UMT PRESS

Planetary Sustainability
Journal Homepage: https://journal.umt.edu.my/index.php/planetsust/
eISSN: 3009-0105
DOI: http://doi.org/10.46754/ps.2026.01.002

CAN HYDROTHERMAL BIOMASS PROCESSING SERVE AS AN ANALOGUE OF MILLENNIA-SCALE NATURAL CARBON MATURATION? A UNIFIED PERSPECTIVE ON CARBONISATION, HUMIFICATION, AND FULVIFICATION

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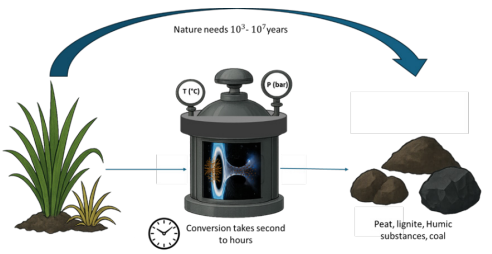
HIGHLIGHTS

- Hydrothermal processing mimics early natural carbon maturation pathways
- A unified scheme maps carbonisation, humification, and fulvification on Van Krevelen
- Hydrothermal products align with early diagenetic organic matter chemistry
- Hydrothermal pathways support soil restoration, peat alternatives, and carbon storage

GRAPHICAL ABSTRACT



ARTICLE INFO

Article History:
Received: 13 December 2025
Revised: 26 December 2025
Accepted: 26 December 2025
Published: 15 January 2026

Keywords:
Hydrothermal carbonisation, hydrothermal humification, artificial humic acids, artificial peat, carbon maturation.

ABSTRACT

Hydrothermal biomass processing provides a rapid and controllable approach to replicating the natural carbon maturation of organic matter, a process that typically spans millennia. Subcritical water treatment at elevated temperatures and pressures converts biomass into products analogous to those found in peat, lignite, and coal. This review examines three principal hydrothermal pathways, namely carbonisation, humification, and fulvification, which yield hydrochar, artificial humic acids, and fulvic-like acids, respectively. These products share similarities with natural soil organic matter in terms of carbon content, polarity, and stability. The Van Krevelen diagram serves as a valuable tool for comparing the transformation trajectories of these materials with those of natural carbon evolution. Analysing the effects of process variables such as temperature, pH, and feedstock composition facilitates the development

of tailored carbon materials for soil amendment, peat substitution, and carbon sequestration. The review also addresses technological challenges and scale-up requirements to advance future bioeconomy applications.

Introduction

The transformation of organic matter into stable carbon-rich solids is one of the most fundamental processes governing the long-term evolution of Earth's carbon cycle (Yang *et al.*, 2021). In natural environments, the conversion of plant residues into increasingly condensed and durable carbonaceous matter occurs through an intricate interplay of biological activity, geochemical alteration, and thermodynamic constraints (HRİSTOV *et al.*, 2021; Sarlaki *et al.*, 2021a). These processes unfold across enormous temporal scales, ranging from centuries in the upper horizons of peatlands to tens of millions of years in deep geological basins. Biomass is composed primarily of cellulose, hemicellulose, lignin, proteins, lipids, and extractives, and its chemical signature reflects the functional diversity of these biopolymers (Davies *et al.*, 2001; Chefetz & Xing, 2009). Over time, this organic matter undergoes progressive hydrolysis, fermentation, oxidative and reductive transformations, dehydration, decarboxylation, and eventual aromatisation (Amir *et al.*, 2006; Miralles *et al.*, 2012).

With progressive burial, the decline in microbial activity is accompanied by slow, geochemically mediated restructuring of organic matter that sequentially produces peat, lignite, sub-bituminous coal, bituminous coal, and ultimately anthracite (Fantle *et al.*, 2010; Sarlaki *et al.*, 2020, 2021b, 2023a, 2023b). Increasing compaction and temperature, rising by ~ 20°C/km to 35°C/km along the geothermal gradient, further constrain microbial processes and increasingly redirect coalification toward thermochemical reaction pathways. Over geologic timescales (10^6 to 10^8 years), dehydration, decarboxylation, aromatisation, and condensation reactions reorganise organic matter, yielding peat at shallow depths (< 10 to 20 m), lignite at intermediate burial (≈ 0.1 to 1 km), sub-bituminous and bituminous coals at deeper levels (≈ 1 to 4 km), and ultimately anthracite under the highest burial pressures, and temperatures (commonly > 4 km). These transformations reflect slow but continuous geochemical rates controlled primarily by temperature, pressure, and residence time within the sedimentary basin, rather than by biological processes. Each step in this continuum is marked by systematic reductions in O/C and H/C ratios, increasing aromatic condensation, and decreasing polarity (Amir *et al.*, 2006).

