residues). Significant
355 trends, that will be further discussed in the following paragraphs, can be observed while varying process
356 temperature, whereas digestate type, and residence time for HTC, scarcely affect char properties.

357

358 *2.2.1. Influence of feedstock type*

359 Digestate type remarkably affects char properties [28,126]. However, due to the huge variety of AD feedstocks
360 composition, clear differences at varying digestate type on char properties are not easily detectable from
361 literature (Figure 2, Figure 3). The convenience of using anaerobic digestate from mono-digestion or co-
362 digestion processes should be evaluated case by case in view of its target application, since changes in char
363 yield and/or properties largely depend upon co-substrates characteristics.

364 As regards pyrolysis, char O/C molar ratio of digestate-derived biochar is often linearly correlated to volatiles
365 content, independently of pyrolysis conditions [127], whereas H/C molar ratio is lower than that generated
366 from other biomasses, due to higher inorganics content in digestate, leading to different reaction pathways and
367 enhancing aromatization.

368 High concentrations of oxy-PAH (oxygenated polycyclic aromatic hydrocarbons) in char were observed in
369 [75] from sewage sludge anaerobic digestate, although PAH, PCDD, and poly-chlorinated dibenzofurans
370 (PCDF) contents resulted in low environmental risk. The importance of feedstocks origin was pointed out also
371 in [85], where the high Zn and Cu concentrations found in biochar produced from manure digestate were likely
372 ascribable to the growth-promoting copper-zinc additives in livestock feeds.

373

374 *2.2.2. Influence of process conditions*

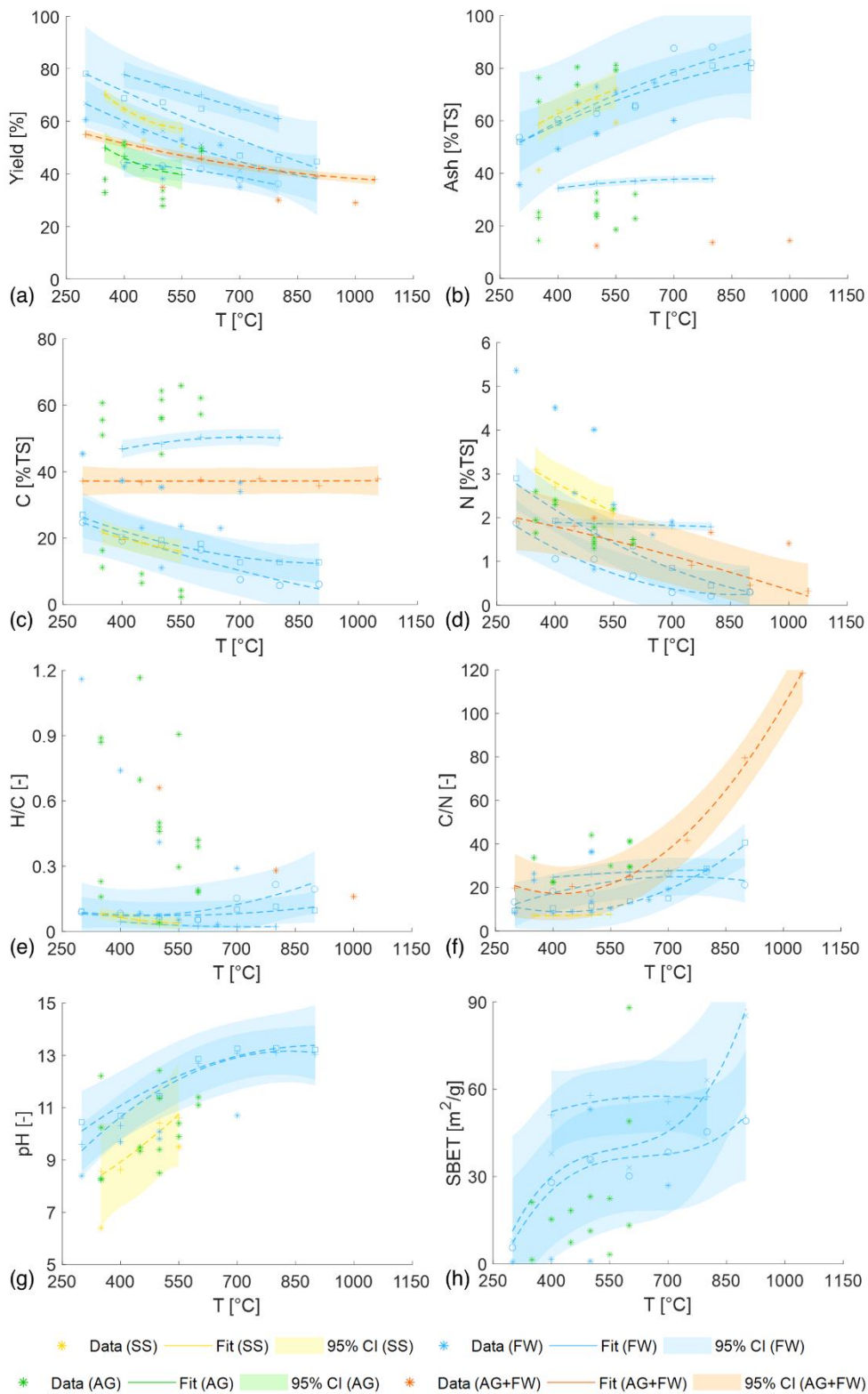
375 Process temperature is the main driver influencing char physicochemical characteristics. However, despite
376 being scarcely discussed in literature, char properties may dramatically change while varying other process
377 parameters, such as: residence time and feedstock to water ratio for HTC; heating rate, particle size, pressure,
378 inert gas flow rate (the latter contributing to microporosity development and hydrophobicity reduction) for
379 pyrolysis [127].

380 *2.2.2.1. Char yield*

381 While increasing process temperature, biochar or hydrochar yields tend to decrease (Figures 2 and 3) due to
382 enhanced solid destruction at increasing of process severity [76,90], leading to further thermal decomposition
383 and gasification of surface groups (as regards pyrolysis) [62].

384 Such decreasing trends are confirmed by several studies on HTC performed with different digestate types (SS
385 [128], AW [87,93]). To improve hydrochar yield, it is recommended to adopt mild temperatures (180-210 °C)
386 and short residence times (30 min). The biomass to water ratio affects hydrochar yield (and, as a matter of fact,
387 energy consumption [87]) but its impact it is not yet clear, as it is strongly dependent on feedstock type [72].
388 Common biomass to water ratios reported in literature for digestates range from 1:3-1:4 for manure digestate
389 [87,88] and 1:6-1:10 for lignocellulosic and energy crops digestates [88,89,93].

390 As regards pyrolysis, some authors [74] found that biochar yield reduction becomes moderate above 500 °C,
391 indicating that carbonization process is almost completed (Figure 2a). During pyrolysis, biosolids thermal
392 decomposition takes place in absence of oxygen to prevent organic material loss at high temperatures [112]:
393 however, excessive N₂ flow rates may reduce biochar yield, due to a reduction in volatiles residence time,
394 minimizing secondary reactions and additional char formation [127]. In [129], biochar yield kept at rather
395 constant level while varying process pressure (atmospheric to 8 MPa). Conversely, heating rate is crucial in
396 controlling char yield: the higher the heating rate, the less efficient is solid product generation [98], though
397 heating rate effect becomes negligible at temperatures above 650 °C [130].



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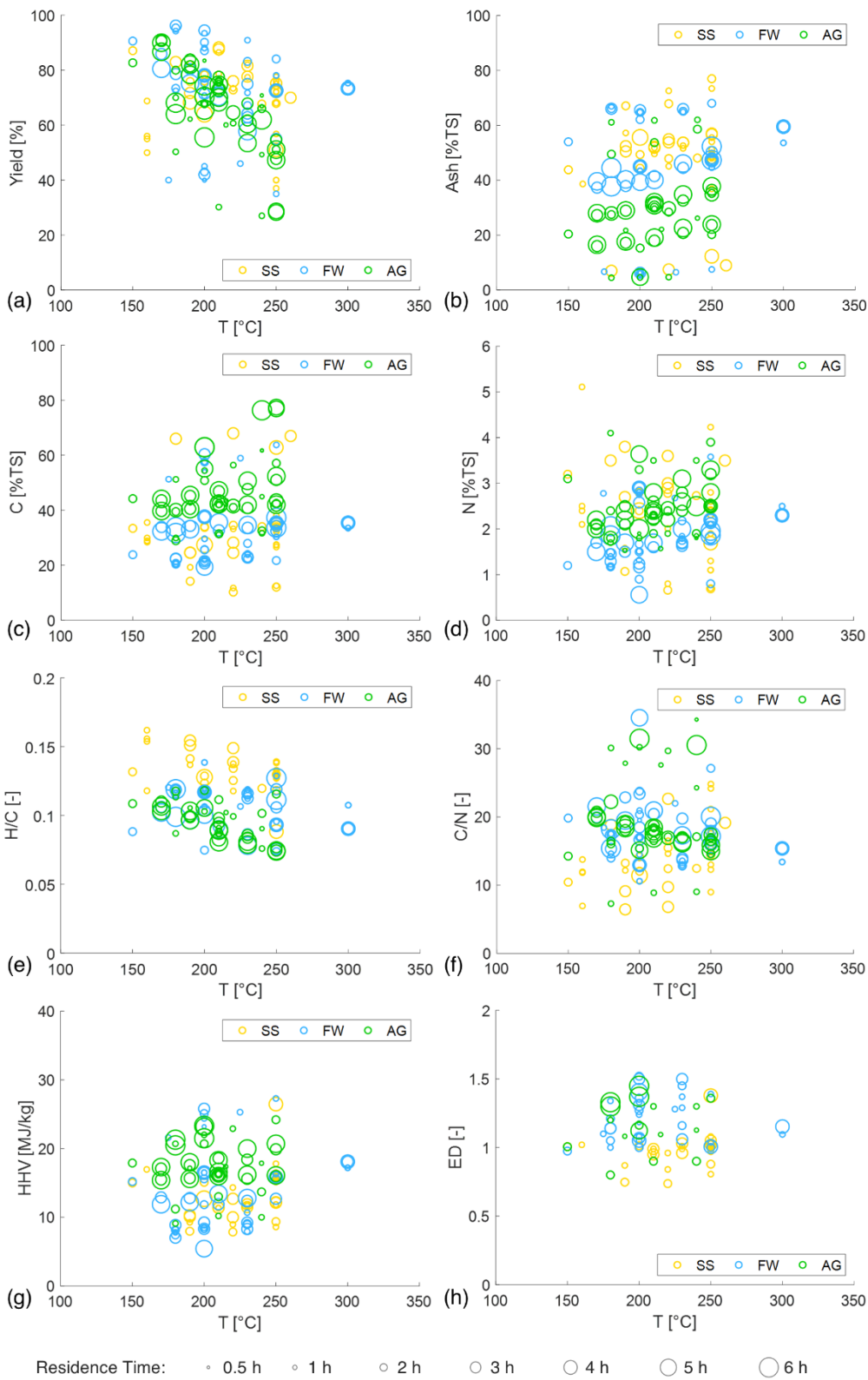
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Figure 2. Pyrolysis biochar properties as a function of process temperature for different digestate types (SS = sewage sludge, FW = food waste, AG = agricultural waste). Asterisks identify results from tests performed by varying one to four process temperatures. Symbols other than asterisks are used to display results from a single study testing the same substrate while varying at least five temperatures: in such cases, fitting with polynomial functions (second or third grade) and 95% confidence intervals (CI) are also displayed.



405

406 **Figure 3.** Hydrochar properties as a function of process temperature (x-axis) and residence time (circles size)

407 for different digestate types (circles color, SS = sewage sludge; FW = food waste; AG = agricultural waste).

408

409 2.2.2.2. Elemental analysis (CHON)

410 The analytical determination of char elemental composition is essential for char characterization, as carbon
411 (C), nitrogen (N), hydrogen (H) and oxygen (O) contents strongly affect char properties (such as porosity and
412 Higher Heating Value, HHV) and its field of application. Temperature is the most influencing factor, and
413 should be carefully set to tailor char elemental composition to the desired range [98].

414 As regards pyrolysis, the influence of process temperature on char elemental composition is still controversial.
415 Some authors [74,131] found that C, N, H and O content decreased as temperature increased, while others [85]
416 claimed that O content increased between 350 °C and 550 °C. The ratios O/C, (N+O)/C, and H/C indicate the
417 hydrophilicity, polarity, and aromatization degree, respectively. The dehydration process associated with
418 increased pyrolysis temperatures commonly decreases H/C and O/C values [63,74], resulting in lower PAHs
419 content due to vaporization from the solid matrix (above 550 °C) [127]. Conversely, the augmented oxidation
420 degree with temperature increase found in [85] resulted in increased hydrophilicity and polarity: the
421 aromatization degree augmented with temperature, but a further temperature increase to 550 °C decreased H/C
422 ratio due to dehydrogenation. Besides, with increase in pyrolysis temperature, a C/N ratio increase was
423 observed in [74], indicative of carbonization and conversion/gasification of organic nitrogen.

424 Regarding hydrochar, carbon content normally increases as temperature rises [91], whereas nitrogen increases
425 or decreases depending on digestate type and other process conditions. In contrast, oxygen decreases as
426 temperature rises [71,93,132]. As a consequence, H/C and O/C molar ratios decrease as temperature increases,
427 indicating that dehydration and decarboxylation are the main occurring degradation reactions [72,77,82,132].
428 In addition, the higher the operating temperature, the higher is the hydrochar dewaterability [76].

429 2.2.2.3. Proximate analysis (ash, fixed carbon and volatiles)

430 As temperature increases, fixed carbon (FC) content increases, while volatile matter decreases [67,72]. Ash
431 content is a crucial parameter affecting char suitability for different applications: it relates to the concentrations
432 of inorganic elements in hydrochar and is of noticeable importance for the selection of the most appropriate
433 combustion technology, since high ash concentrations may cause fouling, slagging and corrosion in energy
434 recovery applications.

435 As clearly shown in Figures 2b and 3b, high temperatures increase char ash content, mainly due to the loss of
436 volatile matter and contemporary mineral retention [63,67].

437 2.2.2.4. pH, nutrients and inorganics

438 An important parameter to consider for applications of char as soil conditioner is pH, as it affects plant's
439 nutrients availability. It is recommended to keep pH in the range of 6.0-7.5, being suitable for various plant
440 species.

441 The original feedstock pH strongly affects hydrochar pH; in addition, a pH decrease is commonly observed
442 during HTC process as temperature increases [86].

443 Regarding pyrolysis, at increasing temperatures, ash content increases, with a positive influence on pH value
444 (Figure 2g) due to ash alkali nature [127], given by the alkalization effects of Ca^{2+} cations, whose concentration
445 increases at higher temperature [59], and the decomposition and volatilization of organic acids phenolic
446 substances [74]. More in general, pyrolysis conditions (rather than feedstock type) mainly affect the pH of
447 produced biochars [85]. Furthermore, at increased temperature, a decreased electrical conductivity (EC) of
448 biochar extracts has been reported for digestates from sewage sludge or food waste [59,62]. This property is
449 crucial as well for soil applications, being an indicator of biochar mineral release.

450 Indeed, char has been often proposed for improvement of phosphorus availability in soils. In general, the total
451 P content in char increases as compared to the corresponding precursor materials, indicating that pyrolysis and
452 HTC are P enrichment processes [85]. High temperatures and residence times were found to increase P
453 concentrations in hydrochar from 1.19-fold to 1.34-fold [79,80].

