

A review on the interplay between bioeconomy and soil organic carbon stocks maintenance.

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Systematic Review

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A review on the interplay between bioeconomy and soil organic carbon stocks maintenance.

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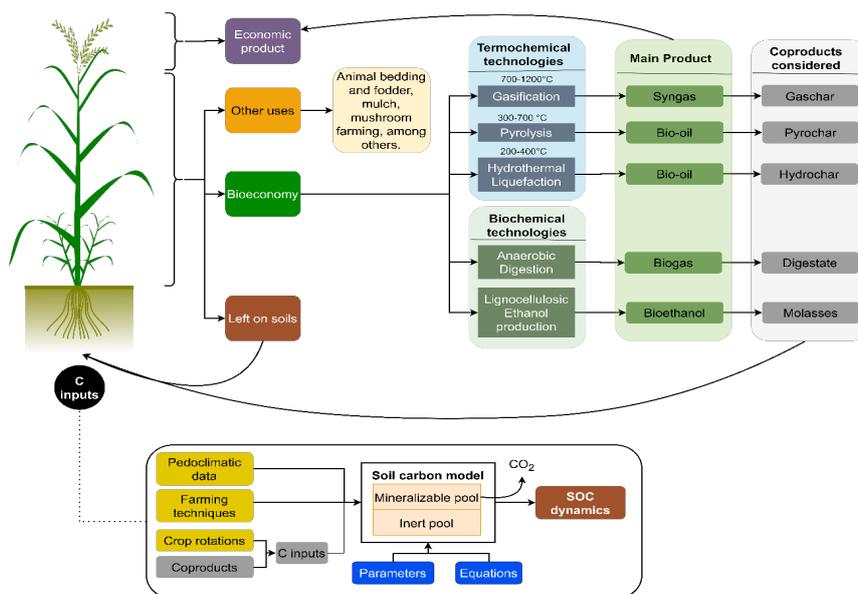
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Abstract

Crop residues potential for the bioeconomy is often limited under the basis of avoiding prospective soil organic carbon depletion. However, when processed in the bioeconomy the biomass carbon can be partially recovered in a stabilized degradation-resistant state in the coproducts. This study interlinks the theoretical basis between the coproducts' characteristics and behavior in soils and the use of soil models to predict the effect of replacing crop residues with bioeconomy coproducts. Stemming from a revision of over 600 datasets we defined conversion coefficients from biomass C to coproduct (C_c) and their inherent recalcitrance in soils (C_R) for pyrolysis (C_c : 48%, C_R : 95%) and gasification biochar (C_c : 20%, C_R : 95%), hydrochar (C_c : 31%, C_R : 83%), digestate (C_c : 36%, C_R : 68%) and lignocellulosic bioethanol solid (C_c : 44%, C_R : 42%) and liquid (C_c : 21%, C_R : 46%) coproducts. Different approaches to incorporate stabilized organic matter in soil models were investigated as well as the data requirements of a variety of soil models to set the basis for model adaptation in a dynamic harvest – return of C to explore future scenarios involving the coproducts return as a strategy to increase the bioeconomy feedstock provision while ensuring the maintenance of SOC stocks.



Graphical Abstract

29 **Keywords:** *bioeconomy, soil organic carbon, biochar, digestate, lignocellulosic bioethanol,*
30 *recalcitrance, soil model*

31 **Abbreviations**

| | |
|---|---|
| IPCC: Intergovernmental Panel for Climate Change | GHG: Greenhouse gases |
| HTL: Hydrothermal liquefaction | AD: Anaerobic Digestion |
| HTC: Hydrothermal carbonization | SOM: Soil Organic Matter |
| HTG: Hydrothermal gasification | SOC: Soil Organic Carbon |
| 2GEtOH: Lignocellulosic ethanol | Cc: Carbon conversion |
| BpC: Coproduct carbon content | Cr: Carbon recalcitrance |
| BmC: Initial carbon in the biomass (DM) | DM: Dry Matter |
| BMP: Biomethane potential | BpY: Coproduct yield |
| EOM: Exogenous organic matter | C _L : Carbon labile fraction |
| SHF: Separate hydrolysis and fermentation | MRT: Mean residence time |
| SSF: Simultaneous saccharification and fermentation | TS: thin stillage |
| CDS: Condensed distiller's solubles | WDG: Wet distiller's grain |
| DDGS: Dried distiller's grain with solubles | Y _{bc} : Yield biochar |
| NFWR: Non-fermentable wheat residue | FOM: Fresh Organic Matter |
| DNDC: DeNitrification DeComposition model | BIO: Microbial biomass |
| EPIC: Environmental Policy Integrated Climate model | IOM: Inert Organic Matter |
| APSIM: Agricultural production systems simulator | CA: Active Carbon pool |
| STICS: Simulateur multIdisciplinaire pour les Cultures Standard | CS: Stable Carbon pool |
| CANDY: Carbon and Nitrogen Dynamics model | h : humification coefficient |
| RothC: Rothamsted carbon model | k: decay rate |
| ICBM: Introductory Carbon Balance Model | PE: Priming effect |
| NCSOIL: Nitrogen and carbon transformation in soil | Db: Bulk density |
| DPM: Decomposable Plant Material | C _{DG} : Carbon in Digestate |
| RPM: Resistant Plant Material | C _{BG} : Carbon in biogas |
| HUM: Humified organic matter | FBC: Fresh biochar |
| NPP: Net primary production | RBC: Resistant biochar |
| IROC: indicator of residual organic carbon | C _m : Carbon mineralized |
| CEC: Cation exchange capacity | UpH: upper oxisol soil pH |
| η: substrate use efficiency coefficient in CANDY | LpH: lower oxisol soil pH |
| CFM: Carbon in Fresh matter | SS: sewage sludge |
| C _{runoff} : Carbon los by runoff effects | |
| C _{down} : Carbon transported from topsoil to subsoil | |
| C _{retained} : Carbon retained in soil after application | |
| C _{remain} : Carbon remaining in soil at a given time | |
| MSW: Municipal solid wastes | |
| PCM: Pelletized cattle manure | |
| RMSE: root mean square error | |
| CR: Carbon recalcitrant fraction | |

32

33

34 **1. INTRODUCTION**

35 In front of the urgency and necessity to transit towards economies using low fossil carbon, as
36 called for in the Paris Agreement [1] and illustrated by the IPCC [2], the European Union is
37 betting on bioeconomy and circular economy as strategies to reach climate neutrality by 2050
38 [3].

39 In its latest bioeconomy strategy [4], the European Commission defined bioeconomy as
40 covering “all sectors and systems that rely on biological resources [...], their functions and
41 principles. It includes and interlinks land and marine ecosystems and the services they provide;
42 all primary production sectors that use and produce biological resources, i.e., agriculture,
43 forestry, fisheries and aquaculture; and all economic and industrial sectors that use biological
44 resources and processes to produce food, feed, bio-based products, energy and services. [...] health
45 biotechnology and biological medicines are not included in the bioeconomy definition”.

46 The biomass used as feedstock for the bioeconomy processes can be derived from agriculture
47 residues, wastes, and byproducts from biomass processing. Byproducts are defined as the
48 wastes resulting from a process or chemical reaction. They are not the principal product or
49 service, sometimes they could be toxic for the ecosystems, or on the opposite, they can be
50 valorized through additional processing. Valorized byproducts are labeled as coproducts [5].

51 Although supplying the most accessible source of renewable carbon, the bioeconomy implies
52 many challenges in particular those posed by tapping into the potential of a large diversity of
53 renewable biological resources (biodiversity, land use changes, ecosystem services) [6], which
54 may disturb the nutrient cycle in the biosphere. Soils play a crucial role in food security,
55 ecosystem services, and climate change mitigation [7]. Among the diverse biomass available
56 for bioeconomy, crop residues play a key role because of their wide availability, low costs or
57 interaction with food security and fast generation [8]. However, crop residues apport C to
58 maintain the soil levels balance and excessive removal may potentially deplete SOC stocks [9].
59 Various studies have proposed limiting removal rates of crop residues in the range 15% - 60%,
60 varying for different biomass, as a mean to ensure the SOC stocks maintenance [10]–[14].

61 Yet, these removal rates have been proposed in a context without considering the actual usage
62 of the crop residues and the potential C returns to soils. Coproducts from bioeconomy
63 processes are rich in stabilized C, which could be returned to soils as means to maintain the
64 SOC balance. The coproducts return to soils may allow to export higher amounts of biomass
65 for the bioeconomy than the rates mentioned above [3], [15].

66 The purpose of this review is to set the theoretical fundamentals to challenge the limitations
67 placed on crop residues mobilization in the context soil organic carbon preservation. It intends
68 to support the vision that the amount of biomass available to supply the bioeconomy with
69 renewable carbon directly depends upon how the biomass is converted and used.

70 To this end, key pathways to convert crop residues into products and services of the
71 bioeconomy are here reviewed, as well as their implications in terms of influence on the soil
72 organic carbon (SOC) equilibrium. Section 2 describes the scope and methodology followed,
73 including an explanation of the variables influencing the SOC dynamics from bioeconomy
74 coproducts application in soils. Section 3 details the operating conditions and overall carbon

75 balance involved in these pathways, the various products and coproducts generated, and the
76 quality or recalcitrance of the carbon in the coproducts that can be returned to soils. The
77 Section 4 presents an overview of the tools used to simulate the long-term changes in SOC and
78 the data they require. Finally, we explore perspectives on the integration of the bioeconomy
79 coproducts as soil amendments within existing SOC development simulation tools.

80 **2. Review Scope and Methodology**

81 **2.1 Bioeconomy technologies included and terminology**

82 Here we review the technical aspects, operating conditions, coproducts C balance and inherent
83 stability (recalcitrance) of five bioeconomy technologies seen as the most common and
84 promising processes using crop residues for the provision of renewable gas and liquid
85 hydrocarbons and involving the possibility of a carbon return to soils through the coproducts .
86 Overall, 137 different scientific papers, industrial data, and grey literature were reviewed, to
87 produce a total of 620 data records. The key bioeconomy technologies considered include
88 pyrolysis (main product: bio-oil; coproduct: pyrochar), gasification (main product: syngas;
89 coproduct: gaschar), hydrothermal liquefaction (HTL) (main product: bio-oil; coproduct:
90 hydrochar), anaerobic digestion (AD) (main product: biogas; coproduct: digestate) and
91 lignocellulosic ethanol (2GEtOH) production (main product: bioethanol; coproduct: molasses).
92 Bioethanol molasses here refer to the residual liquid fraction obtained from the ethanol
93 production process, mainly composed of hydrolyzed C5 and unconverted C6 sugars.

94 It should be noted that the co-product from pyrolysis is typically referred to as biochar, yet,
95 this term is more and more expanded to encompass a large variety of char originating from
96 biomass, either from a pyrolysis or gasification process [16]. To avoid confusion, the term
97 pyrochar is therefore used herein to designate the specific char stemming from the pyrolysis
98 process. Moreover, it should be highlighted that the focus is here on the coproducts that can
99 be returned to soils. Yet, these technologies also generate additional coproducts not
100 considered within this review. For instance, pyrolysis generates a non-compressible gas
101 coproduct that can be used for energy, and the bio-oil can be fractionated in a heavy (oil) and
102 light (vinegar) phase having biofungic properties [17]. Similarly, gasification generates tar, a
103 mixture of organic compounds condensable at room temperature that can affect the gas
104 quality and equipment efficiency [18], and ashes with very low C content that are typically
105 disposed in landfills [19]). Besides molasses, 2GEtOH also produces a solid fraction (separated
106 from the molasses) that is mainly composed of fibers (lignin and unhydrolyzed sugars) and
107 essentially used for energy (and to some extent for ruminant feed) (ref.).

108 *2.2 Carbon flows from crop residues to coproducts from bioeconomy technologies*

109 To understand the C flow from different crop residues to the coproducts, we used a mass
110 balance approach based on a non-exhaustive literature revision (until July 2021) of reported
111 yields and composition (i.e., C content) of the coproducts per technology. Only crop residues
112 were included as feedstocks to the extent possible, and when not possible due to data scarcity,
113 the most representative proxies (wood and grass) were considered. If the results were present
114 in more than one publication (consecutive publications for extended experiments), we used
115 the most actual and complete study. This approach resulted in the revision of 171 datasets for
116 all the technologies (pyrolysis:44, gasification:25, HTL:31, AD:68, 2GEtOH:3), stemming from

117 73 studies. The fraction of C from the original biomass remaining in the coproduct, hereafter
118 referred to as carbon conversion (Cc), was determined using Eq 1 for the pyrolysis, gasification,
119 HTL, and 2GETOH production pathways.

$$120 \quad Cc = \frac{BpY * BpC}{BmC} \quad (\text{Eq 1})$$

121 where BpY is the coproduct yield (kg Bp kg biomass⁻¹), BpC is the carbon content in the
122 coproduct (kgC kgBp⁻¹), and BmC is the initial carbon content in the biomass (kgC kg biomass⁻¹).