The natural carbon maturation of organic matter is governed primarily by temperature, heating rate, residence time, and pressure, with the thermal regime being especially decisive. From a chemical standpoint, natural carbon maturation represents a protracted, low-temperature, high-pressure transformation akin to slow pyrolytic decomposition, during which volatile species are progressively expelled. Under atmospheric conditions (~ 0.1 MPa), this process initiates near 230°C (Basu, 2010) or ~ 280°C (Demirbas, 2009). However, because lithostatic pressure increases by roughly 25 to 30 MPa/km of burial depth, the onset of organic matter breakdown can occur at much lower temperatures, around 120°C, or even as low as 70°C or 85°C to 95°C (Straka & Sýkorová, 2018).

Elevated pressures also favour the formation and preservation of the solid carbonaceous fraction (Straka & Sýkorová, 2018).

The genesis of humic substances occurs on geological timescales, controlled by a tightly coupled network of microbial transformations and abiotic reactions. Over the last century, both humus reserves and total soil carbon have progressively declined relative to their original baselines. In chernozem soils of Moldova, for instance, annual humus losses of about 0.51 to 0.71 t/ha indicate sustained depletion associated with long-term agricultural exploitation (Yang & Antonietti, 2020b). Such trends arise because natural humic substances are produced only through exceedingly slow microbial conversion of papyrus and sphagnum peat, a process that unfolds over more than 15,000 years (Yang & Antonietti, 2020b; M. Xu *et al.*, 2025; Meng *et al.*, 2025). Although humic substances typically represent just 2 to 8 wt% of topsoils, they occur at substantially higher concentrations in peat, brown coal, weathered coal, leonardite, and lignite deposits (Sarlaki *et al.*, 2024b).

The extraction and combustion of fossil carbon represent a rapid reversal of an ancient sequestration pathway, contributing substantially to planetary-scale perturbationsf the carbon cycle and the crossing of several planetary boundaries (Lehmann *et al.*, 2020; Reichenbach *et al.*, 2021). Hydrothermal processing provides a controlled, accelerated analogue of the earliest stages of natural carbon maturation (Luo *et al.*, 2025). Unlike pyrolytic or torrefaction-based thermochemical technologies that rely on dry, high-temperature conditions, hydrothermal processes operate in water rich environments under moderate temperatures and autogenic pressures (Sarlaki *et al.*, 2024a, 2024b). These conditions, typically occurring between 180°C and 250°C, mimic the physicochemical milieu of water-saturated sediments and early diagenetic settings (Ghaslani *et al.*, 2024). While hydrothermal processing reproduces the dominant chemical vectors of early carbon maturation, namely dehydration, decarboxylation, condensation, and aromatisation, it fundamentally differs from natural systems in pressure history, mineral mediation, and residence time, which remain orders of magnitude shorter and less geochemically complex. In these environments, the unique solvent and catalytic properties of subcritical water support ionic reactions, hydrolysis, dehydration, decarboxylation, and condensation, enabling chemical transformations that are analogous to those occurring naturally in peatlands but on far shorter timescales (Gu *et al.*, 2025; Wu *et al.*, 2025).

Hydrothermal carbonisation (HTC), hydrothermal humification (HTH), and hydrothermal fulvification (HTF) represent three mechanistically distinct but interconnected pathways within the broader hydrothermal domain (Ischia *et al.*, 2024; Marzban *et al.*, 2024b; Sarlaki *et al.*, 2024a). “Hydrochar” refers to the solid carbonaceous product of HTC dominated by dehydration and aromatisation reactions, “humins” denote insoluble polymeric condensation products formed primarily from sugar-derived intermediates in alkaline media like HTH and HTF solid products, and “artificial humic acids (AHAs)” describe alkali-extractable, oxygen-rich macromolecules generated via hydrothermal humification that are chemically analogous, but not identical to natural humic substances. Each hydrothermal pathway yields a characteristic class of carbonaceous materials. The HTC process produces hydrochar, a solid product with reduced oxygen content, intermediate aromaticity, and enhanced chemical stability (Cavali *et al.*, 2025). HTH produces AHAs with structural motifs similar to those of natural soil humus (Gu *et al.*, 2025). HTF yields dissolved oxygen-rich molecules similar to natural fulvic acids (Kohzadi *et al.*, 2023). Whereas HTC solid products (hydrochars) are more suitable for biofuel production due