454 The effect of pyrolysis temperature on P speciation and plant availability on biochar derived from digested
455 sludge is relevant. Organic P content decreases with pyrolysis temperature, being decomposed into inorganic
456 P by heating [85]. In [95] a negligible effects of low temperatures on P speciation (mainly in the form of
457 calcium phosphates, struvite or other magnesium phosphates) was found while, above 600 °C, phosphorus
458 gradually became more thermodynamically stable (apatite), with formation of reduced P forms above 1,000
459 °C. Due to the presence of less soluble P species in biochar produced at higher temperatures, the ratio of
460 bioavailable to stable phosphorus generally decreases: thus, when considering biochar utilization as slow-
461 release P fertilizer, high pyrolysis temperatures should be avoided.

462 While phosphorus and potassium concentrations commonly increase at increasing temperature, nitrogen in
463 biochars was found to decrease slightly until 500 °C and was substantially lost at 700°C [64], as evidenced in
464 Figure 2d. N depletion is due to volatilization; moreover, its availability for plant uptake remains questionable
465 due to its gradual transformation into pyridine-like structures [74]. The influence of pyrolysis temperature on
466 seed germination index (GI) and water holding capacity (WHC) of biochar-amended soils has been also
467 investigated: the first one resulted positively affected, whereas the second one was negatively affected, likely
468 due to the lowered production of carboxylate and ionizable functional groups [64].

469 Inorganic compounds, including nutrients and micronutrients, were shown to concentrate in hydrochar as
470 temperature rises: e.g., depending on feedstock type and temperature increase, K, Ca, Fe and Al contents raised
471 1.16-fold to 1.40-fold [79,86], with the only exception of Na, whose concentration decreased from 4.9 to 4.4
472 mg/g [86].

473 Regarding pyrolysis, inorganics concentrate but, similarly to what observed on phosphorus [95], when
474 increasing pyrolysis temperature above 450 °C, heavy metals fractions with higher bioavailability (metal-
475 exchangeable state, carbonate state, iron/manganese oxide binding state) decrease significantly, indicating
476 that the leaching risk of heavy metals from biochar is controllable [85]. Other authors [64] found that copper
477 is more sensitive to pyrolysis temperature, when compared to other micronutrients (Ca, Fe, P, K and Zn),
478 that appeared to be stable throughout the wide tested temperature range (300-700 °C). Considering heavy

479 metals content, it is common to find an increase in their concentrations as temperature increases [79,86] but
480 a decrease in Hg was observed, likely due to its volatility [79,86].

481 2.2.2.5. Higher Heating Value (HHV)

482 Proximate and elemental analysis are often used as indicators of char energy content and suitability as fuel: C
483 increase, together with H and O decrease, indicate the generation of C-C bonds having greater energy than C-
484 O and C-H bonds. The ash content, HHV, energy densification (ED) and energy yield (EY) are the main
485 parameters commonly evaluated as regards energy aspects.

486 Hydrochar is characterized by a high carbon and energy content (e.g., 15-20 MJ/kg), potentially making it an
487 attractive material for (coal) co-firing [76]. Literature studies evidenced the increase of HHV by increasing
488 process temperature (Figure 3g), whereas increasing residence time slightly reduces the HHV, but improves
489 most hydrochar slagging and fouling indices [133]. Regarding feedstock type, higher HHVs were observed for
490 hydrochars derived from agro-industrial digestate [69], while lower values were obtained using sewage sludge
491 digestate [69,134] and MSW digestate [120] as hydrochar precursors.

492 Overall, to improve energy recovery, mild temperatures (180-210 °C) and short residence times (30 min) are
493 recommended. As a result, high HHV, moderate ash content and high COD concentration in the liquid fraction
494 may suggest the co-combustion of hydrochar and process water recirculation in the biogas digester as desirable
495 application fields [79–82].

496 ED is the ratio between hydrochar HHV and feedstock HHV, both on dry basis. As pointed out in [69], low
497 lignin and high ash content in the feedstock can lead to a lower HHV of the produced hydrochar, resulting in
498 ED ratios below 1. Feedstocks such as sewage sludge digestates usually show low ED degree (1.02-1.08) if
499 compared to lignocellulosic feedstocks [69,132,134]. ED ratios in the range of 1.08-1.13 (190-240°C) were
500 found for corn stalk digestate-derived hydrochar [93]. Higher ED values were obtained for MSW digestate-
501 derived hydrochar: 1.37 at 230 °C (30 min) and 1.52 at 200 °C (60 min) [120].

502 To link mass yield and energy densification, EY parameter is introduced, referring to the product of
503 hydrochar/mass yield and ED, indicating the energy embedded within the hydrochars [72]. In [72] an EY
504 increase in FW digestate-derived hydrochar was observed while increasing the temperature up to 225 °C,
505 whereas the reaction time had a weak influence. The same trend was found for AW digestate-derived hydrochar
506 [87,93] and for SS digestate-derived hydrochar [134].

507 Similarly to HTC, temperature increase commonly results in biochar HHV decrease in pyrolysis processes;
508 despite high biochar HHV can be obtained with pyrolysis (22.3-24.6 MJ/kg using AW digestate as precursor),
509 it is suggested to use the dried digestate instead of its biochar as solid fuel [84,135]. For this reason, for the
510 majority of the reviewed papers concerning pyrolysis, HHV, ED and EY are poorly discussed. The relatively
511 high ash, nitrogen and sulphur contents commonly found in digestate-derived biochars, boost for their
512 applicability as soil amendments, instead of fuel sources: fuel-bound nitrogen/sulphur/ash contribute to the
513 emission of nitrogen oxides (NO_x), sulphur oxides (SO_x) and particulates in combustion, negatively affecting
514 the environmental quality of fuels [131,135].

515 2.2.2.6. Porosity, surface area, and adsorbent capacity

516 Surface properties, including surface area and pore size distribution, are commonly determined based on
517 Brunauer-Emmett-Teller (BET) theory by N₂ adsorption/desorption tests.

518 No significant changes in biochar surface area (SBET) are commonly observed at temperatures between 300-
519 550 °C [84,85,135], while critical pyrolysis temperatures (600 °C [63], 700 °C [84,131] and 800 °C [135])
520 sharply increase biochar surface area. High temperatures enhance biochar aromaticity (H/C), which is
521 beneficial for a higher surface area due to additional pores generation [84,135]. A pore structure with a huge
522 specific surface area may provide outstanding performances for adsorption and/or catalytic reaction sites for
523 contaminant removal [63]. However, at elevated temperatures, collapse or coalescence of newly formed
524 micropores may take place, resulting in a mesoporous (rather than microporous) pore distribution in chars.
525 Digestate-derived biochars contain Ca-minerals like CaCO₃ that decompose into calcium oxide (CaO) and CO₂
526 when heated above 700 °C: CO₂ release from carbonates stimulates char oxidation to CO, causing pores loss
527 [84].

528 Accordingly, an increase in BET surface area and pore volume at increasing process temperature is commonly
529 reported also for HTC: the volatile matter content decreases, making the pores more accessible [86,120].
530 Nevertheless, above 260 °C a specific surface area decrease was observed in [73], probably due to the
531 condensation of aromatic structures and pore collapse.

532 Few studies addressed the adsorptive capacity of digestate-derived chars: a higher removal capacity was
533 commonly related to a higher surface area and functional group density [62,74]. Due to reduced carbonization,
534 biochars pyrolyzed at lower temperatures have relatively lower adsorption capacities, while higher
535 temperatures can cause as well a decline in the adsorption capacity, because of the loss of surface functional
536 groups from dehydrogenation, dehydration and condensation, and due to higher pH values. However,
537 depending on target pollutants, surface area is not the most important factor influencing char adsorption
538 capacities. In [136] it was found that char calcium and magnesium contents have a stronger influence on
539 ammonium adsorption capacity than specific surface area.

540

541 2.2.3. *Digestate-derived char vs. raw biomass-derived char*

542 Limited data are present in literature regarding the comparison of physicochemical characteristics and
543 application fields between char produced from raw biomass and char produced from digestate; however, some
544 interesting outcomes are mentioned hereafter. A relatively low impact of AD on the yields of gas, liquid and
545 solid fractions obtained from pyrolysis of raw and digested food waste was highlighted in [131], with
546 comparable gas (respectively 7.4% and 5.3% for food and digested waste) and bio-oil (respectively 60.3% and
547 52.2% for food and digested waste) percentages. However, by considering char physicochemical
548 characteristics, a significant increase in ash content was observed in char produced from digested food waste,
549 together with a remarkable reduction in C content (especially in its recalcitrant fraction), due to the stabilization
550 effects given by the upstream anaerobic treatment [131,137]. As regards pore size and distribution, char

551 produced from raw food waste showed an improved surface area with large open pores, when compared to
552 that obtained from digested waste, the former showing a better suitability for application in adsorption
553 processes. Different results were obtained by [85] when comparing cow manure and dairy manure: the char
554 obtained from the respective digestates showed a higher yield, an improved specific surface area and a slightly
555 higher pH. An improved char yield (from 24% to 38%), together with a reduced energy requirement for
556 pyrolysis, was noticed also in [138] in the treatment of digested roadside grass when compared to the raw
557 feedstock. As regards product distribution, comparable results were obtained after pyrolysis of raw and
558 digested organic fraction of MSW, with a remarkable increase (about 8%) of char yield and a contemporary
559 decrease of heavy organics and gas in the latter [137].

560 Generally, the high ash content and the reduced volatile carbon fraction, normally found in digestate (and
561 consequently in its char), pushes for uses other than energy recovery, due to the limited HHV [137], while fuel
562 utilization is more appropriate for chars derived from raw biomasses. Also, phosphorus and heavy metals
563 (together with all inorganic fractions) tend to be more concentrated in chars produced from digestates than in
564 chars produced from raw biomasses [85].

565 Coherent considerations can be drawn for HTC: in [72], hydrochar produced food waste and its digestate
566 showed comparable yields and similar characteristics for utilization as fuel. As concerns physicochemical
567 characteristics, the only highlighted difference was in ash percentage, that was obviously higher in digestate-
568 derived hydrochar. The increased ash content in digestate-derived hydrochar was confirmed also in [87] and
569 [71], with a negative effect on hydrochar HHV: thus, it was suggested to prefer soil application rather than
570 energy recovery when selecting digestate as main substrate for HTC, due to hydrochar stability and absence
571 of pathogens. The reduction in C content in digestate-derived hydrochar, observed in [71] when treating food
572 waste pulp, was coupled with an increase in N, Ca, Fe and S contents, due to their higher concentration in
573 digestate when compared to the original feedstock.

574

575 **2.3. Other processes**

576 Table A3 summarizes the most recent literature studies concerning char produced from digestates using
577 processes other than pyrolysis and HTC: these include gasification, microwave HTC, processes combination,
578 catalytic processes, co-pyrolysis/co-HTC, pyrolysis/HTC integrated with physical/chemical/magnetic
579 modification.

580 Combination of processes may help to valorize anaerobic digestates fully. HTC followed by pyrolysis proved
581 to be effective for producing a char with improved characteristics as soil amendment (higher carbon content,
582 reduced PAH concentrations) compared to HTC and pyrolysis alone [139,140]. The combination of HTC and
583 supercritical water gasification (SCWG) applied on AHL [141] or the combination of HTC and steam
584 gasification on hydrochars [142] allowed to efficiently convert digestate into valuable biofuels, hydrochar and
585 H₂-rich gas, while minimizing waste production and management costs. Microwave-assisted low-temperature
586 hydrothermal treatment (MLHT; temperatures: 100-180 °C) [143] and microwave assisted hydrothermal

587 carbonization (MLHC; temperatures: 180-260 °C) combined with pyrolysis [144] are promising method to
588 produce hydrochar with high energy value and fuel properties, despite the ash content remains a limiting factor.
589 Autogenic pressure carbonization (APC) may also improve syngas yield and quality, favoring the generation
590 of bio-chemicals (pyrenes, phenols) with relatively high purity, and enhancing the nitrogen content in char
591 [145].

592 Few examples of catalytic processes were found in literature: in [146] the effectiveness of using steel slag
593 catalyst and CO₂ as reactive gas media during pyrolysis was evaluated to manipulate carbon distribution; in
594 [147] zeolite catalyst (ZSM5) was used to speed-up process kinetics and enhance aromatic hydrocarbons yield
595 in bio-oil, demonstrating that catalytical pyrolysis may reduce energy requirements as compared to non-
596 catalytic systems.

597 Conversely, co-pyrolysis/co-HTC, and char physical/chemical activation or functionalization have been
598 extensively investigated to optimize process conditions and product yields: given the predominant share of
599 studies, a detailed discussion is provided in the following.

600 *2.3.1. Gasification*

601 Compared to pyrolysis and HTC, gasification of anaerobic digestate is scarcely investigated for char
602 production whereas it is an attractive technology for syngas generation. Depending on its heating value (which
603 is mostly a function of the temperature) [148] and on the adopted gasification agent, syngas can be further
604 exploited as fuel (after purification from main pollutants, including tar) [149] or as hydrogen source for
605 biomethanation processes [150]. A combined system AD + HTC + gasification of hydrochars was tested in
606 [72] to increase the amount of produced hydrogen. An advantage of integrating AD with gasification regards
607 the possibility of reusing the CO₂ separated from biogas as a gasification agent [151].

608 Despite it is widely reported that gasification char yields are low [152], char yields up to 46% were observed
609 using anaerobic digestate as feedstock [151,153]. The char yield changes inversely with the equivalence ratio,
610 since at depleted oxygen conditions, a higher amount of carbon from the original biomass remains in the char
611 product [154]. Char yield is also affected by kinetic limitations of char oxidation/gasification reactions when
612 the reactor volume is insufficient to allow an adequate char residence time [155]. The huge amount of ash in
613 digestate may result in operational issues such as ash slagging during gasification process, reducing the
614 accessibility of raw material for complete gasification, and adversely influencing process efficiency. It is
615 therefore crucial to carefully manage solid-phase ash handling according to the ash melting behavior [152].

616 Char can be used as fuel for gasification [156], recycled to the anaerobic digester for biogas yield enhancement
617 [151,155], or applied on agricultural lands as fertilizer [152]. According to [152], char generated from
618 gasification of digestate from agricultural waste has low specific surface area and carbon content, and high
619 amount of inorganic components, thus being not suitable as fuel or activated carbon precursor. In [148], it was
620 shown that the formation of micropores happens from 650 °C to 950 °C, while specific surface area and pore
621 volume decrease at 950 °C, promoting the formation of macropores. Increasing the temperature, however,
622 reduces the amount of aliphatic side chains while promoting the generation of aromatic rings, causing a decline

623 in char reactivity. In [154] the characteristics of agricultural waste digestate-derived char were thoroughly
624 investigated: no N and S enrichment was noticed since such compounds volatilize above 200 °C and 375 °C,
625 while other macronutrient (P, K, Ca and Mg) and micronutrient (Fe, Cu, Mn, Ni, Zn) concentrations increased
626 significantly compared to the original feedstock.