123 The AD technology Cc was determined using a compilation of the biomethane potential (BMP)
124 values reported for different feedstocks and process conditions. BMP is defined as the specific
125 methane production from a given substrate under specific digestion conditions [20]. Details on
126 these calculations are in the supporting database.

127 2.3 Assessing coproducts recalcitrance

128 The coproducts considered herein all result from processes aiming to convert biomass' easily
129 degradable C into bioeconomy products. As a result, the C remaining in these coproducts tend
130 to be more resistant to microbial degradation than the raw feedstock it stems from, when
131 applied as soil exogenous organic matter (EOM). In soils, the fraction of carbon degraded and
132 emitted as CO₂ (mineralization) is known as *labile* (C_L), while the stable fraction that remains
133 undegraded and stored in the soil through the humification process is regarded as *recalcitrant*
134 (C_R).

135 Understanding the stability of each co-product and its effects on soils is of major importance in
136 climate, environmental and agronomical sciences, yet it remains unclear, and further
137 investigation is required. Part of the reason why it has been poorly understood is because of
138 the different conditions between studies: different properties of the wide variety of
139 feedstocks, diverse process conditions, and diverse methods to measuring and modeling the
140 data, resulting in a wide range of estimated stability values [21]. The methods include the
141 analysis of the carbon structure, carbon oxidation resistance using chemical aging tests,
142 thermal degradation, proximate analysis, laboratory incubation studies, field trial assays, and
143 modeling [21], [22].

144 Naisse et al. [23] found that the C stability of biochar and hydrochar cannot be reliably
145 characterized by chemical reactivity, while incubation and field trials experiments tend to
146 show the most realistic results [22]. Although most abovementioned methods are less reliable
147 than incubations and field trials, they are frequently used as proxies to estimate the C
148 degradation of products due to their simplicity and time of execution [24].

149 Common drawbacks of the laboratory incubations and field trials assays are the difficulties of
150 mimicking actual conditions in controlled environments or proper monitoring in natural fields.
151 Short-term laboratory incubations measure the fluxes of CO₂ from the studied product alone or
152 in a mixture with soil under laboratory conditions. This method allows understanding the
153 effect of different parameters in the degradation process but fails to replicate the interactions
154 happening in real environments [21], [25]. Field trials are long-term studies (>2-3 years) that
155 help to determine the degradation of the coproducts applied in actual fields. The drawback of
156 this method is the difficulty to separate the CO₂ fluxes from other sources than the coproduct

157 and other carbon losses resulting from soil erosion, runoff water, and other environmental
158 processes. Besides, the results tend to be explicit for the studied place, and it requires long
159 periods. The most prolonged field trial for biochar lasted only 8.5 years [26] compared to the
160 hundreds of years of expected stability. Some authors consider that incubation experiments
161 are weak to determine the long-term C stability, especially for chars, and suggest that multi-
162 carbon compartment modeling (Eq. 2 a,b, Eq. 3) would allow a better understanding of the
163 long-term recalcitrance. However, there is general agreement that incubation studies provide
164 the most faithful proportion of C_L [27] which is key to understanding the C_R fraction behavior
165 and thus is the most popular method.

$$166 \quad C_m = C_L(1 - e^{-k_L t}) + C_R(1 - e^{-k_R t}) \quad (\text{Eq. 2a})$$

$$167 \quad C_{\text{remain}} = C_L * \exp(-k_L * t) + C_R * \exp(-k_R * t) \quad (\text{Eq. 2b})$$

168 Where C_m is the C mineralized at time t , C_{remain} is the C remaining at time t , C_L and C_R represent
169 the labile and recalcitrant C pools, respectively, and k_L and k_R represent the mineralization
170 rates of labile and recalcitrant pools, respectively. The mean residence time (MRT) of the
171 organic matter in soils is defined as the inverse of the decay (or mineralization) rate [28].

$$172 \quad \text{MRT} = 1/k$$

173 We reviewed the available literature regarding the recalcitrance of the studied coproducts,
174 considering only incubation, field trials, and modeling studies. We included all the available
175 studies per technology, until September 2020, without differentiating by the duration or type
176 of soil used in the assays. If results from the same experiment were in more than one
177 publication, we selected only the data for the studies with the lengthiest duration. This
178 selection yielded a database including 87 studies with 449 data records (pyrolysis:144,
179 gasification:36, HTL:104, AD:114, 2GEtOH:51) after removing outliers. We recorded the
180 amount of C remaining after the assay as the C_R fraction of the coproduct reported by each
181 study. MRT values are presented as conveyed by the original authors or as calculated in
182 previous publications, and when not reported it was not calculated (unless explained). The C_R
183 was determined as the average recalcitrance per group for an average incubation time, after
184 removing outliers.

185 The complete database with all the records for C_c and C_R data is available in
186 doi.org/10.48531/JBRU.CALMIP/WYWKIQ

187 *2.4 Review of SOC models*

188 To understand the ability to link the soil application of the bioeconomy coproducts with the
189 long-term SOC stocks, we reviewed the characteristics, data inputs, outputs, and applicability
190 of **12** different soil models to assess the SOC changes in croplands. We included the most used
191 and cited models in the literature reviews and simulations across different pedoclimatic
192 systems and included in the FACCE-JPI project CN-MIP ([https://project-wheel.faccejpi.net/cn-](https://project-wheel.faccejpi.net/cn-mip/)
193 [mip/](https://project-wheel.faccejpi.net/cn-mip/)), namely CENTURY, Daycent, DNDC (DeNitrification DeComposition), EPIC (Environmental
194 Policy Integrated Climate), Daisy, APSIM (Agricultural production systems simulator), STICS
195 (Simulateur multIdisciplinaire pour les Cultures Standard), CANDY (Carbon and Nitrogen
196 Dynamics), ORCHIDEE, RothC (Rothamsted carbon model), AMG, CTOOL (Table S2). This review

197 permitted to understand the requirements and capabilities of modeling the SOC dynamics
198 resulting from the interchange of crop residues with the bioeconomy coproducts, and to
199 define the most promising models for including the coproducts as soil EOMs.

200 **3. Bioeconomy**

201 **3.1 Bioeconomy conversion pathways description**

202 The technologies covered in this study are well explored in previous separate reviews
203 regarding the process conditions and products characteristics. The goal of our study is to
204 compile all the key aspects of each technology to understand the variability in the composition
205 of the coproducts and their behavior in soils, to clarify the interplay between bioeconomy
206 coproducts and soil carbon dynamics.

207 **3.1.1 Pyrolysis**

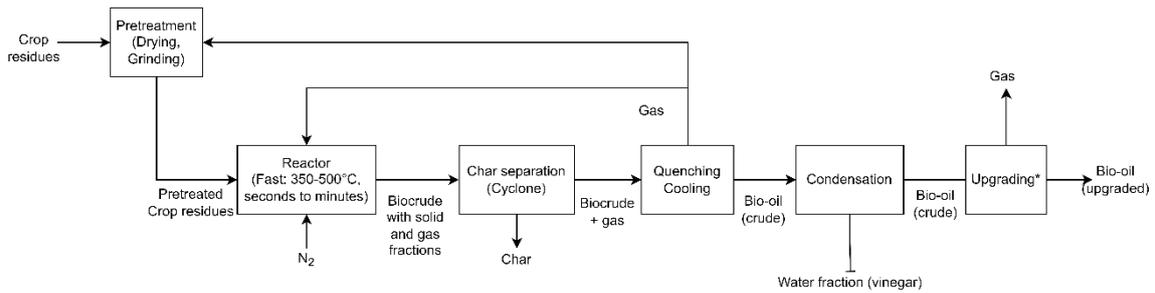
208 Pyrolysis is a thermal process where biomass is decomposed in an oxygen-free environment, in
209 a range of temperatures from 300 to 700°C, to produce bio-oil, gas, and biochar hereon
210 referred as pyrochar (Fig.1) [29], [30].

211 Bio-oil, which releases lower amounts of SO_x and NO_x than fossil fuels, can be combusted in
212 turbines for power and heat generation or upgraded to be used as transportation fuels [31].
213 Biochar can be used for pollutants sorption, as a precursor for activated carbon production, as
214 negative emissions technology, and as a soil amendment to improve soil quality and fertility
215 [32]–[34].

216 The yields of the products depend on the feedstock characteristics and the process conditions,
217 such as residence time, temperature, pressure, etc. [31], [35], [36]. A recent review on biochar
218 [30] found correlations between the residence time and products yields as well as between the
219 process temperature and the characteristics of the products in pyrolysis processes.

220 Pyrolysis processes can be classified as slow or fast depending on the heating rate. Slow
221 pyrolysis is characterized by slow heating of the feedstock ($<10^{\circ}\text{C s}^{-1}$) during minutes to hours
222 at temperatures above 400°C [29], [37], [38]. Fast pyrolysis employs higher heating rates for
223 shorter times ($>10^{\circ}\text{C s}^{-1}$, $<2\text{ s}$) [39]. Fast pyrolysis is optimal for bio-oil production, with yields
224 of around 75% bio-oil, while slow pyrolysis delivers approximately equal ratios of products and
225 favors biochar production with typical yields of 35% biochar [30], [35].

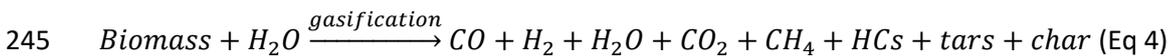
226 Pyrolysis temperature plays a key role in the chemical and structural properties of biochar.
227 During pyrolysis, an array of reactions such as dehydration, cleavage, and decarboxylation take
228 place, which is favored at higher temperatures [30], [31]. High temperatures promote the
229 volatilization of other elements, mainly H and O, hence increasing the C content and producing
230 biochar with fewer O- functional groups. Moreover, longer exposures to heat allow the
231 production of a higher number of aromatic compounds resulting in more recalcitrant biochar
232 [40], [41]. Large proportions of aliphatic compounds in biochar are related to more lability and
233 solubility in soils [42].



235 Fig. 1. Generic process flow diagram of the pyrolysis process, here with crop residues as an
236 input feedstock.

237 3.1.2 Gasification

238 Gasification is a thermochemical conversion technology in which biomass resources are
239 converted to bioenergy in the form of heat and a gaseous mixture of H₂, CO, CH₄, and CO₂,
240 often referred to as syngas [43], [44]. Gasification is performed at high temperatures (700-
241 1200 °C) in the presence of a limited amount of oxidizing agent (i.e., air, steam, oxygen, carbon
242 dioxide, or a combination of these) in insufficient amounts to reach combustion [45], [46].
243 Besides syngas, other light hydrocarbons, as well as a mixture of residual materials, composed
244 of char, ashes, and tar, are produced by gasification, as shown in Eq 4 [47] (Fig. 4).



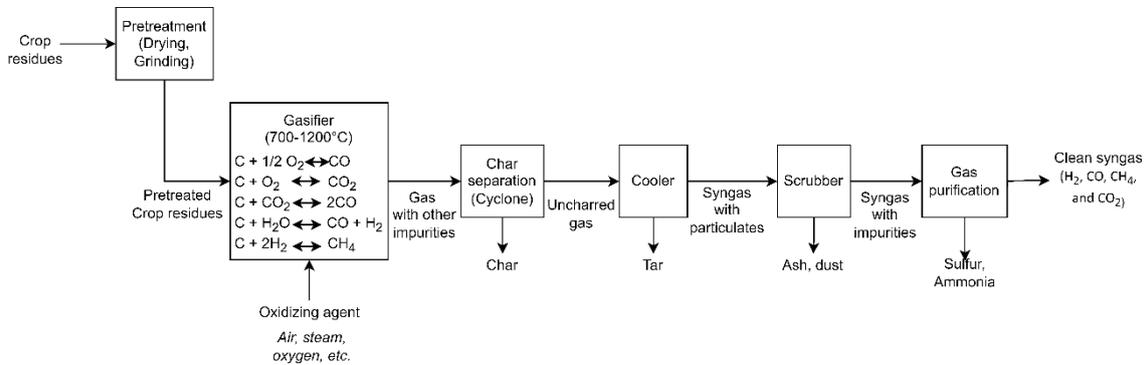
246 Gasification is a complex process that encompasses a series of steps as volatilization of the
247 biomass, cracking and reforming of the volatiles, and gasification of the chars formed [48], the
248 reactions involved in these processes are the water-gas, Boudouard, water-shift, steam
249 reforming, and methanation reactions [49]–[51].

250 Syngas can be directly used for heat and power generation, upgraded to produce
251 transportation fuels, or used for chemical production [48]. Like pyrolysis biochar, gasification
252 char can be valorized for different uses, including soil health management [52].