to their higher degree of carbonisation, HTH products, AHAs, and hydrochars are better aligned with soil and plant growth applications. In contrast, HTF products, namely artificial fulvic acids (AFAs), are particularly well suited for hydroponic cultivation systems (Wu *et al.*, 2025).

Although HTC technologies have been extensively reviewed in the literature (Funke & Ziegler, 2010; Khan *et al.*, 2019; Ischia & Fiori, 2021; Djandja *et al.*, 2023; Wu *et al.*, 2023, 2025; Cavali *et al.*, 2025; Gu *et al.*, 2025), the emerging perspectives of HTH and HTF as purposeful routes to tailor the functional performance of hydrothermal products have only recently begun to take shape. In this article, we move beyond conventional reaction summaries and focus instead on how humification- and fulvification-driven pathways can be deliberately engineered to enhance the value and applicability of hydrothermal products. Specifically, we synthesise and reinterpret recent advances through (i) a unified, process-oriented mechanistic framework describing the staged maturation of carbon under hydrothermal conditions, (ii) a comparative analysis of how reaction environments steer the formation of artificial humic and fulvic acids versus hydrochar, and (iii) a property-function perspective linking molecular transformations to agronomic performance, contaminant control, and climate-smart soil applications. The article provides a novel synthesis that connects process design, chemical pathways, and practical deployment, thereby advancing existing reviews that primarily catalogue technologies without fully articulating their humification-centred potential.

Together, the HTC/HTH/HTC pathways allow the controlled design of functional carbon materials that span a broad region of the chemical space associated with natural organic matter and early coalification intermediates (Yang & Antonietti, 2020a, 2020b). This work develops a conceptual, mechanistic, and geological framework for interpreting hydrothermal biomass processing as an analogue of natural carbon maturation. It synthesises the fundamental reaction mechanisms that control hydrothermal transformation, evaluates the role of water-mediated chemistry, and highlights the structural and compositional evolution of hydrothermal products. The Van Krevelen diagram is used as a unifying analytical tool to visualise changes in the atomic hydrogen-to-carbon and oxygen-to-carbon ratios throughout hydrothermal reactions. This diagram shows how hydrothermal trajectories parallel the natural movement of biomass toward peat and early lignite precursors. The article also examines geological carbon maturation timescales to contextualise the dramatic acceleration achieved through hydrothermal engineering.