627 *2.3.2. Co-pyrolysis/co-HTC*

628 Co-pyrolysis/co-HTC of different wastes can solve the issue related to limited feedstocks availability,
629 synergistically improving product quality. Kinetics and gas yields were enhanced during co-pyrolysis of
630 microalgae and swine manure digestate [157], or during co-pyrolysis of microalgae and digested MSW [158].
631 In both cases, an increase in microalgae fraction in the mixtures led to higher H₂ production, likely due to the
632 catalytic action of alkali metals available in ashes. Accordingly, in [159] the potential for biochar derived from
633 co-pyrolysis of fruit wastes, sewage sludge and anaerobic digestates from food wastes as a long-term, stable
634 carbon sink in soils was confirmed. More than aromaticity, the presence of Si, Fe, alkali and alkaline earth
635 metals derived from the blends on the biochar matrix affected its recalcitrance, which was higher than
636 conventional biochar (prepared from single biomasses). In [160] it was showed that co-pyrolysis of sewage
637 sludge digestate and lignocellulosic biomass enhanced volatiles release and reduced char yield; char stability
638 and nitrogen content were improved, resulting in higher potential for use as fertilizer and carbon sink. In
639 addition, the reaction pathways of proteins, lipids and carbohydrates pyrolysis were deeply investigated,
640 providing guidance for optimizing co-pyrolysis processes, leading to the production of higher-quality products.
641 Co-HTC was tested as well to improve the combustion properties of hydrochar produced from digested sewage
642 sludge: the addition of digested cow dung resulted in increased carbon content and improved hydrochar HHV.
643 Besides, hydrochars activation energy was increased: during HTC, cellulose and hemicellulose in cow dung
644 digestate interacted with proteins to form higher energy C-N bonds, resulting in a N-rich hydrochar [161].

645 *2.3.3. Physical/chemical char modification*

646 Char modification, including physical activation with steam, chemical treatment with acids, oxidizing agents
647 and alkalis, is generally applied to improve its properties for application as water or gas phase adsorbent.
648 As regards chemical modification, char treatment with H₂O₂ increases the presence of functional groups
649 containing oxygen (carboxyl groups) on the surface, while the treatment with KOH increases hydroxyl groups
650 and surface basicity. Heavy metals removal from water is frequently addressed in literature by using char
651 adsorption; the main mechanisms involved in heavy metals sorption are [162]: electrostatic interaction (mainly
652 determined by pH_{PZC}), ion exchange (with Ca²⁺ and Mg²⁺, but also with K⁺ and Na⁺), surface complexation
653 (carboxyl and hydroxyl groups), surface precipitation (phosphate, PO₄³⁻ and carbonate, CO₃²⁻) and physical
654 adsorption (onto active pore sites). Target contaminants for testing chars modified with KOH and H₂O₂ include
655 As(III), As(V), Cd(II) and Pb(II) [162–164]: compared to untreated chars, in activated chars the sorption
656 capacities were found to be up to 5.3-fold, 20-fold and 3.8-fold higher for As(V), Cd(II) and Pb(II),
657 respectively. Despite this, chemical modifications may induce organic matter and mineral ash leaching from

658 biochar pore sites. After treatment, char washing with water is required until pH becomes stable or neutral;
659 however, this procedure induces the release of organic or inorganic compounds (e.g., PO_4^{3-} and CO_3^{2-}) from
660 biochar, which may influence biochar metals sorption itself [164]. Chemical modification with KOH was also
661 tested on hydrochars to obtain highly porous media with large surface area and stronger affinity towards CO_2 ,
662 for biogas upgrading to biomethane [165], or towards phosphate [166] and methylene blue adsorption, the
663 latter intended for cationic dyes removal from aqueous solutions [167].

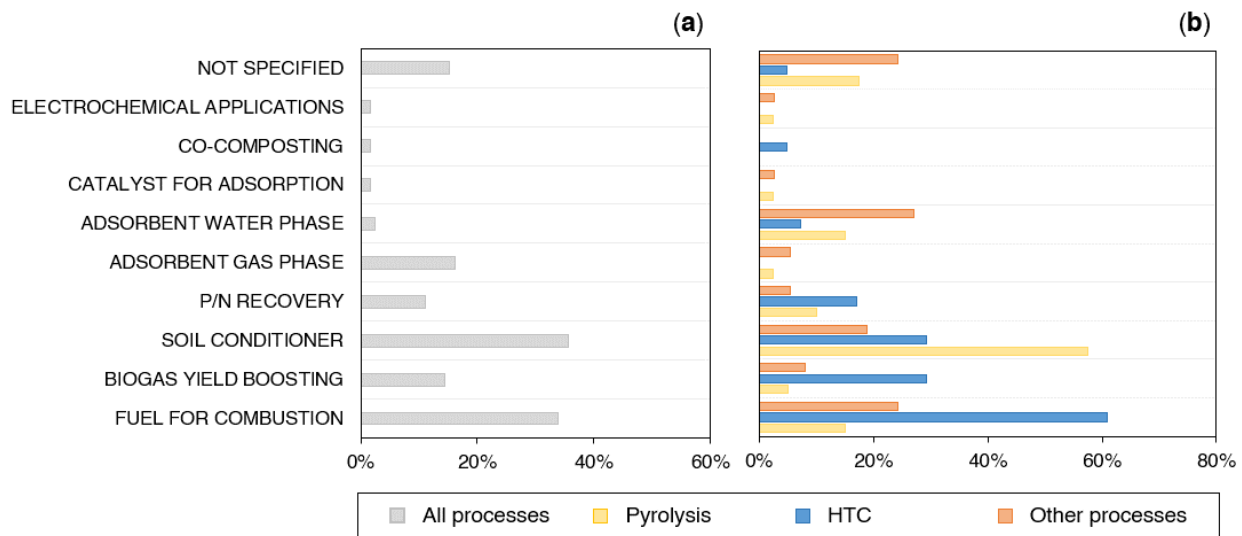
664 Other examples of chemical modification of digestate-based chars were provided using different reagents, such
665 as salts (Na_2CO_3 , NaHCO_3 and NaCl) to increase carbon content and specific surface area of hydrochars for
666 adsorption of phosphorus in wastewater and carbon dioxide in gas [168]. The modified biochars prepared in
667 [169] using HCl , $\text{NH}_3\cdot\text{H}_2\text{O}$ and KMnO_4 were negatively charged, showing larger specific surface area and
668 total pore volume, together with higher contents of specific functional group (C–O, O–H, P–O and Si–O–Si)
669 for heavy metals (Cu and Zn) and antibiotics (sulfadimidine and tyrosine) removal.

670 High concentrations of iron, naturally present in digestates [100] or added in the form of zero valent iron (ZVI)
671 particles for sludge dewatering amelioration [170], proved to be effective for the synthesis of magnetic chars
672 with high reactivity towards organic contaminants, by transforming Fe_3O_4 into FeO at increased temperature.
673 The possibility to anchor metals or metal oxide nanoparticles (NPs) on char surface was investigated given
674 their outstanding performances in water contaminants removal. The presence of reactive surface functional
675 groups on chars, their large surface area, and highly porous structure, make them one of the most promising
676 precursors for the preparation of nanoscale-metal-based composites, such as Cu-NPs/chars [171,172], that
677 were successfully tested to remove model organic contaminants (such as tetracycline and octocrylene).

678

679 **3. Biochar and hydrochar applications**

680 Considering the reviewed research papers (Figure 4a), biochar and hydrochar produced from anaerobic
681 digestates are mainly investigated for applications as fuel (energy recovery) or as soil conditioner (fertilizer,
682 soil improver, soil stabilizer). Figure 4b shows the distribution of reviewed literature by type of application
683 and process: HTC studies are mainly aimed at producing a solid fuel to be used in combustion, including the
684 possibility of recirculating HTC liquors (AHL) to anaerobic digesters to boost biogas yield. Biochar produced
685 from pyrolysis, instead, is commonly intended for soil application. Unconventional processes, including
686 chemical or physical modification of chars (grouped into “Other processes”), are predominantly developed for
687 target-oriented applications, such as adsorbent media production to remove organic/inorganic compounds from
688 water or gas phases.



690

691 **Figure 4.** Percentage distribution by type of application of literature published (2016-2022) on
 692 thermochemical valorization of anaerobic digestates: (a) all literature; (b) literature grouped by type of
 693 process applied.

694

695 Table 3 links possible char applications (soil conditioner, fuel for energy generation, adsorbent media) with
 696 biochar and hydrochar properties while varying digestate type and process conditions. As regards the influence
 697 of feedstock type, the use of SS digestate derived char on agricultural fields is limited by the presence of
 698 emerging pollutants (both organic and inorganic ones); likewise, the mechanisms of contaminants desorption
 699 when using char as adsorbent medium should be carefully evaluated. Caution should also be used when dealing
 700 with AW digestate derived chars, especially when manure is fed to agricultural digesters, due to the wide use
 701 of antibiotics and growth-promoting additives in livestock feeds.

702 Regarding process conditions, the most influencing parameter is temperature that can be raised or reduced in
 703 to tailor and control char properties. Caution should be used when increasing temperature for the generation
 704 of chars to be used as soil conditioner: if on the one side P, micronutrients and heavy metals tend to concentrate,
 705 on the other side their bioavailability is reduced, N content decreases and the pH may increase to alkaline
 706 values that are not suitable for plants. A temperature increase positively affects the energetic content of chars
 707 (H/C decrease, HHV and EY increase) but a compromise should be made since the greater ash content
 708 measured at high temperatures reduces char suitability as fuel. To improve char properties as adsorbent media,
 709 high temperatures reduce H/C ratio then improving pore structure and specific surface area. However, for both
 710 pyrolysis and HTC, SBET reduces at very high temperatures (900/1000 °C for pyrolysis, 260°C for HTC) due
 711 to pore collapse.

712 In this Section, the main char applications, including energy recovery (Section 3.1) and agricultural reuse
 713 (Section 3.2) are highlighted. Other minor applications are also briefly introduced (Section 3.3).

714

715 **Table 3.** Range of variability of biochar and hydrochar properties while varying feedstock type and process
 716 temperature (T) according to literature reviewed and influence on potential applications. The direction of
 717 arrows indicates growing trends as a function of temperature. The applications are evaluated using red, yellow
 718 and green circles (respectively not recommended, with caution, feasible) for each feedstock type. The grey
 719 circle indicates a missing evaluation due to lack of data.

		Biochar from Pyrolysis			Hydrochar from HTC				
Feedstock Type		Sewage sludge digestate	Food waste digestate	Agricultural waste digestate	Sewage sludge digestate	Food waste digestate	Agricultural waste digestate		
Char properties	Process T	[°C]	350-500 →	300-900 →	350-600 →	150-260 →	150-300 →	150-250 →	
	Yield	[%]	50.5-70.3 ←	35.0-78.0 ←	27.8-52.0 ←	37.0-88.3 ←	35.0-96.2 ←	27.0-91.0 ←	
	Ash	[%]	41.2-72.4 →	34.3-88.1 ↗↘	14.5-81.2 →	7.00-77.0 →	6.00-68.0 ↘↗	4.50-62.0 →	
	C	[%]	15.7-22.0 ←	5.78-50.4 ↘↗	2.25-65.9 ↘↗	10.2-68.0 ↘↗	19.3-63.8 ↘↗	28.9-77.5 →	
	N	[%]	2.10-3.10 ←	0.21-5.36 ←	1.30-2.60 ←	0.66-5.11 ←	0.56-3.58 ↘↗	1.53-4.10 →	
	H/C	[-]	0.04-0.08 ←	0.02-1.16 ↘↗	0.04-1.17 ↗↘	0.09-0.16 ↘↗	0.07-0.14 ←	0.07-0.12 ←	
	pH	[-]	6.40-10.6 →	8.39-13.3 →	8.24-12.4 →	5.3-6.1 ←	7.8-8.4 ↘↗	5.77-9.7 ←	
	HHV	[MJ/kg]	N.A.	6.30-13.0 ←	22.3-24.6 →	7.86-26.5 ↘↗	5.44-27.3 ↘↗	9.10-24.2 ↗↘	
	SBET	[m ² /g]	N.A.	0.66-85.3 →	1.43-88.0 ↘↗	4.92-27	N.A.	1.53-6.78 →	2.82-52.0 →
	Applications	Soil conditioner		●	●	●	●	●	●
Fuel for energy			●	●	●	●	●	●	
Adsorptive media			●	●	●	●	●	●	
References		[27,59,74,85,90,96,97,127,129,131,137,138,173–177]			[67–71,73,77–82,86,88–90,92,93,117,120,127,128,132,134,142,178–182]				

Notes. The direction of arrows indicates growing trends as a function of temperature: → always increasing with T; ← always decreasing with T; ↘↗ increasing or decreasing with T; ↗↘ decreasing and then increasing with T; ↗↘ increasing and then decreasing with T.

720

721

722 3.1. Energy recovery

723 Energy recovery is one of the most investigated end-uses for hydrochar, rather than for biochar. A schematic
 724 view of the possible options for AD integration with thermochemical conversion processes is reported in
 725 Figure 5: a fundamental distinction is made between pyrolysis (Figure 5a) and HTC (Figure 5b). The following
 726 strategies, alone or in combination, may be considered for energy recovery from thermochemical processes:

727 (i) char utilization as fuel; (ii) char recycle to AD; (iii) recycle of HTC liquor to AD; (iv) thermal energy
728 recovery from pyrolysis vapors; (v) enhancement of H₂ production.

729 *3.1.1. Direct char utilization as fuel*

730 As previously discussed, the first approach is mainly limited by high ash content in digestates, which is mainly
731 dependent on feedstock type. In digestate-derived chars, the ash content can reach 60% on dry basis, which is
732 a relatively high value if compared to traditional fuels [87,131]. Compared to other precursor biomasses (e.g.,
733 lignocellulose or carbohydrates-rich feedstocks), in fact, digestate-based chars show an increased ash content,
734 as the organic fraction already underwent a biochemical stabilization process [67]. During AD, the organic
735 matter is mainly converted into CO₂ and CH₄, resulting in a concentration of inorganic compounds [93].
736 Thermochemical processes carbonize the residual digestate organic fraction, leading to a stable or even reduced
737 carbon content, and an increased ash fraction, which is redistributed among the generated products [67]. Ash
738 contents found in biochars and hydrochars, which may cause issues such as slagging, fouling, and corrosion
739 in the downstream combustion units, raise the question of whether digestate is a suitable feedstock for the
740 combustion of digestate derived-chars [143].

741 Depending on feedstock type, applied process and adopted operating conditions, literature is controversial on
742 this point. Some authors found that it is more convenient to directly use the raw precursor instead of its
743 digestate, especially when dealing with HTC. According to [87], the net energy gain was higher for HTC of
744 manure or manure combined with whey, compared to the integrated AD-HTC process. As a result, if on the
745 one hand AD can slightly [72,89] or adversely change [93] the hydrochar fuel properties, on the other hand, it
746 modifies its surface functional groups, improving its characteristics for a stable combustion. In [143] it was
747 claimed that an increased treatment temperature is required to improve hydrochar carbon content and thermal
748 stability, which may lower the net energy gain due to increased energy consumption. Besides, co-processing
749 (especially with other lignocellulosic feedstocks) is suggested by various authors [69,160,161] to improve
750 hydrochar/biochar fuel quality. Considering pyrolysis, there exist specific cases when the direct use of dried
751 digestate as a solid fuel (i.e., without thermochemical conversion) is demonstrated to be energetically more
752 convenient [84]. In other studies, the coupling of slow pyrolysis and AD was shown to significantly improve
753 the energy balance compared to separate processes: sufficient energy was available in biogas and non-
754 condensable pyrolysis gases to sustain the pyrolysis energy need. If required, biochar combustion can provide
755 additional energy [175]. Co-digestion can be considered as well to improve char characteristics and overall
756 process energy balance. However, since digestate pre-treatment (drying) is the most impacting factor on energy
757 balance in pyrolysis processes, the benefits are strongly dependent on specific co-substrate characteristics (e.g.,
758 solid/liquid, highly or poorly degradable). Thus, in addition to enhanced biogas and char production, a greater
759 amount of undigested material is generated, requiring drying prior to conversion in pyrolysis reactors [28,183].
760 Recently, acid leaching was proposed to reduce the ash content in char produced from HTC of digested sewage
761 sludge, yielding lignite-like hydrochar with HHV of 20.5-23.1 MJ/kg [80] and allowing for P recovery through

762 stripping or leaching [78]. However, a complete extraction of digestate ashes is unfeasible, since most of the
763 inorganic matter is bound in a stable matrix, and re-dissolution is possible only partially and with great effort.
764 Overall, no remarkable differences between biochar (6.33-24.6 MJ/kg) and hydrochars HHV (5.44-27.3
765 MJ/kg) were observed from reviewed literature. A direct comparison on chars derived from agricultural
766 feedstocks was provided in [90] by using the same precursors. The HHV of hydrochar was about 1.07 times
767 higher than biochar's (26.5 MJ/kg compared to 24.6 MJ/kg), whereas hydrochar ash content was 2-5 times
768 lower than biochar's [90,127]. Apart from the lower ash content, which always depends upon digestate type,
769 authors agree that, compared to pyrolysis, the larger interest in HTC process for energy recovery applications
770 is due to the theoretically more favorable energy balance. The lower process temperatures and the possibility
771 to treat wet substrates without a preliminary drying phase are the main benefits. Furthermore, from a thorough
772 energy perspective, digestate hydrothermal pre-treatment significantly improves its dewatering efficiency,
773 being a relevant positive factor, as digestate drying is known to be an energy-intensive process [70].