253 Full-scale gasification facilities commonly operate at atmospheric or higher pressures up to 33
254 bar and temperatures ranging between 800-1100°C [48], [53], albeit agriculture residues are
255 typically treated at 750-850°C [49]. The moisture content of the biomass has to be kept below
256 35% with recommended levels around 10-20% to avoid tar formation and failures in the
257 system [48], [51]. Typical conversion efficiencies range between 50-70%, with the amounts of
258 tar formed and the heating value of syngas dependent on the oxidizing agent. The use of air as
259 oxidizing agent introduces high amounts of nitrogen to the process, which dilutes the CO and
260 H₂ concentrations, and yields syngas with heating values of 4-10 MJ Nm⁻³. Pure oxygen can
261 produce syngas with heating values up to 28 MJ Nm⁻³ and the highest CO concentration,
262 nevertheless its use is limited due to elevated costs. Steam is an attractive agent as it yields
263 high H₂ concentrations and heating values in the range of 10-18 MJ Nm⁻³, as well as low
264 fractions of tar (0.2%) and char (7.9%) [49], [50].

265 The main challenges of gasification are tar formation and moisture control of the biomass.
266 Various authors have comprehensively reviewed the implications of the feedstock and
267 operating conditions for biomass gasification, as well as the chemical reactions involved, the

268 reactors design, pretreatments, tar removal processes, and novel gasification technologies
 269 using catalysts or supercritical fluids [43], [45], [46], [48]–[51], [53]. Still, there is scarce
 270 information regarding the char C recalcitrance and its behavior when used as a soil
 271 amendment.



272

273 Fig 2. Generic process flow diagram of the gasification process, here with crop residues as an
 274 input feedstock.

275 3.1.3 Hydrothermal Liquefaction

276 Both gasification and pyrolysis require the use of dry biomass (< 10% moisture, [54]), which
 277 may involve a previous extra process to prepare the feedstock. Hydrothermal Liquefaction
 278 (HTL) is a thermochemical process carried out in a liquid-phase media, acknowledge as a
 279 promising technology for biofuels production, alternative to pyrolysis and gasification [55]–
 280 [57]. Compared to other thermochemical processes, HTL is considered a more energy effective
 281 technology as it allows the use of a wide variety of feedstocks, from lignocellulosic to algal
 282 biomass [58], without previous drying steps, it produces a biocrude with less oxygen content,
 283 yields less tar, and requires lower amounts of chemical additives and heat consumption [56],
 284 [59]–[61].

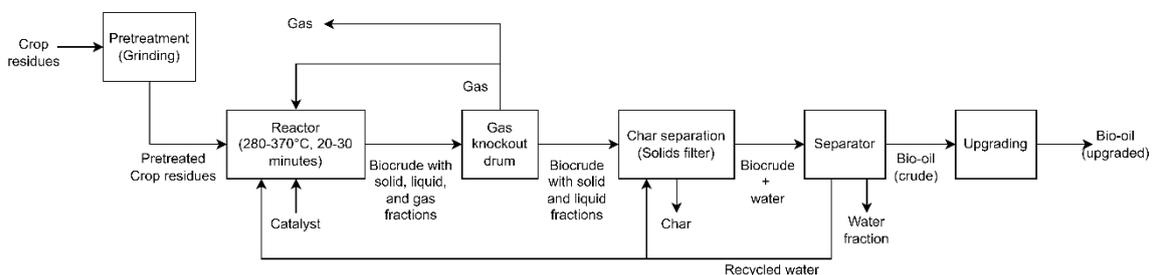
285 HTL allows to input a feedstock with only 5-20% DM [62] and is carried out at low
 286 temperatures around 250-374°C, pressures of 4-25MPa, and retention times around 20-30
 287 minutes [63], [64].

288 During HTL biomass undergoes multiple reactions, including hydrolysis, dehydration,
 289 polymerization, Maillard reaction, decarboxylation, and repolymerization reactions [56], [61],
 290 to convert the carbohydrates in the feedstock into biocrude, biochar and gases (Fig. 3). The
 291 bio-oil produced by HTL has a lower water and oxygen content than fast pyrolysis bio-oil, but a
 292 higher viscosity [64] and the HTL biochar is commonly referred to as hydrochar.

293 Catalysts can influence the HTL processes to improve the bio-oil yield and properties, decrease
 294 the hydrochar yield [58], reduce operation times, hindering secondary reactions, and reduce
 295 pressure and temperature dependency of the process [63]. The effect on the process is
 296 influenced by the type of catalyst, process conditions and biomass used [59]. Basic catalysts
 297 are preferred on HTL operations over acid catalysts, to avoid the system corrosion. For
 298 instance, K_2CO_3 in low temperatures HTL processes accelerates the water-gas shift reaction.
 299 Zhu et al. [55] found that C conversion from the feedstock to hydrochar decreased from 41%
 300 to 9% when K_2CO_3 was applied.

301 It has to be noted that there is a similar process called Hydrothermal Carbonization (HTC),
 302 where instead of bio-oil, the main product intended is hydrochar. Similarly, an alternative
 303 process referred to as hydrothermal gasification (HTG) has been developed to focus on the gas
 304 as the main product. The HTC processes are normally carried out at temperatures above 400°C
 305 [62] and for longer times comprising hours. Higher temperatures cause the decomposition of
 306 biooil, leading to char formation at higher rates than in HTL [65] and with different
 307 composition.

308 The effects of different parameters and catalysts application on HTL yield and products
 309 characteristics has been well reviewed by different authors[57], [58], [60]–[62], [66], [67].
 310 However, the focus of HTL reviews has been the biocrude and when the interest is on the
 311 yields and characteristics of hydrochar the HTL literature is rather scarce since the hydrochar
 312 attention has been given to HTC.



313

314 Fig 3. Generic process flow diagram of the hydrothermal liquefaction process, here with crop
 315 residues as an input feedstock.

316

3.1.4 Anaerobic digestion

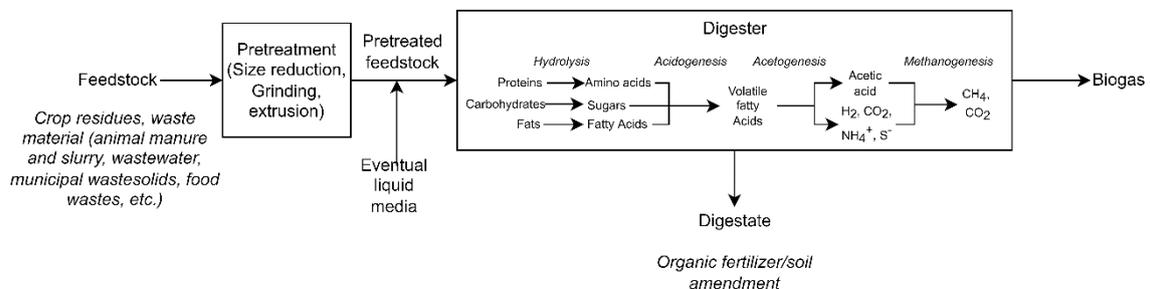
317 Anaerobic digestion (AD) is a biological process where, in the absence of oxygen,
 318 microorganisms decompose organic matter into i) biogas, which could be used to generate
 319 renewable energy, and ii) a solid-liquid by-product known as digestate, typically used as a soil
 320 amendment or fertilizer [68]. Through this process carbohydrates, proteins, lipids, and other
 321 organic compounds are transformed into biogas, which is composed of methane (CH₄, 50-
 322 70%), carbon dioxide (CO₂, 30-50%), and traces of other gases (H₂S, NH₃, 1-5%) [69]. AD is
 323 among the most cost-effective and environmentally friendly technologies for renewable
 324 energy due to its simplicity, low costs, and adaptability to different types of wastes and
 325 biomass. Therefore, the number of AD facilities is rising worldwide, with a subsequent increase
 326 in digestate production [69], [70].

327 The co-digestion of a mixture of two or more substrates, typically organic wastes, and animal
 328 manure is commonly used to enhance biogas quality and process stability. Moreover,
 329 incorporating biorefineries byproducts into the digestion process is a way to reduce external
 330 feedstocks requirements [71].

331 The process consists of a series of complex microbiological reactions that take place in four
 332 consecutive stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Fig.
 333 4). The reactions, influenced by the feedstock selection and operating parameters, govern the
 334 overall yield and characteristics of the products [72].

335 Different organisms with different responses to temperature participate in the process in a
 336 syntrophic association. The majority of biogas systems operate at temperatures around 30-
 337 40°C or 50-60°C [73]. Although some organisms can produce biogas at higher or lower
 338 temperatures, lower methane rates have been observed at psychrophilic temperatures
 339 (~10°C), and accumulation of fatty acids is associated with temperatures above 60°C [74]. The
 340 process can be carried out in wet (10% DM or less) or dry conditions (15-35% DM) [75] with
 341 optimal retention times between 10 and 25 days [72].

342 During AD, the more readily degradable components are converted to biogas while the non-
 343 degradable materials remain in the digestate [68], [76]. Digestate is a material rich in C and
 344 nutrients such as N and P, which is key to maintain soil fertility. Digestate is mainly composed
 345 of lignin, cellulose, and hemicellulose [77]. During AD, cellulose and hemicellulose degrade in
 346 about 50% and 80%, respectively, while the lining remains unconverted. Digestate commonly
 347 contains 9-13% dry matter, of which between 28 and 47% correspond to the total carbon
 348 content [78], [79]. Besides carbon, digestate is rich in nitrogen, potassium, phosphorus, and
 349 other minerals, which makes it attractive as a fertilizer or soil conditioner [70].



351 Fig. 4. Generic process flow diagram of the anaerobic digestion process, here with the input
 352 feedstock including crop residues, waste material, wastewater, animal manure and slurry, and
 353 eventual mixture with a liquid media.

354 3.1.5 Second-generation ethanol production

355 Bioethanol is a high-octane number biofuel produced by yeast fermentation of sugars, typically
 356 used in transportation as a mixture with gasoline [80]. The energy content of cellulosic
 357 bioethanol ranges between 16.7-21.2 MJ L⁻¹ depending on the feedstock, which represents
 358 around 66% of the energy content in gasoline [81]. In contrast with gasoline, bioethanol
 359 contains 35% oxygen, denoting a 15% higher combustion efficiency [82].

360 Wheat, rice, corn, and sugarcane residues are the most common feedstocks for lignocellulosic
 361 bioethanol, also called second-generation biofuel. For bioethanol production, biomass must
 362 follow a series of steps (Fig. 5), involving i) a physical, chemical or thermal pretreatment to
 363 release hemicellulose and cellulose from the matrix, ii) the hydrolysis of polymers to simple
 364 sugars aided by enzymes, and iii) the fermentation of sugars by microorganisms followed by iv)
 365 a distillation process to purify the bioethanol [83], [84]. During the process, approximately 95%
 366 of soluble sugars are transformed into ethanol and CO₂, while 1% becomes yeast cellular
 367 matter, and 4% are byproducts [82].

368 The enzymatic hydrolysis usually occurs at mild conditions (low pressure, long retention times
 369 in the range of 48-72h, pH around 5, and temperatures below 50°C), the efficiency conditioned

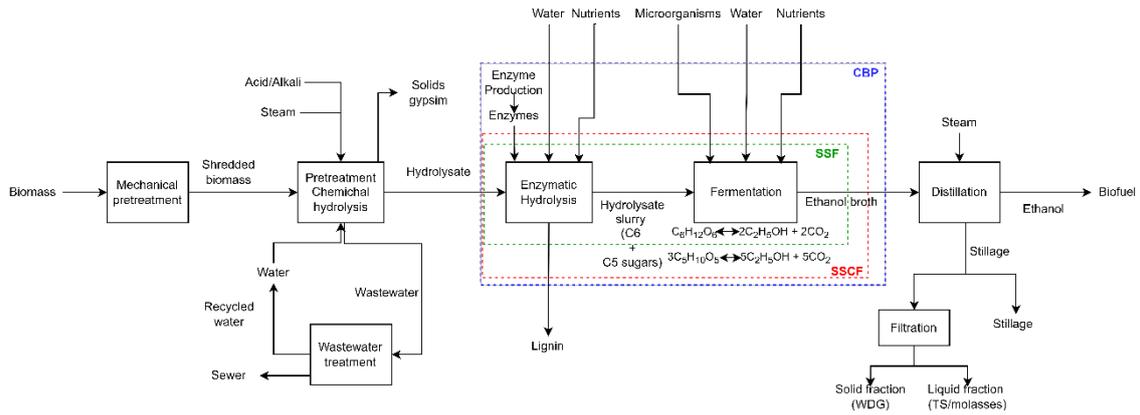
370 by the pretreatments [80], [82], [85]. The fermentation process could be carried out by
371 different microorganisms, including yeast, bacteria, and fungi, of which the
372 yeast *Saccharomyces cerevisiae* is the most frequently used, with efficiencies of 90 to 93% of
373 the theoretical yield. The reaction in Eq 5 corresponds to a typical ethanol conversion from
374 glucose fermentation by yeast, with a theoretical yield of 51.1% of ethanol and 48.8% of CO₂
375 [86].