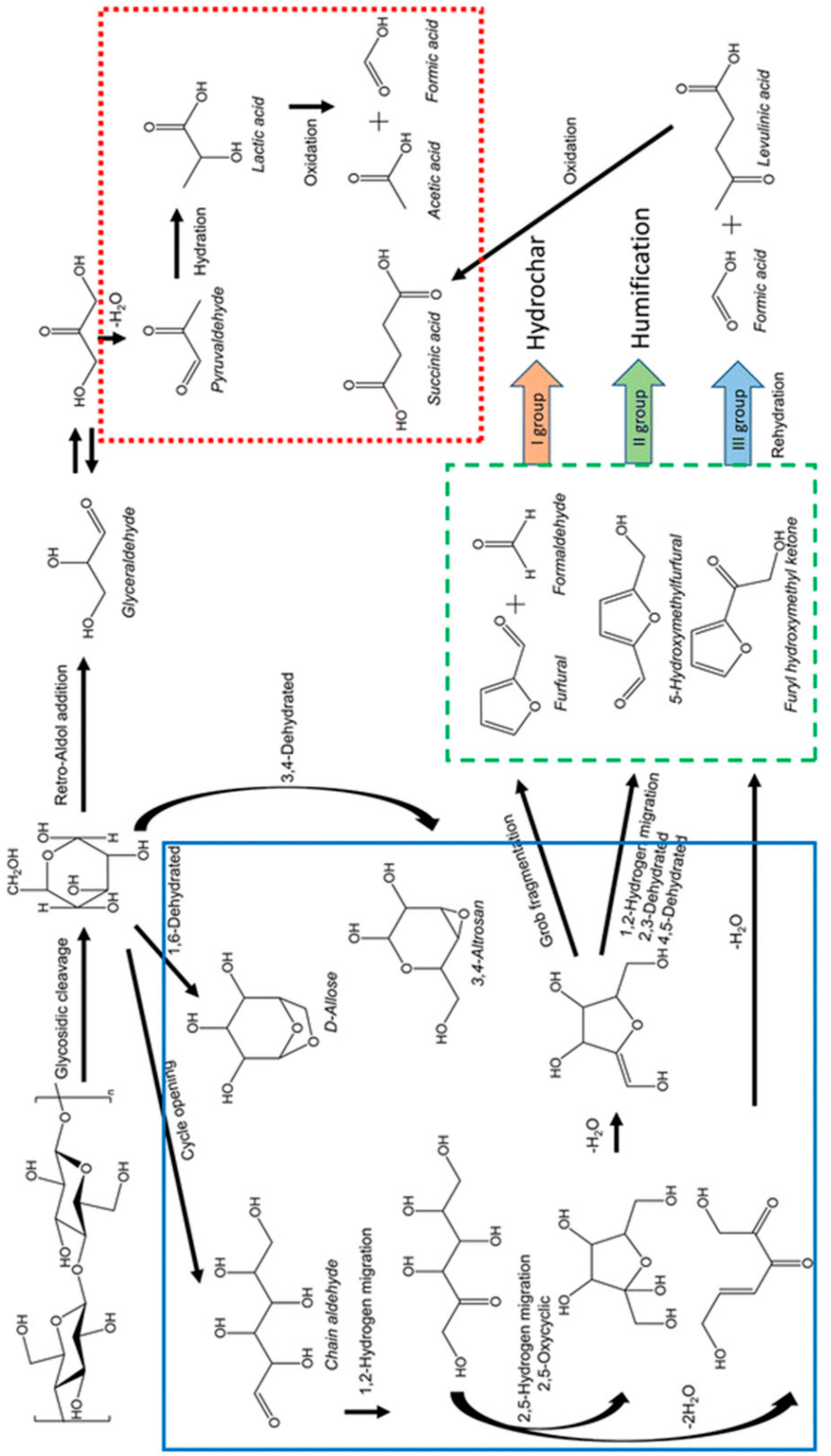
Hydrothermal Processes in The Boundary of Carbonisation

Hydrothermal processes involve the transformation of biomass in liquid process water at temperatures typically between 180°C and 250°C under autogenic pressures generated by the confined water phase (Cavali *et al.*, 2023). However, the pressure is not always purely autogenic, since additional pressure (10 bar or more) can be generated by gaseous reaction products, mainly carbon dioxide, which is strongly influenced by the acidity or alkalinity of the hydrothermal medium (Marzban *et al.*, 2024b). Subcritical water exhibits physicochemical properties that make it a uniquely reactive medium for organic transformations. As temperature increases, the dielectric constant of water decreases, and its ionic product increases by several orders of magnitude, which significantly enhances both acid- and base-catalysed reactions (Akiya & Savage, 2002). In contrast to natural carbon maturation, which is strongly mineral-mediated, catalytic effects in hydrothermal systems are