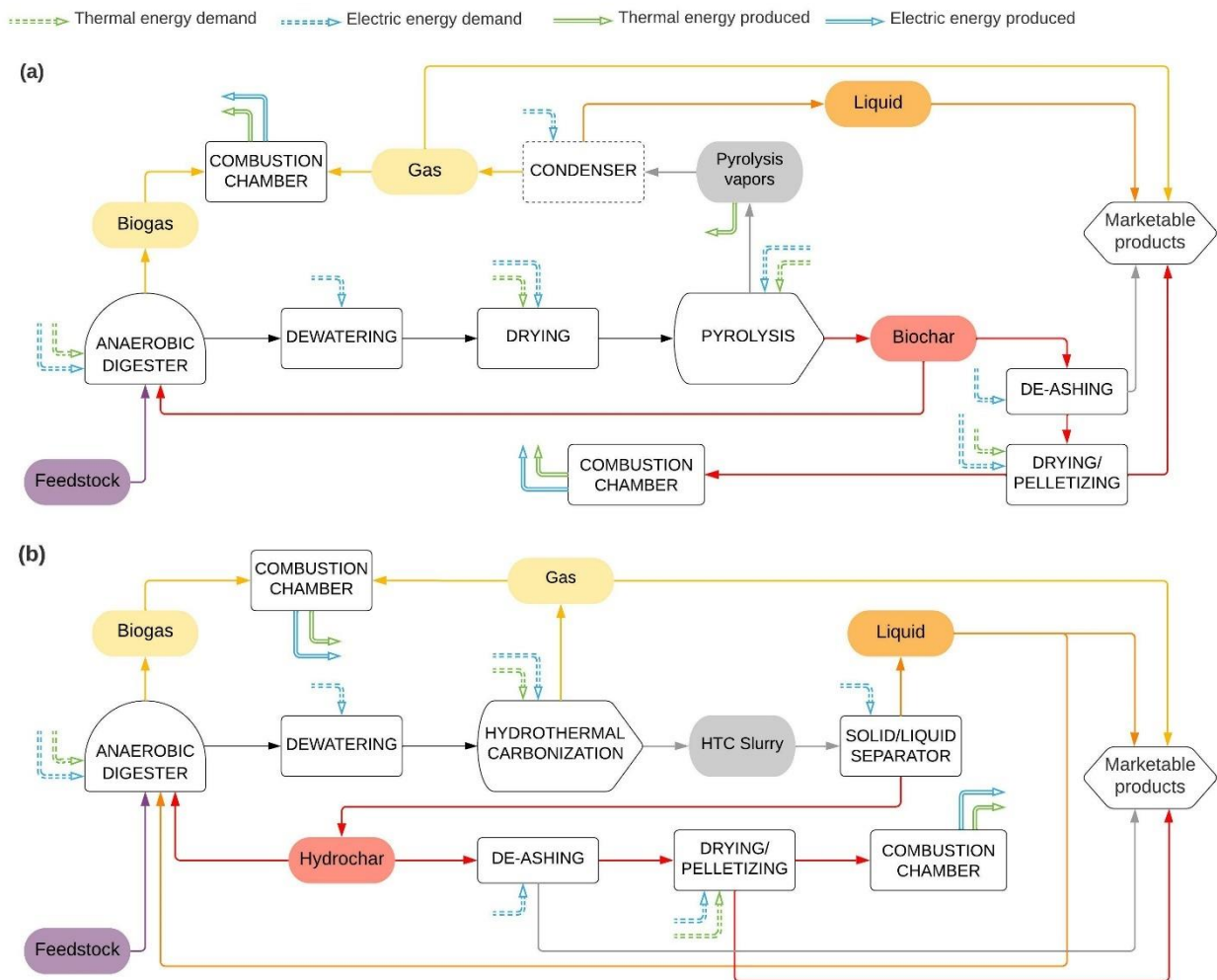
774 *3.1.2. Char/HTC liquor recycle to AD and other strategies*

775 As previously highlighted, chars produced from digestate have commonly a higher ash content than the ideal
776 one for combustion application. Hence, recycling of chars or process waters back into the anaerobic digester
777 raised interest for optimizing energy recovery. Char addition to AD reactors can increase biogas production:
778 the presence of nutrients and trace elements may play a key role in determining its effectiveness in biogas
779 production enhancement [31]. Also, char surface microstructure strongly influences microorganisms'
780 immobilization, potentially improving direct interspecies electron transfer (DIET) mechanism [31,151]. Char
781 in AD can also act as a pH control agent due to its alkaline properties, preventing pH drop due to volatile fatty
782 acid (VFA) accumulation [59]. Recently, biochar and hydrochar performances in the enhancement of biogas
783 yield from sewage sludge and swine manure were compared, highlighting a higher energy production in
784 hydrochar-amended digesters. Compared to biochar, the incomplete hydrochar carbonization leads to the
785 release of char-derived, biodegradable organic matter that contributes to the overall methane yield. Besides,
786 the increased abundance of functional groups in hydrochar promotes electron transfer between microorganisms
787 [184].

788 Due to organic compounds solubilization, a significant amount of organic matter is concentrated in HTC
789 effluents, that may be digested with the main feedstock [120]. Depending on HTC process conditions and
790 feedstock type, process water can contain up to 15-20% of the carbon originally present in the feedstock,
791 resulting in extremely high COD concentrations (up to 90-110 g/L) [185]. Recycling HTC liquor to AD reactor
792 could even double methane yield in sewage sludge AD, reaching 102 mL CH₄/g COD (from 55 mL CH₄/g
793 COD), further increasing to 187 mL CH₄/g COD with concurrent hydrochar recirculation [186]. In most of the
794 studies [69,79,132] inhibition due to ammonia from HTC liquor was not observed, but it may occur under
795 specific conditions [80], and thus proper reactor monitoring is mandatory. However, care should be taken when
796 measuring methane production enhancement through traditional batch assays (such as biochemical methane
797 potential-BMP tests), as the properties of process water and digestate might not be stable when continuously

798 recycling the former back to the original AD system. Long-term negative impacts on biogas production may
 799 arise due to possible toxic compounds accumulation and increased ammonium concentrations inside the
 800 digesters [92]. A possible solution could be the installation of a separate anaerobic digester to treat the HTC
 801 liquor, although this implies an additional energy and economic burden [76].
 802 Further energy recovery, finally, is commonly achieved by using vapors released from pyrolysis step to support
 803 the drying phase or to run the pyrolysis unit [99,126]. Indeed, gasification of HTC liquor [141] or hydrochar
 804 [72] was also proposed to emphasize potential H₂ generation, besides producing a solid fuel. Steam gasification
 805 may also be used to produce activated carbon starting from chars for application in areas other than the energy
 806 sector [120].

807
 808



809
 810 **Figure 5.** Integration of AD with (a) pyrolysis, (b) HTC: strategies for energy recovery.
 811

812 **3.2. Soil application**

813 Two main strategies are mainly proposed to recover nutrients from chars. The first option is linked to direct
 814 char application as soil fertilizer (often after pre-treatments to prevent pollutant accumulation), while the
 815 second one is related to indirect phosphorus and nitrogen recovery from char, producing a high-quality N/P-
 816 fertilizer.

817 *3.2.1. Direct char application to soil and comparison with digestate*

818 Regarding the first approach, as previously introduced, digestates are often directly applied to agricultural
 819 soils. Thermal conversion processes modify the physicochemical properties of organic matter in digestates.
 820 The comparison between digestate and char as soil fertilization media is summarized in Table 4, highlighting
 821 their main specific features.

822

823 **Table 4.** Comparison between digestate and char as soil fertilization media.

	Raw digestate	Char
Main components	Labile and partially stabilized organic fractions	Fixed carbon structures chemically stable and inorganic compounds
Nutrients	About 30-50% of carbon; good nutrient concentration (NPK)	Enrichment of P, K and micronutrients; N content similar to raw digestate
Effect on microorganism activity in the soil	Slow decomposition, with nutrient release for plants and formation of humus components	Poor degradability, chemical stability (recalcitrance)
Advantages	Directly improves soil structure, favoring the aggregation of soil particles and a long-lasting stabilization of the aggregates; capable to neutralize soil acidity	Long term carbon sequestration; improved surface area, water holding capacity and higher carbon recalcitrance; lower risks of heavy metals leaching; capable to neutralize soil acidity
Concerns	Excess digestate application can lead to nutrient run-off with environmental pollution; pathogen exposure; high transportation and application costs	Pretreatments may be required before soil application to reduce phytotoxicity, especially regarding hydrochar; unsuitable as long-term fertilizer, due to the readily available nutrient content

824

825 Char is often referred to as a “carbon sink” [159,160], potentially playing a role in climate change mitigation
 826 as long-term carbon capture and storage media. As appears from Table 4, both digestate and char show good
 827 soil amendments properties but, since they have been processed differently, with complementary effects [27].
 828 Thus, it is suggested to use both digestate and char as fertilization media to exploit the relevant benefits given
 829 by both of them. Besides, the potential synergy of coupling biochar with liquid digestate for soil amendment
 830 has been proposed and successfully tested [187]. Compared to digestate, and thanks to its improved stability,
 831 char can be stored and used on the fields when more appropriate, thus lowering the issues related with residual
 832 methane and carbon dioxide emissions from digestate (when stored or applied on soil) or with improper land

833 spreading. In addition, being dried, char can be more easily, safely and cheaply transported, then resulting in
834 reduced carbon emission related to truck transportation and in the possibility of optimizing fertilizer supply
835 and demand at the local scale.

836 Phosphorus availability in char decreases at increasing processing temperatures, thus low pyrolysis
837 temperature should be selected when char is to be used for crops with an instantaneous need for P [85,95]. In
838 [182] the fertilization effects of hydrochar were investigated, observing no germination inhibition after 5%
839 hydrochar application. However, they reported its unsuitability as long-term fertilizer, due to the readily
840 available nutrient content. In [79], hydrochar use as fertilizer was suggested but due to Hg content above the
841 legislative limit, an additional treatment before reuse was required. In [82], instead, the use of hydrochar
842 derived from secondary sludge as a potential soil amendment was suggested, reporting heavy metals content
843 below International Biochar Initiative (IBI) standards. However, inappropriate oxygen and volatile matter
844 content may pose additional limitations. At the same time, in [91] the need for long-term experiments both at
845 laboratory and in field conditions was highlighted to assess the long-term stability of carbon compounds after
846 hydrochar soil application. By comparing the properties of biochar and hydrochar produced from agro-
847 industrial digestate, in [90] it was found that biochar had a better quality in terms of O/C and H/C molar ratios,
848 as well as regarding specific surface area. In addition, biochar displayed a PAH concentration lower than 4
849 ppm, falling within the “premium” class according to the European Biochar Certificate (EBC). Compared to
850 other “marginal” feedstocks (e.g., plants grown on contaminated land, demolition wood), food waste digestate
851 proved to be a suitable substrate for biochar production with interesting applications as fertilizer, due to high
852 nutrients concentrations, complying with EBC guideline values for heavy metal content [188]. However, more
853 generally, digestate composition can differ widely, and reasonable monitoring procedures for the assessment
854 of biochar quality would be advisable.

855 Due to different physio chemical characteristics of hydrochar (mostly related to feedstock type and HTC
856 temperature), hydrochar pre-treatment and modifications may be required before direct soil application. In
857 [189] it was revealed that through HTC of digestates pre-contaminated with organic pollutants (e.g., PAH),
858 the toxicity of generated hydrochars could be increased under treatment temperatures above 220 °C. Therefore,
859 HTC process conditions and pollutant concentrations in the digestate should be carefully controlled. By
860 coupling pyrolysis and HTC, lower PAH concentrations were measured in [139] on pyro-hydrochars,
861 compared to chars produced by HTC and pyrolysis alone. Other important properties for application as soil
862 amendment, such as carbon content, pH and BET surface area, were improved by processes combination.

863 In [86] the importance of hydrochar phytotoxicity was underlined, which may be evaluated through the
864 characterization of hydrochar water extracts. Phytotoxins such as furan compounds were found in the extracts,
865 which may be responsible for plant growth limitations. In addition, a high abundance of Na and a high pH (>
866 7.5) may hinder plant growth, since nutrients (e.g., Mg, P, Fe, Cu, and Zn) availability and solubility can be
867 lowered. To solve this issue, dilution and mixing of hydrochars with other substrates was suggested. For the
868 same purpose, in [85] acid leaching treatment was proposed to decrease Zn and Cu contents in biochar before

869 land application. Overall, contamination issues in chars are either attributed to organic compounds formed
870 during carbonization process or to pollutants present in the raw feedstock; nevertheless, another source of
871 contamination by Ni and Cr results from high-grade steel used in some high-temperature reactors, with
872 important consequences for design and operation of industrial units [188].

873 Generally, the applicability of either raw digestate or char as fertilizer depends on original substrate
874 characteristics: char tends to accumulate the inorganic elements present in the original feedstock, so if a
875 significant amount of heavy metals is present in the raw digestate, soil application should be avoided, as their
876 concentration would actually increase in char. A more conscious digestate management, including its (at least
877 partial) conversion into char through thermochemical processes and with focus on fertilizer amounts and crops
878 needs, could improve the fertilization effects on plants, limiting at the same time the negative impacts on the
879 environment. Finally, since char-soil interaction is a complex process that depends on the physicochemical
880 properties of both char and soil, two main advices should be considered: (i) a careful soil application is
881 necessary to avoid nutrient deficiency or toxicity effects, which may negatively impact plant growth and long-
882 term soil productivity; (ii) a dedicated assessment is necessary to properly manage char agronomic use [27,97].
883

884 *3.2.2. Indirect phosphorus and nitrogen recovery from char*

885 As regards the second approach for nutrient recovery from chars, few studies investigated acid leaching from
886 hydrochars for nutrient recovery. N and P recovery in hydrochar are maximized at different process conditions
887 (pH and temperature), so a compromise should be found to reach the desired N/P ratio in the product for
888 agricultural applications [190]. In [77] a nutrient recycling strategy was proposed to extract phosphorus from
889 hydrochar, precipitating it with nitrogen and magnesium to recover struvite, a well-known slow-release
890 fertilizer. Phosphorus was extracted from hydrochar via acid leaching (citric acid 2 M, liquid to solid ratio
891 10:1, contact time: 2 h) resulting in a phosphorus extraction rate of 58.5-94.8%, with low co-dissolution of
892 heavy metals (only Zn detected in the leachate). Having collected the leachate, the process liquid was used as
893 nitrogen source and, after magnesium chloride addition, pH was increased with NaOH till 9 to promote high-
894 quality struvite formation. As a result, up to 90% of phosphorus was recovered, leading to a high phosphorus
895 content in the precipitated material (up to 113.85 mg/g). Acid leaching was also tested in [167] on hydrochars,
896 recovering more than 82% of phosphate at pH=2 using sulphuric acid. In addition, in [78] two ways were
897 proposed to recover phosphorus and nitrogen from hydrochar: stripping and leaching. The results showed 84%
898 and 71% of phosphorus extraction efficiency, respectively, together with 53% and 54% of nitrogen extraction
899 efficiency. However, the high content of sulphur and heavy metals in hydrochar may limit its potential use,
900 suggesting the need for further investigations and the definition of proper qualitative standards.
901

902 **3.3. Other applications**

903 Several alternative char end-uses to conventional energy recovery and soil application have been recently
904 proposed, including contaminants adsorption (Section 3.3.1), catalysts preparation (Section 3.3.2),
905 electrochemical technologies (Section 3.3.3).