377 The hydrolysis and fermentation stages can occur in a separate hydrolysis and fermentation
378 (SHF) system or a simultaneous saccharification and fermentation (SSF) process. While the SHF
379 systems allow setting optimal temperatures for each process (50°C for hydrolysis, and 28-32°C
380 for fermentation), the SSF configuration involves one reactor operated at temperatures
381 around 38°C where the hydrolyzed sugars are fermented immediately. Higher bioethanol
382 yields and lower times and costs have been observed for SSF processes, compared to SHF, and
383 are the most common system at pilot scale [80].

384 After removing the cellulose and hemicellulose from the biomass for bioethanol production,
385 the more complex sugars, such as lignin, remain in the grains at a 3-fold higher concentration
386 than the original substrate [87]. Before distillation, the non-fermentable components are
387 removed as a stream called stillage. Whole stillage is rich in waxes, yeast cells, soluble
388 nutrients, and lignin content [83], [88]. Stillage can be utilized as animal fodder, fertilizer, or to
389 produce biogas [89]. The liquid fraction is known as thin stillage (TS), of which approximately
390 15% is recycled as process water [90] and the remaining fraction is condensed by evaporation
391 as condensed distillers solubles (CDS). The solids fraction, composed of small unfermentable
392 grain particles is known as wet distillers' grain (WDG). CDS and WDG are often combined and
393 dried, resulting in a mixture known as distillers' dried grains with solubles (DDGS) which allows
394 longer storage times than the separate fractions [91].

395 Around 10.2% and 17.8% of wheat straw are converted to stillage in bioethanol production
396 [89]. Lignin content in stillage from wheat-based bioethanol is ca. 17 – 24 % (DM)[92] and 70%
397 for corn stover bioethanol [93]. For corn-based bioethanol, it is estimated that 10.6 L of
398 bioethanol could result in more than 17 pounds of distiller grains [83]. Bioethanol byproducts
399 have a higher C concentration than the original crop residues [93], with the largest fraction of
400 C in the solid residue. Due to their rich nutrient composition, DDGS is commonly used as a
401 livestock diet supplement, a precursor for bio-composites production, and burned for energy
402 production in power plants. Moreover, the bioethanol coproducts lignin and N content can
403 triple the raw feedstock, which makes them attractive as soil amendments [93].



404

405 Fig 5. Generic process flow diagram of the lignocellulosic bioethanol production process. SSF:
 406 Simultaneous saccharification and fermentation. SSCF: Simultaneous saccharification and
 407 cofermentation CBP: consolidated bioprocessing . CHP: Combined heat and power. WDG: Wet
 408 distillers' grains. TS: Thin stillage

409 **3.2 Carbon conversion from feedstock to coproducts**

410 The initial C in the biomass remaining in the coproducts (Cc) was "determined" for each
 411 technology for the process conditions and the coproducts defined in Table 1. Fig 6 summarizes
 412 the average BpY, BpC, and Cc per technology. The complete database with all the records for
 413 Cc and C_R data is available in doi.org/10.48531/JBRU.CALMIP/WYWKIQ and the complete
 414 summary and references are detailed in Table S1

415 Table 1. Process conditions, coproducts, and feedstocks included in this study per technology.

| Process | Process Conditions | Coproduct | Feedstocks included ^a | MRT ^b years | n C _c | n C _R |
|---------------------------|--|-----------|--|------------------------|------------------|------------------|
| Pyrolysis ^b | 350-700°C (<300°C, 300-500°C, >500°C) , DM>90%, seconds to 2h | Pyrochar | Crop residues (wheat straw, maize straw, maize stover, maize silage, rice straw, rice husks, rapeseed straw, rye straw, barley roots, soybean stover, sunflower straw, sugarcane bagasse), temporary grassland (switchgrass, ryegrass), peanut shell, poultry litter, digestate, green waste | 383 | 44 | 144 |
| Gasification ^c | 600-1200°C dry gasification. 300-550°C hydrothermal gasification, DM>90% | Gaschar | Crop residues (wheat straw, maize stover, maize silage, rice straw), switchgrass, forestry residues (Vermont wood, pine wood), citrus peel, peanut shell, walnut shells | 141 | 25 | 36 |

| | | | | | | |
|--------------------------------|---|-----------|--|-----|----|-----|
| HTL ^d | 180-400°C, K ₂ CO ₃ catalyst, DM<20%, | Hydrochar | Crop residues (wheat straw, maize stalks, <i>maize silage</i> , rice straw, barley straw), <i>forestry residues (wood chips, poplar wood)</i> , <i>straw digestate, draff, miscanthus, sugar beet pulp, vinasse, yeast</i> | 11 | 31 | 104 |
| AD ^e | Mixture of manure/slurry with crop residues. Mesophilic conditions (30-50°C). 1-3 months. | Digestate | Wheat straw, rice straw, maize straw. <i>Cattle manure, cattle slurry, pig slurry, poultry manure, food waste, paper, green waste, household waste, maize silage.</i> | 0.4 | 68 | 114 |
| 2GEtOH production ^f | Pretreatment, acid and enzymatic hydrolysis, fermentation <i>S. cerevisiae</i> , distillation | Molasses | Wheat straw. <i>Wheat starch, corn stover, non-fermentables from wheat bioethanol, DDGS, yeast concentrate, rapeseed meal, vinasse from sugarcane bagasse, vinasse from sugar beet</i> | 1 | 3 | 51 |

416 ^a Feedstocks in italic are included only in the C_R review.

417 ^b For the C_R review, the minimum and maximum pyrolysis temperatures were 250 and 800°C,
418 respectively, and the assays were grouped by temperatures in low (< 300°C), medium (300-
419 500°C), and high temperatures (>500°C).

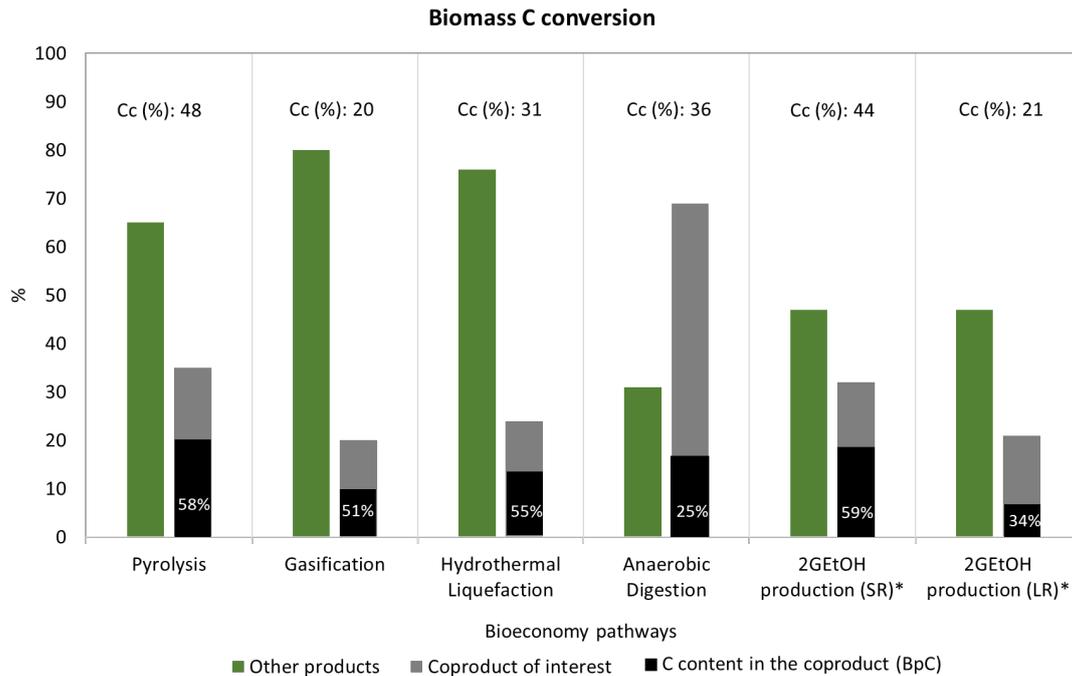
420 ^c The use of wet biomass in gasification processes (hydrothermal gasification) is increasing as
421 an energy wise strategy, thus this process conditions were included in this study.

422 ^d Due to increasing use of catalysts in HTL processes to modify the products yields and quality,
423 we included processes with and without catalysts.

424 ^e Only the crop residues C is accounted in the C_c .

425 ^f For the lignocellulosic bioethanol production, the coproducts were grouped as solid fraction,
426 liquid fraction, and meal, for the C_R coefficient

427 ^g Mean Residence Time corresponding to crop residues feedstock, medium temperatures for
428 pyrolysis, and molasses in the 2GEtOH case. The MRT showed for the AD technology stems
429 from different conditions and incubation assays with different timeframes (including studies
430 carried out for less than a month), thus it is not representative of the real recalcitrance
431 observed in the digestate.



432

433 **Fig. 6.** Coproduct yield, C content, and biomass C transformation into coproduct (DM). Only
 434 the coproducts considered for a return to soil are included in the figure. SR: Solid residue from
 435 the 2GEtOH production; LR: Liquid residue from the 2GEtOH production. *The 2GEtOH other
 436 products includes the bioethanol and CO₂ produced. Data obtained from a non-exhaustive
 437 review of 23 (n= 44), 5 (n= 25), 10 (n= 31), 34 (n= 68), 1 (n= 3), papers for pyrolysis,
 438 gasification, hydrothermal liquefaction, anaerobic digestion, and lignocellulosic bioethanol
 439 production, respectively (n represents the number of datasets included).

440 In average, the lignocellulosic biomass is composed of 38-50% cellulose, 23-32% hemicellulose,
 441 15-30% lignin and 10% of other components [84], which corresponds to a C content of 45-50%
 442 [94].

443 Since our interest in this review is to analyze the potential of crop residues for the
 444 bioeconomy, we selected process conditions that favor the production of the main economic
 445 product per technology (i.e., bio-oil, syngas, biogas, bioethanol). However, most of the studies
 446 regarding the C pathway in pyrolysis processes consider operating temperatures from 300-
 447 700°C with retention times from a couple seconds to hours, thus the process conditions
 448 included in this study were not strictly those of a fast pyrolysis process. These conditions yield
 449 in average 35% of pyrochar(n= 44), composed of 58% C, which means that 48% of the original
 450 C is in the pyrochar (Fig 6) (44% for the specific wheat straw based pyrochar). Our findings
 451 agree with Ippolito et al. [30] who determined a 58% C in crop residues derived pyrochar (300-
 452 400°C) and Qambrini et al. [39] who found a pyrochar yield of 35% for processes lasting from
 453 minutes to hours, while lower yields (<20%) have been reported for fast processes shorter
 454 than 2s [36].

455 // Woolf et al. [16] proposed Eq X to estimate the dry ash free biochar yield (Y_{bc}), as a function
 456 of the pyrolysis temperature (T) and the feedstock lignin content (L). This equation yields
 457 around 25-29% biochar for a low temperature (350-450) pyrolysis of wheat straw, with a 59%
 458 carbon content [16], which is accordance to our findings.

$$459 \quad Y_{bc} = 0.1261 + 0.5391e^{-0.004T} 0.002733L \text{ Eqx //}$$

460 Gasification processes are typically constrained by the feedstock moisture content. Advances
 461 on the technology have allowed to conduct gasification at lower temperatures and in the
 462 presence of moisture (DM 20-35%) in HTG processes. Due to its fast development, we included
 463 HTG studies [95] besides the dry process. Moreover, the typical carbon conversion efficiencies
 464 (50–70%) can be increased by 17-37% if catalysts are used [51], thus catalytic processes were
 465 also included.

466 In highly efficient processes, the fraction of C in wood-agricultural biomass that ends in the tar
 467 is less than 1% [96]. In average, the gaschar yield is 20% DM (Fig 6, n=25), with reported values
 468 from 7% to 28%. The gaschar yield is highly influenced by the oxidant agent, being the double
 469 for oxygen (15.5%) compared with the use of steam (7.9%) [62]. Accordingly, the C content in
 470 gaschar varies in a wide range (20-90%, average 51%) depending on the process conditions (Fig
 471 6). The C balance in gaschar has been suggested to be around 20-60% [97] with a typical
 472 average of 38% [16]. However, You et al. [97] showed that the total carbon content in gaschar
 473 attains fractions well over 60% (wt). In average the biomass Cc to gaschar is 20% (Fig 6). This
 474 value is significantly lower than in pyrolysis process because the oxygen in the gasifier
 475 reactor oxidizes the C to CO₂, while it remains in the biochar in the pyrolysis reactor.