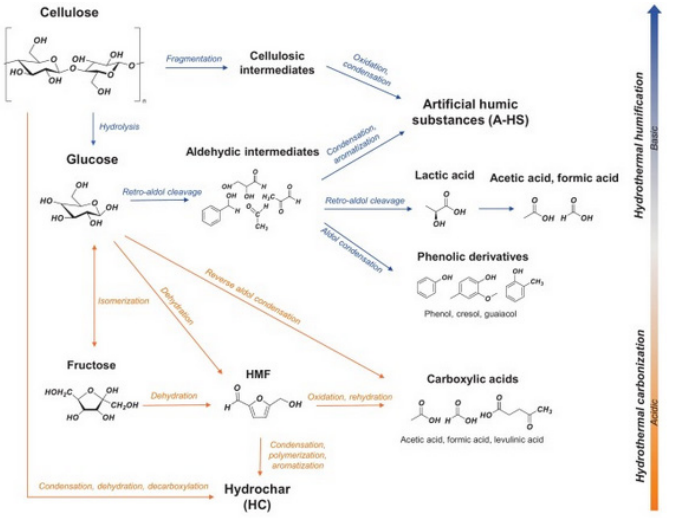
primarily influenced by feedstock-derived ash, organic acids generated during biomass decomposition, added acids or bases, dissolved inorganic species, and reactor materials. The contributions of these factors to pH buffering, intermediate complexation, and promotion of secondary reactions, however, remain insufficiently quantified. These effects were extensively discussed in early research, which established fundamental concepts in the HTC field under slightly acidic or neutral water conditions (Titirici *et al.*, 2007; Titirici & Antonietti, 2010). They were later quantified for polymer and biomass systems under moderate alkaline hydrothermal conditions, known as HTH (Yang & Antonietti, 2020b). Most recently, these principles have been demonstrated for a broad range of real biomass feedstocks under strongly alkaline hydrothermal conditions, leading to what is now known as the process (Marzban, 2024).

Across acidic, neutral, and alkaline conditions, hydrothermal environments facilitate dehydration, decarboxylation, depolymerisation, rearrangement, aromatisation, and condensation reactions at temperatures far lower than those required for dry thermochemical processes such asyrolysis (Libra *et al.*, 2011). Hydrothermal environments, therefore, occupy the chemical space between biological degradation and geological diagenesis, enabling reaction pathways that resemble early natural carbon maturation but on accelerated timescales. This analogy to natural early diagenetic chemistry is consistent with studies on soil and geological carbon formation by (Yang *et al.*, 2021), and is further supported by the recognition of artificially produced humic substances as one of the International Union of Pure and Applied Chemistry's (IUPAC) Top Ten Emerging Technologies in Chemistry in 2021 (Gomollón-Bel, 2021). Within the broader domain of hydrothermal processing, three major pathways can be distinguished: HTC, HTH, and HTF (Ischia *et al.*, 2026, 2024). Although these pathways share a familiar aqueous environment, they differ in reaction severity, product distribution, and mechanistic emphasis.

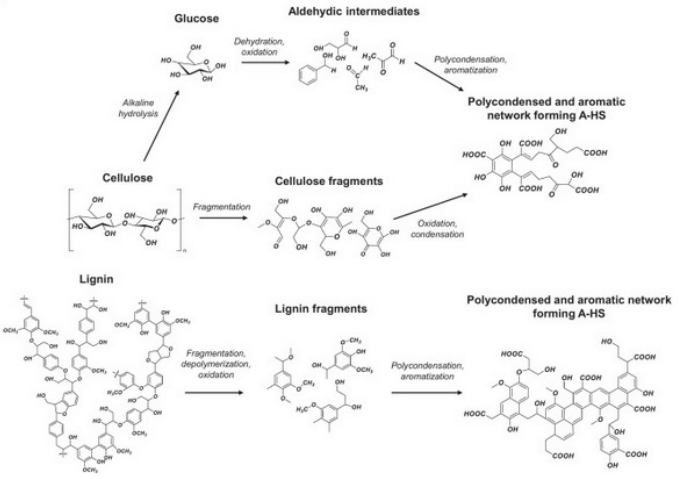
HTC yields a predominantly solid carbon product known as hydrochar and mechanistic studies by Tkachenko *et al.* (2023) and Marzban *et al.* (2024b) clearly describe dehydration and decarboxylation as the controlling reactions that lower the oxygen-to-carbon ratio. HTH emphasises the formation of humic acid-like macromolecules with colloidal and sorptive properties similar to those natural humus (Ischia *et al.*, 2026). HTF yields highly oxygenated, low-molecular-weight acids, and aromatic fragments that resemble natural fulvic acids (Marzban *et al.*, 2024b). The distinction between HTC, HTH, and HTF is illustrated in Figure 1 (a) reproduced from Tkachenko *et al.* (2023) and Figures (b) and (c) from Ischia *et al.* (2026). Collectively, these pathways generate a continuum of carbon-rich materials and dissolved organic compounds analogous to those found in soils, peatlands, and early geological deposits (Sarlaki *et al.*, 2024b). The following section outlines the key differences between HTC, HTH, and HTF, examining their distinct reaction conditions, mechanisms, and resulting products.