906 *3.3.1. Contaminants adsorption*

907 Several literature studies proposed the utilization of digestate-derived char as adsorbent medium for pollutants
908 in gas and water phases. In both cases, char modification (chemical activation/functionalization) is required to
909 improve its adsorption capacity towards target contaminants, achieving comparable properties to conventional
910 adsorbents (such as activated carbon) [162]. Adsorption capacity is determined by char physicochemical
911 properties such as specific surface area, pore properties, special functional groups and surface charges [74].
912 Besides, according to [169], different contaminants show diverse adsorption mechanisms: e.g., physical
913 adsorption, which is strongly correlated to specific surface area and pore properties, is weakly involved in
914 heavy metals removal from water, whereas it is the main mechanism for antibiotics removal. Accordingly,
915 biochar coupled with metal or metal oxide nanoparticles show increased surface area, improved pore structure
916 and, more importantly, it could be coupled with free radicals for organic pollutant (e.g., personal care products
917 [171] and antibiotics [172]) degradation.

918 The main advantage of using digestate-derived chars, compared to other feedstocks, lies in their higher
919 stability, owing to VS reduction during AD process. However, a poor adsorption capacity towards heavy
920 metals was obtained using sewage sludge digestate compared to MSW digestate as biochar precursors, even
921 after chemical modification [162]. Hydrochars normally have lower surface area and porosity than biochars,
922 but proper chemical activation may improve their microporosity and considerably increase (up to ten-fold) the
923 adsorption capacity towards methylene blue [73,167]. Char adsorption efficiency towards ammonium was
924 studied in [74] using both synthetic and real municipal wastewater, proving the importance of assessing
925 interferences from undesired compounds for full-scale applications. The ability of biochar to adsorb phosphate
926 from wastewater [173,174] and liquid digestate [191] has also been investigated, displaying improved removal
927 rates compared to both activated carbon and zeolite [173], with relevant potential of extracting P or reusing P-
928 loaded chars as slow-release P fertilizers. Further research, however, is needed to engineer char application as
929 contaminant adsorbent, e.g., by investigating regeneration methods and process operational conditions [59].

930 *3.3.2. Catalysts and chemicals production*

931 Chars, often chemically activated to enhance their sorption potential, can be applied as catalyst materials for
932 enzymatic and heterogenous catalytic reactions in applications such as biodiesel production, tar removal from
933 syngas, syngas production, biomass hydrolysis, bio-oil upgrading, but also water and gas (deNO_x catalyst)
934 purification [192]. Hydrochar use in biotechnological processes may enhance the economic sustainability of
935 industrial applications [193]. More specifically, digestate-derived biochar has been investigated as inexpensive
936 heterogeneous catalyst (in comparison to traditional metal precursors) for catalytic removal of organic

937 contaminants. In [65] the potential of using food waste digestate-derived biochar to activate
938 peroxymonosulfate (PMS) was evaluated to remove azo dye from simulated textile wastewater, compared to
939 traditional metal-based materials. The results showed that biochar and PMS addition to wastewater could
940 remove >99% of a representative azo dye pollutant (X-3B, 1 g/L) within 10 min. Digestate dewatered by a
941 combined system of zero-valent iron and peroxydisulfate (PDS) was used in [170] to produce magnetic Fe-
942 biochars for PDS activation and consequent sulfamethazine removal from water. Compared to commercial
943 catalysts, biochar-derived catalysts are easier to recycle, show a wider abundance of functional groups and are
944 characterized by lower cost. On the other hand, they have a relatively low efficiency and low abrasive
945 resistance [194]; furthermore, much more practical research is needed to ascertain the commercial applicability
946 of these solutions.

947 3.3.3. *Electrochemical technologies*

948 Char may be potentially applied in electrochemical technologies, such as supercapacitors and batteries, due to
949 its surface area, porosity, polarity, aromaticity and stability; hydrochar-derived supercapacitors demonstrated
950 higher cycle stability and power density, while rechargeable batteries showed lower cycle stability, higher
951 energy density and lower discharge/charge rate [193]. Biomass pre-treatment or biochar post-treatment could
952 optimize the combination of properties (e.g., electrochemical conductivity, capacitance, porosity distribution,
953 superficial redox-active and electroactive surface groups, capacity to host electroactive microbial
954 communities), leading to the production of the so-called *e-biochar*. Furthermore, biochar appears as an
955 excellent candidate for large-scale applications of microbial electrochemical technologies (MET), that may be
956 implemented in soil/water bioremediation, biomass processing, CO₂ fixation and wastewater treatment [195].
957 Examples of digestate-derived chars potentially exploitable in electrochemical applications include magnetic
958 chars [100] and N-doped biochars [196]. Despite relatively low cost and intriguing biomass structure of chars,
959 however, unaffordable performances may be sometimes achieved in these applications [194], and consequently
960 scale-up feasibility still appears challenging.

961

962 4. **Economic and environmental aspects**

963 Besides considering technical and energy features, it is fundamental to account for economic and
964 environmental aspects when comparing alternative char production and application processes. Recent literature
965 started to focus on these aspects, even if at present limited data is available for digestate-based
966 biochar/hydrochar [197,198]. The economic feasibility of treatment chains depends on energy yield in the
967 products, biochar application value, GHG reduction (due to reduced N₂O emissions and carbon sequestration)
968 [199], value of other produced chemicals [194]. Biochars from slow and fast pyrolysis have been reported to
969 cost 18.30 and 8.14 US\$/ton, respectively; however, a recent survey in USA from 23 biochar-producing
970 companies highlighted a much higher average price (2,512 US\$/ton), while globally an extremely wide price

971 range was reported (80-13,480 US\$/ton) [200]. All these economic data are typically referred to woody
972 biomass-derived char, rather than digestate-derived char, so attention must be paid when using literature data
973 as such. Local factors, such as raw substrate availability and cost, are supposed to influence significantly char
974 economic balance; however, digestate valorization through thermal technologies could potentially lead to more
975 sustainable platforms than traditional ones, as char is locally generated and reused. Nonetheless, a remarkable
976 study aimed at studying economic aspects linked to digestate-derived hydrochar showed that hydrochar
977 production has almost double price than natural gas, despite being based on synergy with AD and low-cost
978 feedstock supply [201]; thus, at present dedicated incentives and further technology development (with plant
979 energy optimization) are needed to boost commercial applications. Most of reported literature studies, in fact,
980 are conducted at laboratory or pilot-scale conditions.

981 Concerning the environmental aspects, char can immobilize carbon from an active cycle and return it to an
982 inactive steady state, reducing atmospheric CO₂ concentration and (more generally) GHG emissions [199].
983 Also, char soil application may reduce N₂O emissions by 50-80% [200], potentially being a significant lever
984 in reducing agricultural GHG emissions. Char utilization as energy recovery medium could reduce fossil fuels
985 utilization, while char application as adsorbent medium may have lower environmental impacts than other
986 removal methods based on fossil materials.

987 Life cycle assessment (LCA) is used to thoroughly assess the environmental impacts of alternative scenarios
988 or processes through standardized modelling tools; if coupled with life cycle costing (LCC), it may give useful
989 insights related to the economic aspects as well [202]. Literature studies related to LCA-LCC applications to
990 biochar were aimed at investigating the economic viability of pyrolysis plants [203], comparing pyrolysis with
991 HTC and incineration [204], investigating GHG emissions of biochar and hydrochar compared to mineral
992 fertilizers [205], estimating biochar GHG emissions and carbon storage potential [206], but again they were
993 mainly focused on woody biomasses rather than anaerobic digestates. A techno-economic analysis dedicated
994 to poultry waste valorization highlighted lower GHG emissions of slow and fast pyrolysis than gasification
995 and hydrothermal liquefaction; GHG balances, however, showed trade-offs with economic results, the most
996 influential factors being carbon credits, product market price, plant capacity [207].

997 In [208] a LCA was conducted concerning sewage sludge AD and pyrolysis, demonstrating that tprocesses
998 combination had better overall environmental performances and energy efficiency than pyrolysis alone.
999 Indeed, AD causes a decrease in NO_x and chlorinated pollutants emissions, but an increase in S-containing
1000 compounds [209]. Regarding pyrolysis, the use of dichloromethane for pyrolysis-oil treatment resulted being
1001 the main contributor to the environmental impacts [210]. To overcome the heat demands of combined AD-
1002 pyrolysis for pig slurry treatment, the use of lignocellulosic biomass was demonstrated to be necessary, as
1003 digestate drying is energy-intensive [211–213]. Generally, the use of biogas and syngas contributes most to
1004 emissions mitigation, while sludge dewatering and drying processes contribute the most to environmental
1005 emissions, due to fossil fuel utilization [204]. The environmental performances of composting, combustion,
1006 and pyrolysis for dewatered sewage sludge digestate were evaluated in [213], showing that digestate

1007 combustion and composting performed better than pyrolysis for most of the selected impact categories.
1008 However, being pyrolysis of sewage sludge still under development, uncertainties arise in relation to the
1009 available technological data.

1010 Consistently, in [81] it was proved through LCA that HTC integration with AD in sewage sludge treatment
1011 may reduce the environmental impacts compared to AD alone (global warming impact decreasing from 72 to
1012 18 kg CO_{2eq}/t sludge), even if the estimated costs were 42% higher (from 66.2 to 94.3 €/t sludge) due to HTC
1013 reactor installation. The feasibility of combining AD of agricultural waste and HTC was assessed in [214],
1014 proving that the high energy demand of the combined configuration required the valorization of a limited
1015 fraction (15%) of digestate. Conversely, in [179] it was showed that HTC treatment of MSW digestate resulted
1016 in a positive energy balance of 110 kWh per ton of MSW digestate treated, together with an increased water
1017 recovery from dewatering. This last aspect is of importance in environmental assessment at commercial scale
1018 [215], and innovative integrated systems were recently proposed for AHL reuse such as growth medium
1019 substitute for cultivating microalgae [178]. In [68] LCA was used to assess the environmental performances
1020 of HTC in treating different waste streams, highlighting that increased plant size leads to improved HTC
1021 performances thanks to a more efficient heat and electricity use; however, feedstock characteristics (especially
1022 moisture content), geographical location and waste management systems greatly influenced LCA outcomes.
1023 In [216] it was showed that sewage sludge direct agricultural application (in contrast to incineration) is
1024 beneficial in terms of GHG emissions, but counterproductive in terms of toxicity and acidification potential.
1025 In these categories, HTC and pyrolysis offer clear advantages, especially with regards to the potential
1026 applicability of the resulting chars [217].

1027 Nevertheless, much more research is needed to broadly analyze through standardized LCA and LCC the
1028 environmental and economic aspects related to alternative digestate-derived char applications, especially in
1029 comparison with traditional practices (e.g., direct digestate soil application or mineral fertilization).

1030

1031 **5. Regulatory framework**

1032 In the absence of a supportive policy framework, the diffusion of thermochemical technologies at commercial
1033 scale remains limited despite promising literature results [218]. However, the regulatory context related to
1034 thermochemical technologies is quickly changing favorably.

1035 Biochar recently made its first appearance in EU legislation, with the upcoming implementation (Reg.
1036 2021/2088) of the modified fertilizing products regulation (Reg. 2019/1009); this act standardizes biochar
1037 definition. The addition of pyrolysis and gasification products as a material category (CMC 14) in EU
1038 fertilizing products has become necessary as the market demand for those materials is growing, and chars can
1039 be used to provide nutrients to agriculture [219]. Reg. 2021/2088 defines the specific requirements on
1040 minimum processing conditions (oxygen-limiting conditions, temperature >180 °C for at least two seconds)
1041 and product characteristics (especially regarding toxic compounds, such as heavy metals and PAH).

1042 In parallel with EU fertilizing regulation, biochar produced via pyrolysis from plant materials has also been
1043 recently included in EU organic products regulation as a potential soil conditioner (Reg. 2019/2164). Other
1044 crucial developments at EU level for biochar sector development include: (i) the proposed reform of the
1045 Common Agricultural Policy (CAP) for the period 2021-2027, in which more robust support for soil carbon is
1046 given; (ii) the adoption of an updated strategy for European Circular Bioeconomy; (iii) the announcement of
1047 an EU certification system for carbon removal by 2023; (iv) the new EU targets for climate neutrality by 2050
1048 and the promotion of renewable energy sources utilization. These developments suggest that a tailored
1049 regulation and policy support for thermochemical technologies may not be very far off in time at EU level.
1050 However, well before EU legislation was emanated, biochar was already mentioned by some national
1051 regulations, such as Italy's and Switzerland's. Furthermore, some international and non-governmental
1052 institutions proposed standardized guidelines for safely producing and using biochar. The most relevant
1053 regulations on biochar production, including quality requirements, are summarized in Table 5. In 2011 the
1054 Ithaka Institute developed the European Biochar Certificate (EBC) as a guideline for biochar production and
1055 usage, aiming to ensure sustainable practices in the whole supply chain. The new EBC version, published in
1056 early 2022 [220], defines biochar as a pyrolysis product (thus excluding gasification, HTC, torrefaction),
1057 defined by its quality characteristics, raw materials used, sustainable production (e.g., emissions, feedstock
1058 storage) and end-use. EBC establishes six biochar application classes with different quality requirements
1059 (Table 5), and a positive list indicates which biomasses types are allowed for each application class. It is
1060 planned to include non-plant biomasses (sewage sludge, livestock manure, manure containing biogas
1061 digestates or bones and slaughterhouse wastes) in the EBC positive list for pyrolysis feedstock by mid 2022.
1062 Regarding biochar properties, the organic carbon content (C_{org}), which was limited in the previous versions of
1063 the EBC certificate to be above 50%, has no threshold anymore, since it is not considered appropriate to
1064 identify pyrogenic carbonaceous materials.