476 HTL is able to input a broad variety of feedstocks with diverse compositions, thus the products
 477 yield varies in a wide range depending on the biomass. Moreover, the use of catalysts may
 478 modify the yields and composition of the streams involved. HTL biocrude has yields ranging
 479 from 12 to 77%, for different process configurations [60], [62], and an average C content of
 480 73% compared as to 58% for pyrolysis biocrude [98]. Various modeling studies have been
 481 conducted to determine the HTL biocrude yield [44], leading to a consensus that the protein
 482 and lipids content in the biomass influence the biocrude yield, while the carbohydrates
 483 content can be correlated with the hydrochar production. In average HTL yields 25% hydrochar
 484 (n=31) with a C content of 56%, which describes a Cc coefficient of 31%.

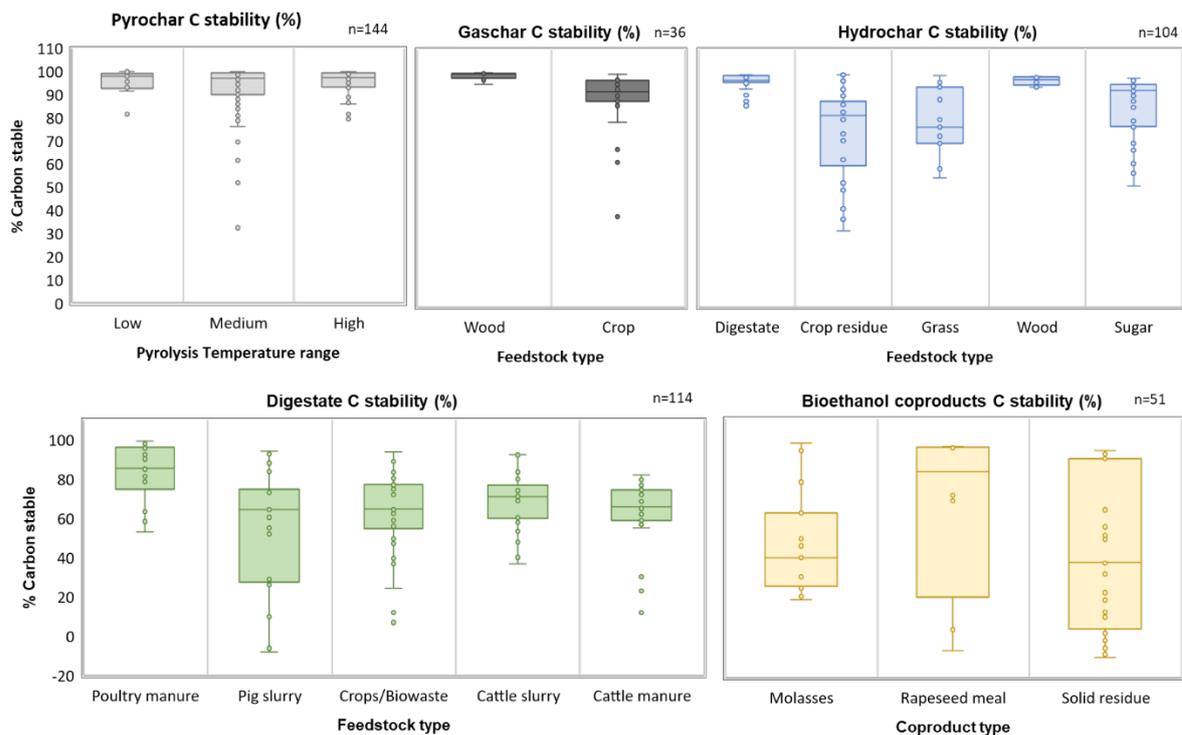
485 The digestate carbon balance was obtained from a mass balance including the reported
 486 biomethane BMP of cereal residues, where the carbon balance from the crop residues has
 487 been determined separately from the C input from the manure and no losses were accounted.
 488 The amount of biomass converted to biogas depends on the initial feedstock, with
 489 methanogenic potentials around 179 – 253 m³CH₄/tonne fresh biomass for agricultural
 490 residues [99] which is in accordance with the average BMP of 215.42 m³ CH₄ tonne⁻¹ dry
 491 biomass reported in our study. In average, of the products and coproducts generated during
 492 AD, digestate represents 69% (n=66). Digestate is composed by solid (10-20%) and liquid (80-
 493 90%) fractions [100], which can be separated to obtain a biologically stable solid. The C
 494 content of digestate ranges from 15% to 55% [101], with an average content of 25% for a
 495 variety of feedstocks (n=66). Based on the volatile solids (VS) reduction reported by different
 496 authors (n=16), approximately 64% of the biomass C is digested to biogas, representing a Cc to
 497 digestate of 36% (Fig 6).

498 Bioethanol production results in 3 main streams in roughly equal proportions i) fuel ethanol, ii)
 499 non fermentable constituents, iii) carbon dioxide [88]. The biomass conversion rates to
 500 bioethanol varies between 22-32% [102]. The average ethanol yield in this study was 0.225 kg

501 kg^{-1} biomass DM ($n=3$), while the CO_2 emissions and coproducts represent a yield of 24% and
 502 53% (32% solid fraction and 21% liquid fraction), respectively. Given the low conversion rates
 503 achieved in the alcoholic fermentation of lignocellulosic biomass, the biggest proportion of
 504 feedstock carbon remains unconverted in the residues. The bioethanol coproducts can be
 505 separated in a solid and a liquid fraction (molasses), the former conserving the biggest share of
 506 biomass unconverted C ($C_c= 44\%$). In average, the solid residue has a C content of 33%, while
 507 the C content of the molasses fraction is 21%, which represents a C_c of 21%. Our results are in
 508 accordance with industrial data, which report a solid fraction (lignin) yield of 32%-39% and
 509 22%-35% molasses, in a dry basis [102].

510 3.3 Recalcitrance of coproducts

511 The C remaining in the bioeconomy coproducts constitutes the degradation-resistant fraction
 512 of C in the untreated biomass, commonly attributed to lignin. The thermochemical processes
 513 change the chemical structure of the recalcitrant C producing different aromatic groups, while
 514 the biochemical processes only remove the labile C from the biomass and the recalcitrant
 515 fraction remains as in the raw material. Therefore, the degree of recalcitrance of the
 516 coproducts varies among the technologies (Fig. 7, Table S2).



517

518 Fig. 7. Carbon recalcitrance and MRT of different bioeconomy technologies coproducts.
 519 Pyrolysis temperatures grouped as low ($<300^\circ\text{C}$), medium ($300 - 500^\circ\text{C}$), and high ($>500^\circ\text{C}$).

520 3.3.1 Pyrochar and gaschar

521 In this subsection we refer to biochar when it is applicable for both pyrolysis and gasification
 522 biochar and when the explanation is specific per technology, we refer to the coproducts by
 523 their specific designation as pyrochar and gaschar. Various studies have demonstrated that
 524 biochar is highly recalcitrant, being able to resist both biotic and abiotic degradation with
 525 approximately 80 – 97% of the organic carbon remaining unmineralized for hundreds to

526 thousands of years [28], [41], [42], [103]. Understanding its recalcitrance is of foremost
527 importance to take advantage of biochar as a carbon sequestration and soil amendment
528 technology.

529 It has been demonstrated that biochar composition can be described by the presence of C_L and
530 C_R fractions [104]–[106], each fraction determined by the characteristics of the raw biomass
531 and the process conditions. The decomposition process of biochar in soils exhibits a rapid
532 degradation of the labile fraction during the first years followed by a high resistance to
533 decomposition with a MRT on the decadal to millennium scale [25], most of them in the
534 centennial or millennial scales.

535 Biochar produced at higher temperatures has a higher proportion of aromatic groups, which
536 makes it more resistant to degradation [40], [41]. It was observed that recalcitrance increases
537 when mineral binding appears, mainly in Fe oxides-rich soils [107]. Also, some evidence
538 indicates that phyllosilicates play a role in biochar soil stability. Regarding the feedstock
539 influence, the high content of ashes in the biomass may act as a barrier impeding the heat
540 diffusion. This hinders the dehydration during the process and favors the production of more
541 dissolved organic carbon (DOC), which is considered the main form of labile carbon in the
542 biochar. This could explain why manure and crop-based biochar, which are biomass rich in
543 ashes, generally contain more DOC and are less recalcitrant [42]. The elemental ratios between
544 C, H and, O can be expressed as the H/C_{org} and O/C ratios, which can be depicted in the Van-
545 Krevelen diagram and are considered simple and reliable identifiers of biochar stability [30],
546 [106]. The H/C_{org} correlates the ratio between hydrogen and carbon to the presence of
547 aromatic compounds and double bonding. This ratio estimates the stability of biochar over
548 100 years (BC_{+100}) as 50% and 70% for an H/C_{org} of 0.5-0.7 and 0.4, respectively [22], [25]. The
549 O/C ratio considers that a higher content of aromatic structures occurs when the ratio of
550 oxygen in biochar is low. The stability is estimated as half-life ($BC_{t1/2}$) and is expressed in three
551 ranges with an estimated $BC_{t1/2}$ of 100 years for $O/C > 0.6$, 100-1000 years for O/C between 0.2-
552 0.6, and 1000 years for $O/C < 0.2$ [30], [108].

553 Metadata analysis on biochar stability in soils by Wang et al. [41] and Han et al. [42] found
554 that the C_L and C_R fractions have different MRT in soils, which varied with the feedstock,
555 pyrolysis conditions, experimental duration, and soil composition. They agree that biochar
556 produced at lower temperatures and shorter times has a higher proportion of C_L than biochar
557 produced at higher temperatures and longer times, and mineralization of biochar is lower in
558 soils with high clay contents and higher in sandy soils.

559 Compared to the raw biomass, biochar mineralizes at a significantly slower rate. In [109],
560 about 77% to 100% of rice husks were mineralized in soils, whereas only 4.4% - 8.5% for rice
561 husks-derived biochar was mineralized. Bruun et al. [29] observed that 53% of C was
562 mineralized from wheat straw added to soils, while only 2.9% and 5.5% were mineralized for
563 the slow and fast pyrolyzed residue, respectively.

564 Based on 24 studies with a total of 128 observations Wang et al. [41] found that about 3% of
565 the biochar composition corresponds to its labile pool, with an MRT of about 108 days, while
566 the more recalcitrant pool has an estimated MRT of 556 years and represents 97% of the BC
567 for different biochar. Zimmerman [110] obtained average C losses of 10.3% after 100 years and

568 28.4% after 1000 years for microbial incubations, and 11.1% after 100 years and 28.8% after
569 1000 years for abiotic incubation of different biochar, by modeling. Using a two-pool model,
570 long-term losses of 2% – 59% were determined for different biochars, whereas considering
571 half-lives on the centennial and millennial-scale losses of 5 – 17 % would be a more accurate
572 estimation [105]. As a response to little mineralization expected, biochar can contribute to
573 increase SOC stocks by 39% with pyrochar addition, according to the meta-analysis (56 studies)
574 reported by Bai et al. [111].

575 The biochar potential to decrease GHG emissions has been extensively documented in various
576 studies [30], [40], [106], [112], however the potential emissions resulting from poor
577 management has been commonly disregarded. Field trials [113], [114] found that plant roots
578 can oxidize biochar, which results in higher mineralization and diminishes the C mitigation
579 potential of biochar. Zhang et al. [115] reported the influence on the rate of application of
580 biochar. Their results showed that application rates from 10 to 40 t BC ha⁻¹ can increase soil
581 CO₂ and CH₄ emissions and decrease N₂O emissions by 15%, 16%, and 38%, respectively,
582 compared to non-biochar situations, while application rates above 80 t BC ha⁻¹ allowed to
583 achieve negative emissions.

584 *3.3.1.1 Pyrochar*

585 We found 34 different studies including a total of 144 different datasets for laboratory
586 incubations, 1 and 2 pool modeling, and field trials . After removing the outliers, we reduced
587 the data to 131 observations and found average recalcitrance of 96%. Since our study
588 considers pyrochar as a coproduct from pyrolysis where the main product is bio-oil, we
589 separated the studies by the process temperature as low (< 300°C), medium (300-500°C), and
590 high (> 500°C) temperatures, with our main interest in the medium temperature group (Fig. 9).