1065 Several European states aligned their national biochar regulations with EBC; for instance, EBC certification is
1066 mandatory for biochar commercialization in Switzerland. Another remarkable voluntary standard for biochar
1067 quality, especially for soil application, was proposed by International Biochar Initiative (IBI); IBI is mostly
1068 adopted in the USA and Canada. As EBC, the IBI standard provides standardized characteristics for a safe BC
1069 use, reporting general criteria for soil amendment [221]. The British Biochar Quality Mandate (BQM) is a UK-
1070 specific initiative, first released in 2014, and follows an approach that specifies the conditions under which a
1071 waste-derived material can be regarded as "non-waste"; BQM also applies to biochar produced from materials
1072 not initially designated as waste [222]. While following EBC and IBI guidelines for toxicant maximum limits,
1073 BQM identifies, in addition, key biochar properties, such as porosity, water holding capacity, cation exchange
1074 capacity, bulk density, specific surface area, labile and long-term stable C, available N/P, P/K/N release
1075 dynamics. Furthermore, BQM stresses the importance of feedstock sustainability, intended as: i) monitoring
1076 biomass source; ii) evidencing that biomass was legally and sustainably managed; iii) utilization of LCA to
1077 ensure GHG emission reduction compared to alternative biomass uses [222]. BQM defines two biochar quality

1078 classes, while EBC and IBI define respectively six and three quality classes. EBC, BQM and IBI are voluntary
 1079 standards and, thus, are not recognized as cogent normative. However, they strongly contributed to the
 1080 implementation of international legislative frameworks.

1081 In the last years, some countries updated their national legislations by adding special sections dedicated to
 1082 char. For instance, in 2015 the Italian decree for soil fertilizers (D. Lgs. 29-04-2010, No. 75) was modified by
 1083 adding biochar from pyrolysis or gasification of wood materials as potential soil amendments, fixing thresholds
 1084 and minimum requirements. As IBI certification, the Italian decree defines three quality classes based on
 1085 biochar characteristics, especially carbon content. According to the German Fertilizer Ordinance, only char
 1086 from chemically untreated wood is listed as a possible input material for soil application. In Austria, it is
 1087 currently not permitted to use biochar on soils because it does not fulfil the requirements listed in the Austrian
 1088 Fertilizer Ordinance , but there is the possibility under the Austrian Fertilizer Law of achieving an individual
 1089 permission to use a fertilizer containing biochar [222].

1090 From the comparison of current legislations and standards (Table 5), it appears evident that H/C_{org} ratio
 1091 (adopted by all standards) is the key indicator of the carbonization degree and therefore of biochar stability,
 1092 and is indispensable for the determination of the C-sink value. The possibility to moisten biochar products is
 1093 forecast by some legislations (EBC, BQM, Italy) to limit the emissions of ultrafine black carbon aerosols, that
 1094 might negatively impact on global warming. The consideration of few potential feedstocks for char production
 1095 (as done in Germany) can reduce pollution risk, on one hand, but severely limits the amount of available
 1096 substrates, on the other hand.

1097 Regarding energy recovery from char, instead, at present no legislation is considering quality thresholds for
 1098 this specific end-use. Consequently, besides technological limitations (Sections 2-3), legislation barriers still
 1099 prevent full-scale application of digestate-derived biochar other than as agricultural amendment, and a further
 1100 effort is needed to overcome these constraints to widen commercial installations. The definition of international
 1101 quality standards for different BC applications appears crucial to boost a broader BC utilization as a valuable
 1102 alternative material obtained from organic wastes, reducing the environmental burdens given by traditional
 1103 sources. In contrast to biochar, to our knowledge there is no guideline or legislation for the characterization
 1104 and classification of hydrochar from digestate, neither for agricultural use nor for its use as a fuel .
 1105

1106 **Table 5.** Overview of European legislation and international voluntary standards involving biochar use in
 1107 agriculture.

Parameter	European Union (EU Reg. 2021/2088) ¹	European Union (EU Reg. 2019/1009) ²	International Biochar Initiative (IBI, 2015) ^{*,3}	European Biochar Certificate (EBC, 2022) ^{**,4}	British Biochar Quality Mandate (BQM, 2013) ^{***,5}
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Organic carbon (C _{org}) ^o	≤ 50	-	Class I: ≥ 60%; Class II: 30- 60%; Class III: 10-30%	-	≥ 10%
H/C _{org} ratio	≤ 0.7	-	≤ 0.7	< 0.7	< 0.7
PAH ₁₆ # (a)	≤ 6	≤ 4 (b)	6-300	< 4±2 (AO) (c)	< 20
PAH ₈ # (d)	-	-	-	< 1 (e)	-
Benzo[e]pyrene #	-	-	-	< 1	-
Benzo[j]fluoranthene #	-	-	-	< 1	-
PCDD/F § (e)	≤ 20	-	≤ 17	< 0.75-20	< 20
PCB #	≤ 0.8 (f)	-	0.2-1	< 0.2 (g)	< 0.5 (h)
As #	-	-	13-100	< 13 (i)	≤ 10 (j)-100 (k)
Cd #	-	-	1.4-39	< 0.7-1.5 (l)	≤ 3 (j)-39 (k)
Cr #	-	-	93-1,200	< 70-90	≤ 15 (j)-100 (k)
Co #	-	-	34-100	-	-
Cu #	-	-	143-6,000	< 70-100	≤ 40 (j)- 1,500 (k)
Pb #	-	-	121-300	< 45-120 (m)	≤ 60 (j)-500 (k)
Hg #	-	-	1-17	< 0.4 - 1 (n)	≤ 1 (j)-17 (k)
Mn #	-	-	-	-	≤ 3,500 (j)
Mo #	-	-	5-75	-	≤ 10 (j)-75 (k)
Ni #	-	-	47-420	< 25-50	≤ 10 (j)-600 (k)
Se #	-	-	2-200	-	≤ 5 (j)-100 (k)
Zn #	-	-	416-7,400	< 200-400	≤ 150 (j)- 2,800 (k)
B #	-	-	-	-	-
Cl #	≤ 30,000	-	-	-	-
Na #	-	-	-	-	-
Tl #	≤ 2 (o)	-	-	-	-

Quality classes: * Class I; Class II; Class III. Threshold values given as range of values from a number of jurisdictions. Reported toxicant levels must be below the maximum allowed thresholds established in the area of jurisdiction where biochar is produced and/or intended for use. ** F: EBC-Feed; AO: EBC-AgroOrganic; A: EBC-Agro; U: EBC-Urban; CM: EBC-ConsumerMaterials; BM: EBC-BasicMaterials. *** HG: High grade; ST: Standard.

*Feedstocks:*¹ Pyrolysis and gasification materials, recovered from waste or by-products within the meaning of Directive 2008/98/EC except for sewage sludge, industrial sludge and animal by-products. ² Pyrolysis products from a wide variety of organic materials of exclusive plant origin, untreated or treated with products included in Annex II. ³ Unprocessed and processed feedstocks (municipal solid waste may not be included). ⁴ Biomasses of different origin: agriculture, forestry and wood processing, landscape management, recycling economy, kitchen and canteen waste, food processing residues on vegetable basis, water maintenance, textiles, paper production, bio-digesters (proportion of animal source materials for biogas plants less than 40%). ⁵ Biomasses.

Unities of measure: ° = [%]; # = [mg/kg DM]; § = [ng WHO-TEQ/kg DM].

Other notes: (a) Sum of congeners PCB 28, 52, 101, 138, 153, 180 (USEPA). (b) Shall be reviewed every second year, considering the risk of accumulation due to multiple applications. (c) < 6±2.2 (A). (d) Sum of Acroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260 (EFSA). (e) < 4 for BM. For EBC-Feed: For dioxin-like PCB, a trigger value of 0.35 ng TE/kg at 88% DM applies. For PCDD/PCDF + dioxin-like PCB, the limit value is 1.25 ng TE/kg at 88% TS. For the sum 6 of dioxin-non-like PCB, a limit value of 10 µg TE/kg at 88% DM applies. (f) Expressed as WHO toxicity equivalents of PCDD/PCDF.

(g) Excluding F*. (h) mg/kg I-TEQ. (i) < 2 mg/kg, 88% DM for F. (j) HG. (k) ST. (l) < 0.8 mg/kg, 88% DM for F. (m) < 10 mg/kg, 88% DM for F. (n) < 0.1 mg/kg, 88% DM for F. (o) In case of applying more than 5 % of pyrolysis or gasification additives relative to the total fresh weight of input material.

1109 **6. Critical aspects and future research needed**

1110 As previously highlighted, at present the number of commercial applications of HTC/pyrolysis technologies
 1111 for digestate valorization is substantially negligible. According to the conducted review and to authors'
 1112 experience on the topic, the critical aspects still hindering full-scale integration of AD with
 1113 HTC/pyrolysis/gasification are summarized in Table 6, together with future research needed. Generally, the
 1114 importance of including all relevant aspects in the assessments, from substrate characteristics and techno-
 1115 economic analysis to environmental/economic impacts and social acceptance, appears unavoidable to
 1116 concretize the vast knowledge made available from scientific literature. Moreover, a careful monitoring of
 1117 digestate characteristics is mandatory, to obtain a char with standardized properties for the selected
 1118 applications; this latter point is particularly critical, as it is known that digestate has a higher variability in
 1119 characteristics compared to traditional lignocellulosic biomasses. Finally, long-term monitoring is strongly
 1120 desirable when applying char to the agricultural soil, to ascertain the absence of negative effects on
 1121 environment and health due to pollutants accumulation.

1122
 1123 **Table 6.** Advantages, critical aspects and future research needed to boost commercial application of integrated
 1124 anaerobic digestion-thermochemical valorization technologies.

1125

Advantages	Downsides	Future research needed
Faster than biological processes ^{1,2,3}	Multi-phase thermal processes with difficult scale-up ^{1,2,3}	Detailed char characterization ^{1,2,3}
Moderate ¹ to high ^{2,3} volume reduction	Raw substrate characteristics and variability impair product standardization ^{1,2,3}	Establishment of a range of variability in physicochemical parameters to tailor legislation ^{1,2,3}
Product valorization towards zero-waste concept ^{1,2,3}	Gaseous emissions require dedicated treatment ^{1,2,3}	Detailed eco-toxicologic assessments (soil application) ^{1,2,3}
Char as carbon sink for CO ₂ sequestration ^{1,2,3}	Ash content in char generates fouling, slagging and corrosion (energy recovery) ^{1,2,3}	Deepened techno-economic analyses ^{1,2,3}
Low temperature process ¹	Contamination due to organic/inorganic pollutants (soil application) ^{1,2,3}	More comprehensive utilization of LCA/LCC ^{1,2,3}
Complete pathogen elimination ^{2,3}	Absent ¹ or limited ^{2,3} legislation standards	Introduction of dedicated standards ¹
Suitable for wet substrates ¹	Corrosion-resistant reactors needed ^{1,2,3}	Adoption of standards for applications other than soil application ^{2,3}
Lower gaseous emissions than incineration ^{2,3}	High temperature and intense digestate drying required ^{2,3}	
Improved sludge dewaterability ¹	Ash melting/slagging limits temperature, which reduces energy yield ³	

1126 ¹= Hydrothermal carbonization; ²= Pyrolysis; ³= Gasification

1127

1128 7. Conclusions

1129 In this work, char production from anaerobic digestates was revised considering processing technologies, fields
1130 of application, legislative framework, energy, economic and environmental aspects. The main aim of the work
1131 was to stimulate a virtuous interconnection between thermochemical technologies and AD, providing an
1132 alternative to direct digestate utilization while minimizing environmental risks. Different digestate-derived
1133 chars were included in the review: sewage sludge, agricultural waste, organic fraction of MSW, manure. The
1134 main applications of char produced from digestates include agricultural reuse, energy recovery, contaminants
1135 adsorption, catalysts preparation and electrochemical technologies. Agricultural reuse (excluding digestate
1136 from sewage sludge) still appears the most favorable application, due to beneficial soil effects and limited
1137 downsides (mainly linked to pollutants present in the original feedstock), while energy recovery could be
1138 restricted due to low heating value and high ash content of digestate-derived chars compared to biomass-
1139 derived ones. As concerns agricultural reuse, however, the combination of digestate and its char may improve
1140 the overall benefits, given their complementary soil fertilization characteristics. HTC has an obvious advantage
1141 over pyrolysis, i.e., it can be applied to wet substrates, including digestates, without an intensive pre-treatment
1142 step (drying). A particular focus was given to energy, environmental and economic aspects, the first showing
1143 a general reduction in environmental emissions thanks to char production and utilization (especially in
1144 agriculture), while the latter still preventing in most cases full-scale applications, due to limited process
1145 efficiency compared to traditional systems (such as incineration or direct digestate reuse). The legislative
1146 framework, which has currently been established only for agricultural application and for biochars, highlighted
1147 a limited availability of international standards for char quality, most of them focusing on woody or
1148 agricultural biomass, rather than digestate. However, a positive shift is being observed by analyzing the most
1149 recent acts (such as those promoted by EU). A paradigm shift should be further encouraged at all levels (from
1150 political authorities to farmers) to include the commercial implementation of thermochemical conversion
1151 processes as possible alternative to valorize anaerobic digestates.

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Appendix

Table A1. Literature studies (2016-2022) on biochar production from anaerobic digestates using pyrolysis.

Feedstock	Pyrolysis type	Process conditions	Purpose/monitored parameters	Scale	Reference
Food waste digestate	Slow pyrolysis	400-800 °C for 2 h, 10°C/min heating rate	Pyrolysis kinetics and characterization of biochar (proximate and elemental analysis and pore properties) and gaseous products: effect of process temperature.	Lab scale	[223]
Food waste digestate	Slow pyrolysis	300-700 °C for 4 h, 10°C/min heating rate	Characterization of biochar for application as soil conditioner (germination index, mineral sorption, water retention/availability): effect of process temperature.	Lab scale	[224]
Food waste and its digestate	Slow pyrolysis	300-700 °C, 10°C/min heating rate	Characterization of biochar (proximate and elemental analysis, surface area and pore distribution) and gaseous and liquid products. Effect of process temperature and comparison between raw and digested feedstocks.	Lab scale	[225]
Food waste digestate	Slow pyrolysis	800 °C for 100 min, 5°C/min heating rate	Evaluation of the potential role of biochar as catalyst to activate peroxymonosulfate (PMS) for pollutants removal from simulated textile wastewater.	Lab scale	[226]
Food waste digestate	Intermediate pyrolysis	250-400 °C	Testing of innovative pyrolysis shaker reactor and characterization of biochar (ash content, electrical conductivity, methylene blue adsorption capacity) and effect of process temperature.	Lab scale	[227]
Municipal biowaste digestate	Slow pyrolysis	540 °C for 1 h, 10°C/min heating rate	Characterization of biochar (elemental analysis, surface area, zeta-potential, functional groups) to be used as N-doped carbons in electrochemical applications	Lab scale	[228]
Raw manure + silage + agro-industrial residues and its digestate	Slow pyrolysis	600 °C for 10 min, 20°C/min heating rate	Characterization (proximate and elemental analyses, nutrients and heavy metal content) and comparison between solid digestate and its biochar for application as soil conditioner.	Lab scale	[229]
Swine manure digestate	Slow pyrolysis	300-900 °C for 30 min, 10°C/min heating rate	Characterization of biochar (proximate and elemental analysis, heating value, trace element analysis, surface area, pore properties) for application as soil conditioner or as fuel: effect of process temperature.	Lab scale	[230]

Feedstock	Pyrolysis type	Process conditions	Purpose/monitored parameters	Scale	Reference
Raw chicken and its digestate, raw dairy manure and its digestate	Slow pyrolysis	350-550 °C for 2 h, 10°C/min heating rate	Characterization of biochar (bioavailability of phosphorous and heavy metal) for application as soil conditioner: effect of process temperature and comparison between raw and digested feedstocks.	Lab scale	[231]
Pig manure digestate	Slow pyrolysis	300-800 °C for 30-120 min, 10°C/min heating rate	Characterization of biochar (chemical composition, heating value, surface area, pore properties) for application as soil conditioner or fuel: effect of process temperature.	Lab scale	[232]
Swine manure + crop wastes + residual glycerin digestate	Not specified	Not specified	Integration between anaerobic digestion and pyrolysis for energy recovery: energy and economic analyses.	Not applicable	[233]
dairy cattle slurry + silage digestate	Slow pyrolysis	Pyrolysis at 400-600 °C with urea for 1 h, 40 °C/min heating rate	Characterization of biochar (proximate and elemental analyses, porous properties, CO ₂ uptake ability) for application as CO ₂ sorbent: effect of process temperature and urea content.	Lab scale	[177]
Cattle manure + duck slurry + agro-industrial wastes + agricultural residues digestate	Slow pyrolysis	500 °C for 1 h, 10°C/min heating rate	Characterization of biochar (chemical composition, water retention and nutrient leaching) and gaseous and liquid products, for application of biochar as soil conditioner.	Lab scale	[234]
Corn silage + manure + vegetable waste digestate	Slow pyrolysis	500 °C for 3 h, 25°C/min heating rate	Characterization of biochar (chemical composition) and application in soil as growth media in comparison with solid digestate.	Lab to pilot scale	[235]
Cocoa waste digestate and cocoa waste + cow manure digestate	Slow pyrolysis	350-500 °C, 10°C/min heating rate	Characterization of biochar (proximate and elemental analyses, heavy metals content and heating value) for applications as soil conditioner and fuel.	Lab scale	[236]
Raw roadside grass and its digestate	Slow pyrolysis	350-800 °C, 2.5-20°C/min heating rate	Characterization of biochar (thermogravimetric and kinetic analysis) for application as fuel: effect of temperature and heating rate and comparison between raw and digested feedstocks.	Lab scale	[138]
Animal slurry + food industry waste digestate	Not specified	300-1,050 °C for 1 h	Characterization of biochar for application as soil conditioner: effect of pyrolysis temperature on P speciation and P availability in the amended soil.	Lab scale	[237]

Feedstock	Pyrolysis type	Process conditions	Purpose/monitored parameters	Scale	Reference
Pig slurry + olive pomace + onion scraps + maize/ sorghum silage digestate	Slow pyrolysis	Up to 800 °C	Evaluation and modelling of pyrolysis kinetics.	Not applicable	[238]
Stillage and straw digested	Slow pyrolysis	370-450 °C for 5-45 min, 5-50°C/min heating rate	Optimization of pyrolysis operating conditions to generate a biochar for application as soil conditioner.	Pilot scale	[239]
Fruit and vegetable peels digestate	Slow pyrolysis	500 °C for 1 h, 20°C/min heating rate	Characterization of biochar (elemental analysis, surface area, pore volume): effect of sole, dual and multi-fermented digestates and evaluation of energy and economic balances.	Lab scale	[240]
Herbaceous biomass + agro-industrial residues digestate	Slow pyrolysis	500 °C for 1 h, 7°C/min heating rate	Characterization of biochar (proximate and elemental analyses, specific area, pore properties, heating value, PAH concentration) and comparison with hydrochar properties for application as soil conditioner.	Lab scale	[241]
Sewage sludge digestate	Not specified	350-550 °C for 15 min	Selection of biochar optimum dosage for improvement of biogas potential from fruit waste in anaerobic digestion.	Lab scale	[242]
Sewage sludge digestate	Not specified	550-700 °C	Characterization of biochar (proximate and elemental analyses) and evaluation of the influence of pyrolysis operating conditions on concentrations of toxic contaminants in biochar for applications as soil conditioner.	Lab scale	[243]
Sewage sludge + grease waste digestate	Slow pyrolysis	Up to 800 °C, 5-40°C/min heating rate	Characterization of biochar (proximate and elemental analyses, heating value) and kinetic analysis for application as fuel.	Lab scale	[244]
Sewage sludge digestate	Slow pyrolysis	370-550 °C for 2 h, 5°C/min heating rate	Characterization of biochar (elemental analysis) and evaluation of ammonium sorption ability from water: effect of process temperature.	Lab scale	[74]
Food waste digestate	Slow pyrolysis	400-800 °C, for 30 min, 160 °C/30 min heating rate	Characterization of biochar (proximate and elemental analyses, surface area, pore properties, heating value, heavy metals speciation) for application as fuel: effect of process temperature and optimization of parameters for integration of anaerobic digestion, hydrothermal pretreatment and pyrolysis.	Lab scale to pilot scale	[99]
Food waste digestate (and other "marginal" feedstocks)	Slow pyrolysis	550 °C for 21.5 min	Characterization of biochar (proximate and elemental analyses, heavy metals concentration) for applications as soil conditioner.	Lab scale	[188]

Feedstock	Pyrolysis type	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge and quinoa residue digestate	Slow pyrolysis	500 °C for 1 h, 10°C/min heating rate	Environmental performance assessment of AD integration with digestate pyrolysis: LCA.	Not applicable	[210]
Seaweed digestated	Not specified	700 °C	Mass and energy balances based on experimental batch results, assuming biochar applications as fuel or for anaerobic digestion enhancement.	Lab scale	[212]
Rice straw digestate	Slow pyrolysis	900 °C for 1 h, 5 °C/min heating rate	Characterization of biochar (proximate and elemental analyses, inorganics and heavy metals concentration) for applications as soil conditioner. Preliminary economic analysis.	Lab scale	[197]
Pulp and paper mill digestate	Not specified	Not specified	Environmental performance comparison between three AD+pyrolysis pathways in different regions of the world: biochar as forest soil conditioner.	Not applicable	[204]
Food waste from restaurant and OFMSW digestate	Slow pyrolysis	300-900 °C for 1 h, 10 °C/min heating rate	Characterization of biochar (proximate and elemental analysis) and phosphate sorption/desorption experiments: influence of process temperature.	Lab scale	[174]
Cattle manure digestate	Slow pyrolysis	350, 550 °C for 1h, 16-19 °C/min	Characterization of biochar (proximate and elemental analysis, image analysis), for application as soil conditioner: influence of process temperature.	Lab scale	[176]
Food waste and manure digestate	Slow pyrolysis	500, 800, 1000 °C for 1h, 5-6 °C/min	Characterization of biochar (proximate and elemental analysis, inorganics and heavy metals content, surface area) and phosphate sorption/desorption experiments: influence of process temperature.	Lab scale	[191]
Sewage sludge digestate	Slow pyrolysis	450-550 °C for 30 min, 25 °C/min heating rate	Characterization of biochar (proximate and elemental analysis, inorganics and heavy metals content, surface area) and phosphate sorption experiments: influence of process temperature.	Lab scale	[173]
Organic waste digestate	Slow pyrolysis	400, 600 °C	Characterization of hydrochar and biochars (proximate and elemental analysis, inorganic concentration, cation exchange capacity) and phosphate and ammonium adsorption/desorption tests, for application as adsorbent media.	Lab scale	[245]

Feedstock	Pyrolysis type	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge and quinoa residue digestate	Slow pyrolysis	500 °C for 1 h, 10 °C/min heating rate	Characterization of biochar (proximate and elemental analysis, inorganic and heavy metal content) and agronomic tests for application as soil conditioner.	Lab scale	[187]
Sargassum horuer digestate	Slow pyrolysis	350-550 °C, 5 °C/min heating rate	Products yields and characterization of syngas and bio-oil: influence of process temperature.	Lab scale	[129]
Raw OFMSW and its digestate		450, 550, 650 °C, 10-20 °C/min	Characterization of biochar (proximate and elemental analyses, HHV), kinetic and thermodynamic study: influence of process temperature and heating rate.	Lab scale	[137]
Corn silage + cow manure digestate	Slow pyrolysis	400-600 °C, 1-10°C/min heating rate	Characterization of hydrochars and biochars (proximate and elemental analyses, surface functional groups, pore properties, thermal stability, nutrients content, PAH concentration, wettability) for application as soil conditioner: effect of process conditions and feedstock.	Lab scale	[127]

Table A2. Literature studies (2016-2022) on hydrochar production from anaerobic digestates using hydrothermal carbonization (HTC).

Feedstock	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate	190 °C for 30 min-3 h, 10% dry matter content	Optimization of HTC operating parameters to improve hydrochar yield, HTC liquor dewaterability, methane yield, and process energy consumption.	Lab scale	[76]
Sewage sludge digestate	160-250 °C, for 30 min, 4.5% dry matter content	Effect of process temperature on hydrochars and process waters characteristics, product yields, biomethane potential and solubilization of organic carbon. Biomethane potential tests were conducted on process waters in combination with hydrochars to assess hydrochar effect on AD processes.	Lab scale	[134]
Sewage sludge digestate	250 °C, for 30 min, 2.5-30% dry matter content	Influence on solid loading on hydrochar and process water composition, products yields, solubilization of organic carbon, biomethane potential of process waters.	Lab scale	[132]

Feedstock	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate	160-250 °C, for 30 min, 2.5% dry matter content	Potential of coupling HTC with AD for sewage sludge treatment. Six scenarios were proposed to assess net waste generation, fate of nutrients, net energy production and economic benefits. Potential struvite production assessment.	Lab scale	[128]
Food waste and its digestate	175-250 °C, for 15 min-2 h, 5 °C/min heating rate	Characterization of hydrochar (proximate and elemental analyses, heating value) and HTC liquor: comparison between undigested and digested feedstocks and effect of HTC process conditions (temperature and residence time) for application as fuel.	Lab scale	[72]
Sewage sludge digestate	180 °C for 2 h, 15% dry matter content in the slurry, nitric acid as catalyst	Phosphate and ammonium recovery as struvite by acid leaching from hydrochar using process liquid from HTC as ammonium source.	Lab scale	[77]
Raw manure and its digestate	180-240 °C for 1 h, 1:3 solids-mass-to-liquid ratio, using deionized water or whey as catalyst	Characterization of hydrochar (proximate and elemental analyses, heating value) and HTC liquor for application of hydrochar as soil conditioner or fuel. Comparison between raw and digested feedstocks, and effect of process conditions on overall energy balance.	Lab scale	[87]
Organic household waste, cow manure, and energy crops digestates	170-250 °C for 2-5 h, 15% dry matter content	Characterization of hydrochar (proximate and elemental analyses, heating value, thermal stability) for application as fuel: effect of process temperature and feedstock type.	Lab scale	[67]
Maize silage digestate	180-220 °C for 30 min, 16% dry matter content	Characterization of hydrochar (proximate and elemental analyses, heating value, combustion behavior) and HTC liquor: effect of process temperature and integration between anaerobic digestion and HTC for energy recovery optimization.	Lab scale	[92]
Cow manure-based digestate	180-250 °C for 1-3 h, 8.8 % dry matter content in the cow manure-based digestate, 4 °C/min heating rate	Characterization of hydrochar (elemental analysis, pore properties, mineral and metal concentrations, phytotoxicity) for using as growing media in soilless culture systems: effect of process conditions (temperature and residence time).	Lab scale	[86]
Corn + sugar beets + beef and swine manure digestate	200 °C for 3 h, 18-20 bar, 2-3 °C/min heating rate	Characterization of hydrochar (elemental analysis, water holding capacity, cation exchange capacity, seed germination and plant growth experiments) for application as soil conditioner.	Lab scale	[182]
Corn digestate	400-600 °C, 1-10°C/min heating rate	Characterization of hydrochars and biochars (proximate and elemental analyses, surface functional groups, pore properties, thermal stability, nutrients content, PAH concentration, wettability) for application as soil conditioner: effect of process conditions and feedstock.	Lab scale	[127]

Feedstock	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate mixed with dewatered digestate	190 °C for 1-3 h, 10% dry matter content	Determination of anaerobic degradability of hydrochar and HTC liquor. Optimization of energy recovery through integration of HTC with anaerobic digestion in wastewater treatment plants.	Lab scale to full scale	[186]
Sewage sludge digestate	200 °C for 4 h, 20% dry matter content in the digestate	Techno-economic feasibility of P/N recovery from hydrochar through stripping and leaching processes. Characterization of hydrochar for application as fuel and of HTC liquor for phosphorus/ nitrogen recovery (elemental analysis, nutrient and heavy metal content).	Lab scale	[78]
Sewage sludge digestate	210-250 °C for 30 min-2 h, 25% dry matter or 15% dry matter digestate	Characterization of hydrochar and HTC liquor (proximate and elemental analyses, nutrient content, heating value, trace elements, heavy metals and pharmaceuticals) for application as soil conditioner or as fuel: effects of process parameters (temperature and residence time).	Lab scale	[79]
Swine manure digestate and rice straw digestate	190-250 °C for 4 h, 3-4 °C/min heating rate, biomass-to-water ratios 1:4 for swine manure digestate and 1:9 for rice straw digestate	Characterization of hydrochar (elemental analysis, surface area and surface functional groups, pore properties, combustion behavior) for applications as fuel and adsorbent: effect of process conditions.	Lab scale	[88]
MSW digestate	180-230 °C for 30 min-2h	Characterization of hydrochar (proximate and elemental analyses, surface area, pore properties, heating value, thermal properties) for application as fuel: effects of process parameters.	Lab scale	[120]
Sewage sludge digestate	180-240 °C for 1 h, 16.5% dry matter content, 3 °C/min heating rate; acid leaching with 1 N HCl (liquid-solid ratio 50:1, extraction time 6 h),	Characterization of hydrochar (proximate and elemental analyses, heating value) and HTC liquor (anaerobic degradability) for application as fuel and as feedstock in anaerobic digestion, respectively. Phosphorous recovery from hydrochar through acid leaching.	Lab scale	[80]
Sewage sludge digestate	Not applicable	Comparison between standalone anaerobic digestion and integration of HTC and anaerobic digestion to treat sewage sludge: techno-economic analysis and life cycle assessment.	Not applicable	[81]
Sewage sludge digestate, thickened and dewatered sludge	190-250 °C for 30-60 min, biomass-to-water ratio 0.17:1	Characterization of hydrochar (proximate and elemental analyses, heating value, nutrients and heavy metal concentrations) for application as fuel: effect of process conditions (temperature and contact time) and feedstock withdrawal point.	Lab scale	[82]
Herbaceous biomass + agro-industrial digestate	200-250 °C for 30 min-3 h, 33.5 to 43.0 °C/min heating rate	Characterization of hydrochar (proximate and elemental analyses, specific area, pore properties, heating value, PAH concentration) and comparison with biochar properties for application as soil conditioner.	Lab scale	[241]