591 Crop residues pyrochar produced at medium temperatures have average recalcitrance of 95%,
592 with an MRT of 632 years (n=74, 249 days average assay). If we only consider studies
593 performed for more than one year (n=30), the recalcitrance remains almost unchanged (93%)
594 while the MRT decreases to 604 years. For high temperatures and an average incubation of
595 193 days, the C_R was 97% (n=49), while for low temperatures and 705 incubation days the
596 average C_R was 97% (n=10). The C_R value obtained for the low-temperature group may be
597 biased by the low number of studies included, thus this value remains highly uncertain. Some
598 authors provided the projected C loss in a 100-year timeframe, for medium temperatures,
599 which resulted in an average 75% C remaining in pyrochar.

600 Our findings are in agreement with Han et al. [42], who determined that manure and crop-
601 based pyrochar have a mineralization percentage of 4.35%, while wood-based pyrochar is
602 more recalcitrant with a mineralization percentage of 1.32%. The 100 year C_R projections
603 reported in this study are in accordance with Woolf et al. [16], who found that 63-82% of the
604 pyrochar remain unmineralized after 100 years, and with the IPCC guidelines [116], which
605 propose an 80% C fraction remaining in soils after 100 years.

606 *3.1.1.2 Gaschar*

607 Higher temperatures tend to produce a more microbial degradation resistant biochar, this
608 explains the less surface functional groups and higher C stability found in gaschar, compared to

609 pyrochar [40], [42], [117]. However, in contrast to pyrochar, there is still scarce information
610 about C recalcitrance of gaschar and incubation trials are required to clarify the gaschar
611 potential on C dynamics [52], [113].

612 Given the scarcity of information regarding gaschar recalcitrance, we included crop residues
613 and woody feedstocks in our review, which yielded 10 publications with a total of 36
614 observations. The mean C recalcitrance was found to be 95% (n=33) for a mean incubation
615 time of 523 days and a mean MRT of 141 years. Data was grouped by type of feedstock into
616 crop residues- and wood derived- gaschar which represented a C_R (%) of 94 (n=20) and ~ 100%
617 (n=10), respectively (Fig. 9).

618 Data was grouped by gasification temperature in three groups: 500-600°C, 700-800°C, 1200°C.
619 For the second and third group C recalcitrance was 95%. The first group showed a recalcitrance
620 near 100%. However, the latter value resulted from only one study where the incubation was
621 carried on for only 143 days. Our results are aligned with the IPCC guidelines [116], which
622 suggest that 89% ($\pm 13\%$) of C gaschar remains in the soil after 100 years. Nevertheless, the
623 MRT values reported in the database included in this study are considerably low and more
624 realistic values are expected to be in the centuries to millennial scale [28], [105].

625 3.3.2 Hydrochar

626 Although HTL is being well investigated, the attention is focused on the bio-oil production,
627 whereas few studies have revolved around the HTL hydrochar, leaving the hydrochar spotlight
628 to HTC processes. Compared to pyrochar, the literature regarding hydrochar recalcitrance is
629 scarce, mainly because the C groups in the latter tend to be less aromatic and have lower
630 surface and porosity than pyrochar [60].

631 From 16 studies (104 datasets), the average stability of hydrochar in soils, obtained from
632 different feedstock was 89% (n=97 after outlier removal, Fig. 9). For crop residues hydrochar,
633 specifically, the reported recalcitrance averages 83% with an MRT of 11 years (n=29).

634 The lower recalcitrant fraction and expected life in soils of hydrochar than gaschar and
635 pyrochar, is attributed to the milder conditions and the water content allowed in the process.
636 These conditions produce hydrochar with a high number of aliphatic groups and O- and H-
637 content, due to the lesser evaporation degree, which is attributed to the formation of DOC in
638 soils and more lability [42].

639 3.3.3 Digestate

640 While the C content of digestate (BpC) is lower than in the feedstock (25% vs 45%,
641 respectively), the return of digestate to the soil can compensate the C loss incurred by
642 removing the crop residues and animal manure from soil, due to lower mineralization rates in
643 the long-term [78]. The digestate recalcitrance is attributed to the high lignocellulosic matter
644 accumulated after the AD, where the more labile components in biomass are converted to
645 biogas [76].

646 Various studies have found that digestate could be even twice more resistant to degradation
647 than the undigested feedstock [118], [119]. For instance, the application of undigested silage
648 maize (100% C) resulted in a 104% loss of CO₂ while the application of digested silage maize

649 (36% C) constituted only a 13% mineralization [120]. It must be noted that the original stable C
650 in biomass is not altered during AD, thus the only difference between the raw and digested
651 biomass lies on the labile C content. Therefore, the higher rate of CO₂ emissions in the raw
652 biomass is attributed to the labile fraction.

653 We found 17 different studies (n=114) regarding digestate recalcitrance. The average digestate
654 C stability for the ensemble feedstocks was found to be 70% (n=104). Since the main focus of
655 this study is to consider the possibility of returning digestate as a mean to harvest more crop
656 residues for AD, we then grouped the different digestates by feedstocks as derived from cattle
657 manure, cattle slurry, pig slurry, poultry manure, and crops/biowastes mixtures. The C stability
658 for the crops/biowaste group was found to be 68% (n=31). When possible, we compared the
659 mineralization of the raw feedstocks vs the digestates. Four studies [121]–[124] observed that
660 in occasions raw feedstock could be more stable than digestate (Bernal and Kirchmann 1992;
661 Cayuela et al. 2010; Dietrich et al. 2020). However, in average (n=20 sets), digestate is 31%
662 more stable than the raw feedstock, specifically, the stability of digestates from
663 crops/biowastes mixtures is 35% higher than the undigested biomass.

664 These results show that although the C content in digestate is only half compared to the the
665 content in the undigested biomass, the removal of the labile C fraction decrease the soil C
666 mineralization if digestate is applied, thus allowing to maintain the SOC levels for longer times
667 than just leaving the crop residues on soils.

668 3.3.4 Molasses

669 The potential soil application of the coproducts resulting from the 2GEtOH production has
670 been poorly investigated, with the majority of studies regarding the behavior of only the solid
671 fraction or molasses produced in first generation bioethanol production, while incubation
672 studies to understand the recalcitrance of 2GEtOH molasses are scarce.

673 Cayuela et al. [125] compared the application of raw wheat residue vs non-fermentable wheat
674 residue (NFWR) from bioethanol production to soils at different rates. They found that NFWR
675 has a stronger stabilization effect on the soil organic matter and long persistence. Research
676 regarding the application of bioethanol coproducts to soils is required as the presence of heavy
677 metals and toxic substances may decrease soil quality, and soil C and N dynamics can be
678 modified by the differences in feedstocks and process.

679 We compiled the available publications regarding the C stability of bioethanol by-products. In
680 our research, we included by-products in form of “non-fermentable solids”, “vinasse”, “yeast
681 concentrate”, “distiller’s grains”, “bagasse pith” and “biodiesel meal” obtained from the
682 bioethanol production from different feedstocks (corn, sugarcane, sugar beet, wheat,
683 rapeseed, potato). A total of 10 papers were included (n=51). The average C recalcitrance for
684 the ensemble of byproducts was 48% (Fig 7) with an MRT of 1.3 years. Separating the residues
685 as liquid, solid and meal resulted in recalcitrance values of 49%, 45%, and 90%, respectively.

686 Evidence has suggested that recalcitrance of bioethanol coproducts can be lower than the
687 recalcitrance of the untreated biomass, probably because the chemical and enzymatic
688 treatments change the lignin condensation, thus allowing greater access to soil microorganism
689 than in the raw biomass [122], [125], [126]. Soil application of molasses has been associated

690 with increased aliphatic groups (in C), salinity and electrical conductivity in the soils, and with
691 higher CO₂ and N₂O emissions than untreated biomass [126], [127]. The high mineralization
692 rate of bioethanol coproducts is associated to an increased microbial activity due to the
693 stimulation of the SOC labile fraction, this is associated with increased fertility and plant
694 growth [83]. More research is required to understand the recalcitrance of bioethanol
695 byproducts and its effects in the long-term soil quality.

696 Some mechanisms have been proposed [23], [52], [113], [128], [129] to understand how the
697 application of bioeconomy coproducts can affect soil C mineralization, commonly referred to
698 as negative priming effect when decreasing the mineralization rate. The key points to consider
699 are:

- 700 a) The soil microbiome may evolve to adapt to use pyrochar or gaschar as a source of C
701 instead of native SOM. Thus, the recalcitrant fraction of C would become the preferred
702 C source affecting the long-term mineralization expected.
- 703 b) BC microporous structure adsorb SOM particles, which reduces microbial accessibility
704 to SOM, thus decreasing the microbial degradation of SOM. Higher process
705 temperatures increase the micro porosity of biochar, which explains the higher
706 negative priming effect for biochar produced under gasification compared to pyrolysis
707 or HTC.
- 708 c) Functional groups in biochar may be toxic for microorganism, thus inhibiting their
709 growth and enzymatic activity. The continued soil respiration even when biochar is
710 added may be evidence to oppose this theory.

711 **4. Soil Organic Carbon (SOC): importance and estimation**

712

713 4.1 SOC storage importance

714 Soil organic carbon (SOC) represents the third largest component of the global C cycle, with
715 approximately 700 Pg in the 30 cm topsoil layer, 1500 Pg to 1 m depth, and 2400 Pg to 2m
716 depth [130], [131]. The SOC stocks represent ca. twice the C stocks in the atmosphere (860
717 Pg) and three times the C stocks in the vegetation (450-650 Pg) [132], [133].

718 SOC is dependent on soil characteristics, climate, and usage, and is modified by anthropogenic
719 disturbances and land use change [134]. Approximately 38% of the global soils surface are
720 dedicated to agriculture, of which one-third is used as cropland (FAO, 2020
721 <https://www.fao.org/sustainability/news/detail/en/c/1274219/>). Soils have lost 140-150 Pg C
722 through cultivation since the onset of agriculture [133], which is related to a C lost between
723 20% and 40% of the C stocks of uncultivated soils [135].

724 Soils can be either a source or a sink of C depending on different management practices, with
725 projected annual storage potential of 1.2 billion tons of C in agricultural soils (IPCC, 2014). The
726 maintenance of SOC impacts the soil fertility, physical structure, water holding capacity,
727 structural stability, erosion resistance, and atmospheric emissions, and thus plays an important
728 role in climate change and food security [136], [137].

729 In agricultural systems, the C inputs from crop residues and organic fertilizers, and the C losses
730 due to decomposition of the soil organic matter (SOM) create a dynamic equilibrium [137]. The
731 changes in SOC stocks can only be really appreciated in the long term, with a minimum of five
732 to ten years to be able to measure the changes. Therefore, soil models are useful to identify
733 the effects of different practices on the soil C evolution and define proper policies and
734 strategies.

735 4.2 SOC modeling

736 The effect of changes in environmental factors and soil management on C evolution is
737 observed only in the long-term, which hinders the understanding of strategies to increase SOC
738 stocks in the short-term. The urgency of sustainable use and management of ecosystems has
739 supported the development of agroecological simulation models [138]. Simulation models play
740 a key role in SOC research because they are mathematical representations that integrate,
741 examine, and test the understanding of complicated soil processes to predict responses to
742 conditions and hypothesis at various temporal and spatial scales [136], [139].

743 The models represent agroecological systems integrating the interaction of biotic elements
744 with soil, weather, and management practices to simulate soil carbon, nitrogen, water, and
745 biomass accumulation [138], [140]. Diverse modeling approaches and continued advances in
746 knowledge regarding the soil-atmosphere interactions have produced the development of
747 more than 250 different soil models, and the number continues increasing [141]. An ideal
748 model must be based on a mechanistic understanding of the SOM dynamics to extrapolate the
749 measured short-term local processes to long-term effects valid at different scales [136].
750 However there remain unresolved challenges regarding understanding of the intrinsic soil
751 dynamics, parameterization, and input data availability, thus no single ideal model exists.
752 Moreover, depending on the purpose of the model the type of process and level of details
753 incorporated in the model may vary. Models must be evaluated across all possible conditions,
754 however due to time and budget constraints this is virtually impossible to achieve, and thus it
755 is preferred to increase the accuracy of a model for particular situations [138] and select the
756 model adapted to the requirements.

757 Large variability in the predictions has been shown across models when using the same
758 conditions [140], thus it complicates the selection of a model. Various authors have reviewed
759 the generalities, limitations, accuracy, and sensitivity of different models without a clear
760 answer on how to define that a model would perform better than other [136], [138], [140]–
761 [143]. Multi-model comparison studies have revealed that using an ensemble of models (i.e.,
762 13 [144]; 2- 4 with site-specific calibration [139]) may provide more reliable results than single
763 models.

764 The models reviewed in this study can be grouped as simple models (RothC, AMG, C-TOOL)
765 dedicated to model the soil C and-or N turnover, and as dynamic agroecosystem models
766 (CENTURY, Daycent, DNDC, EPIC, Daisy, APSIM, STICS, CANDY, ORCHIDEE) which predict the
767 interactions plant-soil-atmosphere [145] and are able to predict C-N dynamics, soil-water,
768 nutrients and energy balance, plant growth, and gaseous emissions. The characteristics of the
769 model and associated input and output data are summarized in SI2.

770 The understanding of SOM processes and interpretation of scientific knowledge varies across
771 the different models in their complexity, fluxes, parameters, inputs, and outputs. The
772 complexity on the inputs required varies among the models, thus the model selection must be
773 based on the research purpose to avoid unnecessary complications. Models with limited input
774 data, easy procedures, and friendly interfaces are commonly preferred by decision-makers
775 [146].

776 In general, models assume that the OM decomposition can be simulated by establishing
777 multiple pools that decay with specific decomposition rate constants commonly represented
778 as k and that define the MRT of the OM in each pool [136], [147]. Different mathematical
779 approaches may describe mass loss utilizing zero-order kinetics, first-order kinetics, enzyme
780 kinetics and microbial growth rate [133]. The number of pools varies among the models,
781 typically between 3 to 5 pools, nevertheless they often include a slow-decomposing pool and
782 an inert non-decomposable pool to represent the complexity of stabilization processes. The
783 OM fraction allocated in each pool, the decay rate, the residence times, and the process
784 regulating SOC retention are distinctive for each model.

785 Soil models commonly incorporate the chemical recalcitrance of the input materials (plant and
786 EOMs) using specific decomposition constants derived from chemically defined fractions (e.g.,
787 chemical digestion, spectroscopy, among others) or kinetically defined fractions fitting the
788 turnover rates and pool sizes to CO₂ emissions observed from incubation experiments [147].
789 The representation of the stabilization process within the model enables the long-term
790 simulation of the persistence of the molecules in soil [140].

791 In general, the inputs required to run the different models are soil characteristics (texture, bulk
792 density, initial SOC stocks), climatic variables (air temperature, precipitations, and
793 evapotranspiration), and management practices (crop rotations, fertilization, tillage, grazing,
794 harvesting, among others). The models require estimates of the decomposability of the plant
795 material and the amount of C inputs from crop residues or other external sources. The C inputs
796 from biomass are estimated from measured yields using allometric functions [133]. Models
797 run in different timesteps (hourly, daily, monthly, or annual), therefore the input data
798 provided has to correspond the time scale. As the model complexity increases, so does the
799 type and amount of input data and computing power requirements.

800 Among the most popular models CENTURY, DNDC and RothC are the most accepted and
801 dominate the SOM modeling literature [136], with CENTURY and RothC being used to set the
802 basis to developing other models.

803 CENTURY [148](Parton et al., 1987) is a biogeochemical plant-soil nutrient cycling model
804 designed to simulate the carbon and nutrient dynamics for different types of ecosystems. It
805 integrates the effects of soil characteristics, climatic conditions, and agricultural management,
806 including crop rotation systems and tillage practices, to analyze the effects of management
807 and global change on productivity and sustainability of agroecosystems. Century is able to
808 simulate the long-term plant growth and soil carbon C, nitrogen N, phosphorus P, sulfur S, and
809 water dynamics to centuries and millennia for grassland, agricultural crop, forest, and savanna
810 systems. The model runs in a monthly timestep and is based on three soil organic matter
811 pools, considered as active, slow, and passive, with different decomposition rates, above and

812 belowground pools and a surface microbial pool. CENTURY has been run and tested across a
813 variety of pedoclimatic conditions across the world [12], [149]–[153]. CENTURY has been
814 further modified into the daily timestep version Daycent [154], [155], which has been used in
815 different studies around the world more frequently than Century in the last times [156], [157].
816 Daycent maintains the same structure, inputs, and simulation outputs as CENTURY but in a
817 daily basis and includes other processes such as GHG emissions assessment.

818 Unlike agroecosystem models, which include a global balance of different, the Rothamsted
819 Carbon model (RothC) 26.3 [158] is a soil process model focused on carbon dynamics. RothC is
820 the most commonly used model to simulate SOC dynamics due to its simplicity and ability to
821 be modified to include different considerations regarding the system. It simulates the SOC
822 dynamics in a monthly timestep, in cropland, forests and grasslands, and has been tested
823 under different soils and climates around the globe [159]–[161]. The standard structure of
824 RothC- 26.3 splits the carbon inputs into five different compartments with a specific decay rate
825 (k) for each compartment following first-order kinetics. Four compartments are considered as
826 active pools, these are the decomposable plant material (DPM, $k_{DPM} = 10 \text{ y}^{-1}$), resistant plant
827 material (RPM, $k_{RPM} = 0.30 \text{ y}^{-1}$), microbial biomass (BIO, 0.66 y^{-1}) and the Humified organic
828 matter (HUM, $k_{HUM} = 0.02 \text{ y}^{-1}$). The fifth pool, the inert organic matter (IOM), is a small
829 compartment resistant to decomposition. The model is based on relatively few soil parameters
830 and requires limited and easily accessible input data, it has been parametrized for C inputs
831 from plant sources and farmyard manure. The uncertainty in SOC stocks predicted by RothC
832 has been estimated to be ± 6.8 – 8.5 % when site specific data on climate, soil, and net primary
833 productivity (NPP) are available (Falloon and Smith 2003).

834 The CSOPRA Project [162] conducted in France, compared the ability of CENTURY, ORCHIDEE,
835 AMG, RothC, and the Tier 1 approach to predict SOC stocks in a specific French situation, and
836 corrected the models errors for the specific context. In this study, AMG proved to better
837 describe the SOC evolution in French conditions, while RothC placed second and provided
838 close results to AMG after appropriate corrections to adapt to French characteristics. Century
839 plant model exhibited wrongs in the parametrization of crops at French conditions at provided
840 poor results.

841 *4.3 Including different Exogenous Organic Matter inputs within SOC models*

842 Evidence suggests that bioeconomy coproducts can affect the soil's physical, chemical, and
843 biological properties, regulating the soil organic carbon dynamics when applied as EOMs.
844 Accurate soil modeling is challenging because of the variation in the composition and
845 characteristics (e.g., stability) of the organic inputs, the slow effects on SOC dynamics, and the
846 uncertainty of extrapolating short-time laboratory observations to long-term periods in real
847 ecosystems. The inclusion of bioeconomy coproducts in soil models is even more complex due
848 to the large variety of characteristics and compositions caused by the feedstock and process
849 conditions combinations and the long times required to observe and understand soil changes.
850 Some authors have set the basics to link the bioeconomy to SOC dynamics by including
851 bioeconomy coproducts in soil models following different approaches.

852 RothC has been the most adapted model for bioeconomy coproducts inclusion, while biochar
853 is the most studied coproduct, followed by digestate. Table 2 summarizes the approaches and

854 parameters used by different authors among all the models that have been adapted to our
855 knowledge. The methodologies for the adaptations have been more or less complex according
856 to the model complexity and data accessibility. All the authors, but Dil and Oelberman [163],
857 considered that the coproducts are composed of C_L and C_R fractions, which are then allocated
858 in the different SOC pools according to specific partition coefficients and mineralize following a
859 first-order decay rate (k).

860 Foreid et al. [164] and Dil and Oelberman [165] followed rather simplistic approaches to model
861 the SOC dynamics from biochar application by not considering different SOC pools in the
862 former and not deploying realistic turnover rates in the latter. Foreid et al. [164] built a biochar
863 soil application model in Microsoft Excel employing laboratory incubation data to define the
864 decomposition rate (k) and data from a field experiment to calibrate the model and describe
865 the leaching effect. The water and temperature inputs were determined using Daycent.
866 Biochar was considered to mineralize according to Eq 2b, for which the labile k was set based
867 on Whitman [166], while the recalcitrant k was defined to fit a turnover of 2000 years in the
868 stable pool. The model considers losses due to erosion and leaching to subsoil introducing an
869 adaptation of the Eq 2b to account for the C fraction prone to erode (f_r) and the erosion rate
870 (k_r). Dil and Oelberman [165] regarded biochar inputs in CENTURY as an organic matter input,
871 representing the recalcitrance by a 95% lignin content. This approach allocated the biochar C
872 in the slow pool following a turnover rate of 10-50 years, which is significantly lower than the
873 reported biochar MRTs.

874 Levavasseur et al. [146] parametrized different EOMs, including anaerobic digestates in AMG
875 based on the indicator of residual organic carbon (IROC, [167]) of the materials. The proportion
876 of EOM input into SOC is represented by the humification coefficient (h), which corresponds to
877 the IROC from the biochemical fractions of 24 EOM (> 600 datasets). The IROC of each EOM
878 was determined based on the C content of the soluble lignin and cellulose Van Soest fractions
879 and the proportion of C mineralized after a 3-day incubation [167].

880 RothC has been modified by Woolf and Lehmann [23], Mondini et al. [132], and Lefebvre et al.
881 [153] to model the SOC dynamics from biochar and digestate inputs. Woolf and Lehmann [38]
882 modified the original decay rates of the decomposable plant material (DPM) and Resistant
883 plant material (RPM) pools in RothC to add the positive and negative priming effects (PE) of
884 biochar addition into soils. The model predicted the 100 years SOC dynamics of exporting 50%
885 of maize residues from arable lands to pyrolysis, followed by the return of biochar to the soil.
886 They found a 30-60% increase in SOC stocks if residues are interchanged with biochar.

887 Mondini et al. [147] built additional SOC pools for eight types of EOM materials, including
888 anaerobic digestates and bioethanol residues. The EOM decomposable (EOM-DEOM) and
889 resistant (EOM-REOM) new pools were added parallel to the standard model, while the
890 humified EOM was directly incorporated into the standard HUM pool. The partitioning factors
891 f_{DEOM} , f_{REOM} , f_{HEOM} , and the mineralization rate constants k_{DEOM} and k_{REOM} were
892 defined through short-time incubation experiments (224 curves). The model was used in later
893 [169] to predict the long-term SOC stocks in Italy, at a national scale, for future EOM scenarios.
894 Lefebvre et al., [168] adapted a biochar submodule composed of a fresh biochar (FBC) and a
895 recalcitrant biochar (RBC) pool. The submodule allocates the C_L in the standard FPM pool and
896 the remaining C_R enters the adapted RBC pool to be mineralized according to a k_{RBC} decay rate

897 representing an 11.9% C lost in 100 years. A fraction of C is subtracted from RBC to represent
898 the leaching (f_l) of biochar in natural ecosystems and a positive PE was included according to
899 the Woolf and Lehmann [38] methodology.

900 RothC is included in the BioEsoil tool[170] to evaluate the effects of bioenergy on SOM by
901 considering the nutrient losses during the process and the potential recoveries from returning
902 the coproducts following a yearly timestep. The bioenergy technologies included are
903 incineration, AD, gasification, ethanol fermentation, and plant oil production. However, only
904 AD digestate, gasification char, and incineration ashes are regarded as soil inputs in BioEsoil.

905 CANDY is an agroecosystem model used in Prays et al. [171] and Witing et al. [172] to predict
906 the SOC dynamics from digestate application. The fraction of C in the FOM pool (C_{FOM}) that
907 enters the SOM pool is labeled as C_{rep} flux and the substrate use efficiency parameter (η)
908 defines the potential to build new SOC. Prays et al. [171] performed incubation assays on six
909 different maize-based digestates and performed inverse modeling to adjust the η and k
910 parameters to fit the mineralization rates observed. The adjusted parameters were used in
911 Witing et al. [172], where they determined the C_{rep} factor for different materials (i.e., crop
912 residues, excrement, and digestate) to model the effects on SOC dynamics from applying
913 digestate. The C inputs from digestate (C_{DG}) were calculated as the difference between the C in
914 the fresh matter (C_{FM}) and the C in biogas (C_{BG}), based on the reported biogas yield for the
915 different EOMs.

916 Digestate was also adapted in C-TOOL [173] by running iterations to determine the C fraction
917 to allocate in the HUM pool which allows a 12% C remaining after 20 years, according to
918 Thomsen et al. [119]. A fraction corresponding to 36.7% and 26.0% of C in manure digestate
919 and straw digestate, respectively, has to be allocated in the HUM pool to fit the Thomsen et al.
920 [119] results. The model was used to predict the SOC evolution of applying digestate in soils in
921 Denmark for a future scenario (300 years).