Feedstock	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate, biosludge, fiber sludge, horse manure	180-260°C for 2 h, 10-22% dry matter content	Characterization of hydrochar (elemental analysis, chemical composition, surface area and functionality, adsorption capacity) for application as water phase adsorbent: effect of process conditions and feedstock type.	Lab scale	[73]
Agricultural biomass digestate, green waste, food waste, MSW	Not applicable	HTC of different wastes: life cycle assessment and evaluation of the environmental performance at commercial scale.	Not applicable	[68]
Agricultural residue digestate, sewage sludge digestate, MSW digestate, vegetable, garden, fruit waste digestate	150-250°C for 1 h, 10-30% dry matter content	Characterization of hydrochar (proximate and elemental analyses, heating value, metal and inorganics concentration) and HTC liquor (methane yield) as fuel and as feedstock in anaerobic digestion, respectively: effect of process temperature and feedstock type.	Lab scale	[69]
Agricultural residues digestate and MSW digestate	200°C for 4.5 h	Characterization of hydrochar (proximate and elemental analyses, pore properties, thermal behavior) for application as fuel: effect of digestate type.	Lab scale	[70]
Raw OFMSW and its digestate	200-300 °C for 30 min-2h, 27% dry matter content	Characterization of hydrochar (proximate and elemental analyses, heating value) and HTC liquor (TOC, TN, primary compounds) for application as fuel: effect of process conditions.	Lab scale	[71]
Lignocellulosic biomass digestate	240°C, biomass-to-water ratio 1:6, 7°C/min heating rate	Characterization of hydrochar (proximate and elemental analyses, heating value) for application as fuel: comparison with torrefaction.	Lab scale to pilot scale	[89]
Straw digestate and poplar wood chips	210-250 °C for 6 h, 10% dry matter content, 1.7 °C/ min heating rate	Characterization of hydrochars (elemental analysis, carbon stability, water holding capacity) for application as soil conditioner: effect of process parameters, post-treatments.	Lab scale	[91]
OFMSW digestate	200 °C for 3 h	Co-composting of OFMSW digestate and its hydrochar mixed in different proportions. Design and assembly of bench-scale batch bioreactors.	Lab scale to pilot scale	[66]
Food wastes + agricultural wastes digestate	180-230°C for 60-390 min, pH 3.3-8	Characterization of hydrochars (elemental analysis, carbon, phosphorous and nitrogen concentrations) for application as soil conditioner.	Lab scale	[190]
Raw corn stalk and corn stalk digestate	190-240 °C for 30 min, biomass-to-water ratio 1:10	Characterization of hydrochars (elemental analysis, fiber composition, heating value, combustion behavior and kinetics) for application as fuel: effect of feedstocks and process temperature.	Lab scale	[93]
Dairy sludge digestate	180, 210, 240°C, for 30 min	Characterization of HTC liquor and hydrochar (proximate and elemental analyses, HHV) for application as fuel.	Lab scale	[142]

Feedstock	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate	180-200-230 °C for 15-30-60-120 min	Characterization of hydrochar (elemental analysis, HHV, dewatering properties) while varying process temperature and retention time for application as fuel and to optimize water recovery.	Lab scale	[179]
Municipal yard waste digestate	180-200°C for 6 h	Characterization of HTC liquor and hydrochar (proximate and elemental analysis, HHV, structural and combustion properties) for application as fuel.	Lab scale	[181]
Cow manure and energy crops digestate	210 °C for 30 min and 5 h	Characterization of HTC liquor and hydrochar (proximate and ultimate analysis, HHV, inorganics and heavy metal concentration, slagging and fouling indexes) for application as fuel and P recovery from ashes. Influence of process residence time.	Lab scale	[133]
Cattle manure and cheese whey digestate	Data from literature	Energy assessment of HTC integration with AD.	Not applicable	[214]
Agricultural waste digestate	200 °C for 4.5 h	Characterization of hydrochar (proximate analysis and HHV) for preliminary evaluation of HTC integration with AD.	Lab scale to commercial scale	[215]
Sewage sludge digestate	200-220-240 °C for 1 h	Characterization of hydrochars (proximate and elemental analysis, metal concentrations) and HTC liquor. Influence of process temperature.	Lab scale	[178]
Organic waste digestate	250 °C for 1h	Characterization of hydrochar and biochars (proximate and elemental analysis, inorganics concentration, cation exchange capacity) and phosphate and ammonium adsorption/desorption tests, for application as adsorbent media.	Lab scale	[245]
OFMSW digestate	180-250 °C, 6 h	Characterization of hydrochar (elemental analysis and HHV) and preliminary techno-economic assessments of integrating AD with HTC.	Lab scale	[198]
OFMSW digestate	180-250 °C for 2-6 h	Characterization of hydrochar (proximate and elemental analyses) and HTC gas, and evaluation of the effects of process water recycle to HTC on hydrochar and HTC gas properties.	Lab scale	[180]

Table A3. Literature studies (2016-2022) on biochar production from anaerobic digestates using processes other than simple pyrolysis and HTC.

Feedstock	Process(es)	Process conditions	Purpose/monitored parameters	Scale	Reference
Manure and straw digestate	Gasification	Air gasification in a downdraft fixed bed gasifier at 600-800 °C, air equivalence ratio of 0.25-0.30	Characterization of gaseous products and biochar (elemental analysis, inorganics and metal content) for application as soil conditioner.	Lab scale	[152]
Corn straw, sludge and cattle manure digestate	Co-gasification with catalyst	Co-gasification with lignite at 650-950 °C in a downdraft fixed bed gasifier, using a steel slag as a catalyst	Characterization of gaseous products and biochar (surface area, pore properties, functional groups): effect of temperature and co-substrate.	Lab scale	[148]
Food and market wastes digestate	Co-pyrolysis	Co-pyrolysis with banana peduncles and sewage sludge at 450°C and 650°C, for 5 min	Characterization of biochar for application as soil conditioner: effect of process temperature and co-substrates blends.	Lab scale	[159]
Municipal solid waste digestate	Co-pyrolysis	Co-pyrolysis with microalgae at 800°C	Evaluation of gas composition, thermal behavior and kinetics during co-pyrolysis: effect of co-substrates blends.	Lab scale	[158]
Food waste digestate	Microwave-assisted Hydrothermal Carbonization (MHTC) + Pyrolysis	MHTC (160-260°C, 20-120 min) + Pyrolysis (300-900°C, under N ₂ , 10-15-20-25 °C/min)	Characterization (proximate and ultimate analysis) of MHTC chars and analysis of pyrolysis kinetics for application as fuel.	Lab scale	[144]
Food waste digestate	Autogenic pressure carbonization (APC)	APC (300-500-700 °C, for 30 min, 5°C/min heating rate)	Characterization of biochar (elemental and proximate analyses, nitrogen content heating value), bio-oil and syngas for application as fuels.	Food waste digestate	[145]
Sewage sludge digestate	Co-pyrolysis	Co-pyrolysis with lignocellulosic biomass at 500°C	Characterization of gas (composition), HTC liquor (elemental analysis, heating value), and biochar (elemental and proximate analyses, heating value, char stability) for applications as fuel or soil conditioner: effect of co-substrates blends.	Lab scale	[160]
Not available	Gasification	Gasification at 730-745-760 °C; 50 Nm ³ /h airflow rate	Characterization of syngas for application as fuel.	Pilot scale	[149]
Sewage sludge digestate	Gasification	Not applicable	Techno-economic evaluation of coupling biomethanation with digestate gasification for wastewater industry.	Not applicable	[150]

Feedstock	Process(es)	Process conditions	Purpose/monitored parameters	Scale	Reference
Food waste plastic-containing digestate	Gasification	Gasification at 800 °C, 60 mL/min N ₂ flow rate	AD performance, microbial communities and energy balance of a combined AD-gasification system where char is recycled to AD and CO ₂ from biogas is used as carrier gas from gasification.	Lab scale	[151]
Not available	Co-gasification	Co-gasification with lignite at 700-950°C	Characterization of syngas and char and investigation of kinetics.	Lab scale	[153]
Agricultural wastes digestate	Gasification	Gasification at 750-850°C, air equivalent ratio 0.14-0.34	Characterization of syngas and char (proximate and elemental analyses, inorganic and heavy metal concentrations, recalcitrance index) for use as soil conditioner.	Lab scale	[154]
Sewage sludge digestate	Gasification and co-gasification	Gasification and co-gasification at 800°C	Techno-economic evaluation of AD integration with gasification, compared to coprocessing of sludge with biomass and animal wastes.	Not applicable	[155]
Not available	Gasification	Gasification at 1000°C	Techno-economic evaluation of AD integration with gasification: comparison with the same system fed with lignocellulosic biomass.	Not applicable	[156]
Swine manure digestate	Co-pyrolysis	Co-pyrolysis with microalgae at 800°C, using Argon as purge gas	Evaluation of gas composition, thermal behavior and kinetics during co-pyrolysis: effect of co-substrates blends.	Lab scale	[157]
Sewage sludge digestate	Co-pyrolysis with catalyst	Co-pyrolysis with cedar wood and algal biomass, at 500°C with/without the catalyst Zeolite ZSM5	Evaluation of kinetics during co-pyrolysis: effect of co-substrates blends, and presence of a catalyst.	Lab scale	[147]
Sewage sludge digestate	Pyrolysis + chemical modification	Slow pyrolysis at 350 °C for 15 min + modification with H ₂ O ₂ or KOH	Characterization and sorption tests of raw and modified biochars for application as adsorbent in the water phase towards As(III).	Lab scale	[164]
Swine manure digestate	Pyrolysis + chemical modification	Oxygen-limiting pyrolysis at 550°C for 2 h + modification with HCl, NH ₃ ·H ₂ O and KMnO ₄ .	Characterization and sorption tests of raw and modified biochars for application as adsorbent in the water phase towards Cu(II), Zn(II), As(III) and antibiotics.	Lab scale	[169]
Sewage sludge digestate	Pyrolysis + chemical modification	Slow pyrolysis at 350 °C for 15 min + chemical treatment for 2 h with 10% H ₂ O ₂ solution or with 2M KOH solution	Characterization and sorption tests of raw and modified biochars for application as adsorbent in the water phase towards As(III), As(V), Cd(II): effect of washing procedure.	Lab scale	[163]

Feedstock	Process(es)	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate and OFMSW	Pyrolysis + chemical modification	Pyrolysis at 350 and 400°C + chemical modification with potassium hydroxide (KOH) and hydrogen peroxide (H ₂ O ₂)	Characterization and sorption tests of raw and modified biochars for application as adsorbent in the water phase towards Pb(II): effect of washing procedure.	Lab scale	[162]
Sewage sludge digestate	Pyrolysis + magnetic activation	Digestate pre-treated by the PDS-ZVI system for dewatering + pyrolysis at 600–1000 °C for 90 min under N ₂ atmosphere.	Characterization and performance tests of raw and modified biochars for application as catalyst for peroxydisulfate (PDS) activation to degrade sulfamethazine: effect of process temperature.	Lab scale	[170]
Cow manure + mixture of industrial food wastes digestate	Pyrolysis + magnetic activation	Commercial-scale thermochemical processing system (800°C, 4 h, airflow input).	Characterization of biochar (elemental and proximate analyses, surface area, iron distribution) for electrochemical applications or as adsorbent.	Commercial scale	[100]
Rice straw digestate	Pyrolysis + anchoring of biochar with Cu nanoparticles (NPs)	Pyrolysis at 500°C for 2 h under N ₂ + Treatment with 0.1 M HCl solution for 6 h + Deposition on the biochar of Cu NPs (synthesized by the reduction of CuCl ₂ ·2H ₂ O using NaBH ₄)	Characterization of biochar-Cu NP composite and adsorption-degradation tests for removal of tetracycline from the water phase: effect of H ₂ O ₂ activation.	Lab scale	[171]
Wheat straw digestate	HTC + pyrolysis + anchoring of biochar with Cu nanoparticles (NPs)	Hydrothermal carbonization (180°C, 6 h) + Pyrolysis (500 °C, 2 h under N ₂ flow rate of 400 mL/min) + Deposition on the biochar of Cu NPs	Characterization of Cu NPs/HDPC (hydrochar-derived pyrolysis char) and adsorption-degradation tests for removal of octocrylene from the water phase: effect of H ₂ O ₂ activation.	Lab scale	[172]
Cattle manure digestate	HTC + supercritical water gasification (SCWG)	HTC at 180-250°C, for 3 h + SCWG at 500- 600 °C, 250 bar, 30 s residence time	Performance evaluation of coupling HTC and SCWG to produce hydrochar and H ₂ -rich gas for application as fuel.	Lab scale	[141]
Sewage sludge digestate	CO ₂ -assisted pyrolysis with catalyst	One stage and two stages pyrolysis using a fixed-bed tubular reactor in the presence of N ₂ or CO ₂	Performance evaluation of using CO ₂ as a reactive gas medium in digestate pyrolysis and a steel slag as a catalyst for controlling carbon distribution in the three pyrolysis products.	Lab scale	[146]
Swine manure digestate	Pyrolysis/HTC + chemical modification	Pyrolysis: 550 °C, 2 h, 10 °C/min heating rate. HTC: 235 °C for 5 h. Chemical modification by soaking chars in FeCl ₃ solution for 24 h.	Characterization of biochars and hydrochars to promote anaerobic digestion. Comparison between biochar and Fe-impregnated biochar.	Lab scale	[184]

Feedstock	Process(es)	Process conditions	Purpose/monitored parameters	Scale	Reference
Sewage sludge digestate	Co-HTC	Hydrothermal carbonization (200-280°C, 1-5 h) with cow dung	Characterization of hydrochar (elemental analysis, heating value) and HTC liquor for application as solid fuel. Effect of process conditions and co-substrates blends.	Lab scale	[161]
Digestate from corn silage and cow manure	HTC + Pyrolysis	HTC at 180, 220 and 260 °C for 1 h + Pyrolysis at 400, 600 and 800 °C for 30 minutes	Characterization of pyro-HTC chars (elemental analysis, surface area, pore properties, PAH and phenolic content) for application as soil conditioner: effect of process conditions.	Lab scale	[139]
Grass silage digestate	Microwave HTC	Microwave (2.45 GHz, 1600 W) assisted low-temperature hydrothermal treatment (MLHT; temperature 100 – 180 °C)	Characterization of hydrochar (proximate and elemental analyses, heating value, surface area and properties) and HTC liquor for application as fuel: effect of acid pretreatment of AD feedstock.	Lab scale	[143]
Maize silage + liquid cattle manure + grass silage digestate	HTC + chemical activation	HTC at 190, 220, and 250 °C for 3 hours + phosphorous leaching (H ₂ SO ₄) + activation process with KOH	Evaluation of phosphate recovery through HTC - acid leaching and subsequent adsorption tests towards methylene blue on acid-leached and untreated hydrochars, chemically activated with KOH. Effect of process temperature.	Lab scale	[167]
Pig manure digestate	Co-pyrolysis	Co-pyrolysis with milk thistle	Characterization of biochar (proximate and elemental analyses, HHV) and energy balance for application as fuel.	Lab scale	[211]
Sewage sludge digestate	Co-pyrolysis	Co-pyrolysis of sewage sludge digestate and wood at 450-650 °C	Environmental performance assessment of sewage sludge digestate management including pyrolysis: LCA.	Not applicable	[213]
40% corn silage, 30% grass silage and 30% cattle manure	HTC + chemical activation	HTC at varying temperature (190-250°C), residence time (3 and 6 h), and pH (5 and 7) + activation with KOH (600°C for 2 h, N ₂)	Characterization of hydrochar (proximate and elemental analyses, surface area and pore properties) and adsorption capacity for removal of CO ₂ in the gas phase: effect of process conditions.	Lab scale	[165]
OFMSW digestate	HTC + Chemical activation	HTC (250°C, 1h, pH = 8.3 and pH = 3) + activation with KOH	Characterization of hydrochars (elemental analysis, surface area, pore properties) for application as adsorbent in the water phase towards phosphate, for the future development of phosphate-enriched carbons to be used thereafter in soil applications.	Lab scale	[166]

Feedstock	Process(es)	Process conditions	Purpose/monitored parameters	Scale	Reference
Fresh and dried cattail digested at the lab scale	HTC + chemical activation	HTC (250°C for 4 h) + activation (Na ₂ CO ₃ , NaHCO ₃ and NaCl at 900°C for 1 h)	Characterization of hydrochars (elemental analysis, surface area, pore properties) for application as adsorbent in the gas-phase and in the water-phase.	Lab scale	[168]
Cow dung digestate	HTC+pyrolysis	Hydrothermal carbonization (190°C, 30 min) + pyrolysis (900 °C; 10-15-20 °C/min heating rate)	Investigation on kinetic and thermodynamic aspects of HTC combination with pyrolysis.	Lab scale	[140]