922 Adaptations were performed in the APSIM and EPIC models to assess the effects of biochar as
923 a soil amendment on other soil characteristics beyond SOC. Lychuk et al. [174] adapted and
924 validated EPIC to determine the maize yield, soil cation exchange capacity (CEC), pH, bulk
925 density, and SOC dynamics in soils amended with biochar. The biochar surface area and charge
926 density were related to biochar additions to model the CEC and pH predictions. The soil-
927 biochar mixture CEC (CEC_{mix}) was determined, and the extra CEC (CEC_{added}) compared to
928 non-amended soil was used to determine the new pH (pH_{new}) using an adaptation of the
929 Magdoff and Barlett [175] equation. The SOC dynamics were modeled by allocating the
930 biochar C in different proportions among the SOC pools. The bulk density is affected by SOC
931 changes and thus was calculated by modifying the Adams (1973) equation to consider the bulk
932 density of the mineral soil (D_m), soil OM (D_{bOM}), and biochar (D_{bBC}) adapting the Adams [176]
933 equation.

934 Archontoulis et al. [177] built a biochar module in APSIM by including ten parameters to define
935 the biochar characteristics and 15 parameters concerning the soil-biochar interactions. The
936 coupled biochar module accounted for changes in soil OC, N mineralization and
937 immobilization, CEC, NH_4 adsorption and desorption, water balance, and bulk density, as a
938 response to biochar application. Unlike the other adaptations, the APSIM biochar module

939 considers a double-exponential decay rate and besides the labile and recalcitrant fractions and
 940 the allocation factors in the SOC pools, it regards the amount of biochar lost during application
 941 and the efficiency to retain biochar in the soil. The C fraction retained in soils is transferred
 942 from the FOM to the metabolic (BIOM) and humified (HUM) organic matter pools and the
 943 positive and negative PE were included as in Woolf et al. (2012). They assessed a range of
 944 values for the different parameters and compared the predictions to field observations,
 945 obtaining a mean relative absolute error (MRAE) from -0.4% to 13.1%.

946 **Table 2. Previous approaches to include the effects of bioeconomy coproducts on soil models**

| Model | Considered coproduct | Approach ^a | Reference |
|---------------------------------------|--|---|-----------|
| Equations embedded in Microsoft Excel | Biochar (pine, oak, and maize stalks pyrolyzed at 500°C) | $f_{C_L} = 0.122$, $k_L = 0.0038 \text{ d}^{-1}$, $f_{C_R} = 1 - C_L$, $MRT_R = 2000$, $k_R = 1.369 \text{ E}^{-6} \text{ d}^{-1}$, $f_r = 0.9$, $k_r = 0.03 \text{ d}^{-1}$ $BC(t) = BC0 \times [f_{C_L} * e^{-tk_L} + (1 - f_{C_L}) * e^{-tk_R}]$ $BCt(t) = BC0 \times [f_r * e^{-tk_r} + (1 - f_r)]$ $C_{m100y} = 11.68\%$, $C_{runoff100y} = 76.09\%$, $C_{down100years} = 0.13\%$, $C_{m2000y} = 20.65\%$, $C_{runoff2000y} = 74.83\%$, $C_{down2000years} = 0.52\%$ BC(T): Mass of Biochar at time t, BC0: Biochar added | [164] |
| RothC 26.3 | Biochar (maize residue, 500°C, slow pyrolysis) | C content = 37% (35-39%), $C_L = 7.5\%$ (5-10%), $C_R = 1 - C_L$, $\ln(2)MRT_L = 3$ (1-5), $\ln(2)MRT_R = 1000$ (500-50000), +PE = 6.9%, (0-13.8%), -PE = 3.6% (1.1-6.1%). f_{BIO} and f_{HUM} as standard RothC. $k'_{RPM} = k_{RPM}(1 + PE[BC])$, $k'_{DPM} = k_{DPM}(1 + PE[BC])$ $BC(t) = BC0 \times [f_{C_L} * e^{-k_L t} + (1 - f_{C_L}) * e^{-k_R t}]$ +PE = C mineralized as CO_2 , -PE = C transferred to HUM | [38] |
| RothC (BioEsoil) | Digestate, gaschar, ashes | FOM is distributed over the DPM and RPM based on h according to $DPM/RPM = 2.02 - 2.174 - h$ Digestate produced: 50%, h: 0.75. Gaschar produced: 50%, h: 1. Incineration ashes produced: 5%, h: 1 | [170] |
| Century | Biochar (wood pyrolyzed at 450°C) | Biochar composition: 61.7% C, 0.24% N, 95% lignin, 257 C:N ratio Biochar added as an organic amendment with C_R represented as 95% lignin content allocated in the slow pool ($MRT = 10-50$). The N input from biochar was considered as a mineral fertilizer. | [165] |
| EPIC | Biochar | Biochar characteristics: $Db_{BC} = 0.64 \text{ Mg m}^{-3}$, 72.9% C, 0.76% N, 4.6% ash, C:N = 120, H:C = 0.018, and O:C = 0.26 Biochar in SOC pools: $f_{Active} = 2\%$, $f_{Slow} = 60\%$, $f_{Passive} = 38\%$ CEC $CEC_{mix} = \frac{CEC_{soil} + \left(\frac{BC_{rate}}{M_{soil}}\right) \times CEC_{biochar}}{1 + \left(\frac{BC_{rate}}{M_{soil}}\right)}$ $CEC_{added} = \frac{(CEC_{mix} - CEC_{soil})10}{OM_{bc\&soil}}$ BCrate is the rate of biochar addition, Msoil is the mass of a slice of soil in 1 ha, CEC biochar is the CEC of biochar. | [174] |

| | | | |
|------------|--|---|-------|
| | | <p>pH: Modified Magdoff and Barlett (1985) equation</p> $pH_{new} = \frac{UpH - LpH}{1 + e^{-a(X_{new}-T)}} + LpH$ $X_{new} = \left(T - \frac{1}{A} \left(\ln \left(\frac{UpH - LpH}{pH - LpH} \right) - 1 \right) \right) + CEC_{added}$ <p>pH=soil pH, UpH= 7.30055, LpH= 3.495, A= 1.08, T= 6.6</p> <p>Db: Modified Adams (1973) equation</p> $Db = \frac{100}{\frac{SOM}{Db_{SOM}} + \frac{100 - SOM - BC}{Dm} + \frac{BC}{Db_{BC}}}$ <p>Db_{SOM}= 0.244 Mg m⁻³</p> <p>Average error= 30% (yield) and 8% (SOC)</p> | |
| APSIM | Biochar | <p>C content= 17-88%, C_L= 3-30%, MRT_L=0.3-25, MRT_R= 50-50000, C_{retained}= 40%, f_{BIO}= 0.05, f_{HUM}= 0.95</p> <p>PE is considered for each pool and k is modified according to Woolf et al., 2012.</p> <p>+PE_{FOM}= 0.1 (0-0.138) m² kg⁻¹ C, -PE_{FOM}= 0.05 (-0.30-0-0.15) m² kg⁻¹ C, +PE_{BIO}= 0.1 (0-0.15) m² kg⁻¹ C, -PE_{BIO}= 0.05 (-0.15-0) m² kg⁻¹ C, +PE_{HUM}= 0.1 (0-0.15) m² kg⁻¹ C</p> <p>MRAE = -0.4% to 13.1%</p> | [177] |
| RothC 26.3 | 8 EOMs. Digestates and bioethanol residues | <p>Additional pools: EOM-DEOM, EOM-REOM, EOM-HEOM</p> <p>f_{DEOM}= 0.09 (0-0.63), f_{REOM}= 0.70 (0.21-0.98), f_{HEOM}= 0.41 (0.06-0.78), k_{DEOM}= 89 y⁻¹ (11-330), k_{REOM}= 0.4 y⁻¹ (0.15-2.51), k_{HEOM}= 0.02 y⁻¹.</p> <p>Mean RMSE = 4.5%</p> | [147] |
| CANDY | Digestate | <p>k= 0.362-0.575 d⁻¹</p> <p>η AOM= 0.802 to 0.890.</p> | [171] |
| CANDY | Digestate | $C_{DG} = C_{FM} - C_{BG}$ <p>C inputs year 2000= 2905 kg C ha⁻¹ (1524 kg C_{rep} ha⁻¹). C inputs year 2011: 2965 kg C ha⁻¹ (1567 kg C_{rep} ha⁻¹).</p> <p>C_{rep} = 53%. η as determined in Prays et al., 2017.</p> | [172] |
| AMGv2 | Manure, digestate, compost, SS, peat, MSW, PCM | <p>h= IROC for the different EOMs in Lashermes et al., 2006.</p> <p>Digestate h= 0.65.</p> | [146] |
| CTOOLv2 | Manure digestate. Straw digestate | <p>C_{remain20y}= 12%</p> <p>Manure digestate: h=36.7%, Straw digestate: h=26.0%</p> | [173] |
| RothC 26.3 | Biochar (sugarcane bagasse, 550°C) | <p>Biochar submodule: FBC + RBC</p> <p>RBC= C_R - C_{leached}</p> <p>C_L= 3%, C_R= 97%, k_{RBC}= 0.00119 y⁻¹, C_{lost100years}= 11.9%, C_{leached}= 5.83%, C_{remain100years}= 83%, +PE= 21% and 91%</p> | [168] |

948 ^aValues in parenthesis represent the whole range of values, L: Labile, R: Recalcitrant, k: decay
949 rate, f: partition factor, C_m : C mineralized, C_{runoff} : C lost by runoff, C_{down} : C transported from
950 topsoil to subsoil, $C_{retained}$: C retained in soils, $C_{leached}$: C lost by leaching, C_{remain} : C remaining at a
951 given time, MRT: Mean residence time (years), PE: Priming Effect, [BC]: concentration of
952 biochar in the soil, Db : bulk density, CEC: Cation exchange capacity, C_L : Labile carbon, C_R :
953 Recalcitrant carbon, k_L : decay rate in labile pool, k_R : decay rate in recalcitrant pool, MRT_L :
954 Mean Residence time in labile pool, MRT_R : Mean Residence time in recalcitrant pool, f_r :
955 fraction of C available for runoff, k_r : runoff rate, +PE: positive priming effect, -PE: negative
956 priming effect, $OM_{bc\&soil}$: organic matter content within the soil and biochar mixture, Db_{SOM} :
957 Bulk density of SOM, Db_{BC} : Bulk density of biochar, UpH = upper oxisol pH, LpH = lower oxisol
958 pH, f_{BIO} : fraction of C transferred to BIO, f_{HUM} : fraction of C transferred to HUM, f_{DEOM} : fraction
959 of C transferred to DEOM, f_{REOM} : fraction of C transferred to REOM, f_{HEOM} : fraction of C
960 transferred to HEOM, h: humification coefficient, η : substrate use efficiency, EOM: Exogenous
961 organic matter, SOC: Soil organic carbon, SOM: Soil organic Matter, FPM: Fresh Plant Material,
962 FOM: Fresh Organic Matter, DPM: Decomposable plant material, RPM: resistant plant
963 material, BIO: Microbial Biomass, HUM: Humified organic matter, LAOC: Labile Added Organic
964 Carbon, DEOM: decomposable exogenous organic matter, REOM: resistant exogenous organic
965 matter, HEOM: humified exogenous organic matter, IROC: indicator of residual organic carbon,
966 FBC: Fresh biochar, RBC: Resistant biochar, SS: Sewage sludge, MSW: municipal solid wastes,
967 PCM: pelletized cattle manure, RMSE: root mean square error, MRAE: mean relative absolute
968 error

969 The understanding of the bioeconomy coproducts potential to build up SOC stocks is still under
970 research and thus the models presented in Table 2 are only a starting step on their inclusion in
971 soil process models and further research, parametrization, calibration, and validation is
972 required to confidently rely on these models for supporting bioenergy development decisions.
973 We categorized the strengths and weaknesses of the models in Table 2 to determine the
974 current SOC models with the major potentials to relate the crop residues export for
975 bioeconomy with the SOC dynamics induced by their use considering the return as coproducts
976 (Fig 8). The models with the highest potential are those cropland-focused, built with simple
977 structures, that require limited data inputs easily accessible at national scales and applicable to
978 different ecosystems.

1005 carbon sequestration and GHG emissions mitigation potential expose the urgency on
1006 developing, calibrating, and validating robust models that allow including the return of
1007 bioeconomy coproducts as soil amendments in an effort to improve the feedstock
1008 provision for bioenergy and biomaterials production.
1009 • We defined C conversion (Cc) and C recalcitrance (Cr) coefficients for pyrochar,
1010 gaschar, hydrochar, digestate, and lignocellulosic bioethanol molasses based on a
1011 comprehensive database including more than 600 records. These coefficients can be
1012 further adapted in soil models to assess the bioeconomy coproducts implications in
1013 SOC stocks evolution.

1014 **Data availability**

1015 The data that support the findings of this study are openly available in "[TBI - Toulouse](https://doi.org/10.48531/JBRU.CALMIP/WYWKIQ)
1016 [Biotechnology Institute - T21018](https://doi.org/10.48531/JBRU.CALMIP/WYWKIQ)" at <https://doi.org/10.48531/JBRU.CALMIP/WYWKIQ>

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