Glycosidic cleavage
Retro-Aldol addition
Glyceraldehyde
-H2O
Pyruvaldehyde
Hydration
Lactic acid
Oxidation
Acetic acid
Formic acid
Succinic acid
Oxidation
Levulinic acid
Formic acid
Rehydration
I group
Hydrochar
II group
Humification
III group
Furfural
Formaldehyde
5-Hydroxymethylfurfural
Furyl hydroxymethyl ketone
3,4-Dehydrated
1,6-Dehydrated
Cycle opening
D-Allose
3,4-Altrosan
Grob fragmentation
1,2-Hydrogen migration
2,3-Dehydrated
4,5-Dehydrated
-H2O
Chain aldehyde
1,2-Hydrogen migration
2,5-Hydrogen migration
2,5-Oxycyclic
-H2O
-2H2O

(a)



(b)



(c)

Figure 1: (a) Proposed degradation trajectories of biomass governed by base-catalysed retro-aldol cleavage and acid-catalysed dehydration across thermochemical humification regimes. Pathway differentiation reflects alkaline loading: Group I: HTC, where KOH is < 1 equivalent relative to carbohydrate content; Group II: HTH, with 1 to 2 equivalents; Group III: HTF, where alkali exceeds 2 equivalents; (b) hydrothermal conversion of carbohydrates, illustrating the transition from HTC (in orange) to HTH (in blue), passing from predominantly acidic or basic conditions; and, (c) formation mechanisms of AHSs from HTH of glucose, cellulose, and lignin

Hydrothermal Carbonisation (HTC)

HTC is an aqueous thermochemical process that converts biomass into carbon-rich solids through ionic reactions driven by the unique properties of subcritical water. The decrease in the dielectric constant and the increase in the ionic product of water at elevated temperaturestrongly promote hydrolysis, dehydration, recondensation, and aromatisation reactions (Titirici & Antonietti, 2010). Cellulose is first cleaved into glucose, which undergoes isomerisation and acid-catalysed dehydration to form hydroxymethylfurfural. This intermediate condenses into polyfuranic structures that assemble into spherical or porous hydrochars enriched in oxygen-containing functional groups (Hu *et al.*, 2010; Titirici & Antonietti, 2010). These features distinguish HTC materials from those formed by dry pyrolysis (Libra *et al.*, 2011). Hemicellulose behaves similarly to cellulose but is more reactive. Using D-xylose as a representative hemicellulose sugar, it has been shown that D-xylose rapidly forms furfural during HTC, with furfural acting as the primary intermediate responsible for hydrochar formation. Reported hydrochar yields fall within the range of approximately 45% to 60%, with feedstock-dependent yields decreasing in the order lignin, wood meal, cellulose, and D-xylose (Kang *et al.*, 2012). Increasing the HTC reaction temperature results in hydrochars with higher carbon content and enhanced aromatic character. For example, hydrochar derived from quince shows an increase in carbon content from 64.6% at 220°C to 70.2% at 250°C, accompanied by a decrease in oxygen from 29.8% to 24.4% and a slight decrease in hydrogen from 2.99% to 2.89% (Table 1). Similar trends are observed for other feedstocks, such as apple, pear, beetroot, and carrot, which also show increasing carbon content and HHV with increasing temperature. In contrast, hydrogen and oxygen contents decrease (Table 1). These elemental changes confirm that higher temperatures promote dehydration and aromatisation reactions, leading to a more carbon-enriched hydrochar structure (Marzban *et al.*, 2022).

Their GC-MS data clearly show furfural formation at 265°C and their FTIR data show the disappearance of ether bonds and the formation of aromatic peaks. Lignin follows a distinct HTC pathway. Because lignin is a phenolic macromolecule, it does not fully dissolve in subcritical water. Lignin was shown to partially hydrolyse at the surface, releasing phenolic fragments that subsequently recondensed into polyaromatic and phenolic-rich hydrochar. The proposed formation pathway involves cleavage of methoxy and ether bonds, generation of phenolic fragments, and surface recondensation into stable aromatic carbon. Among all tested components, lignin produces the highest char yield due to its intrinsic aromatic stability and its tendency toward solid–solid conversion under HTC conditions (Kang *et al.*, 2012). Lignin converts via non-radical fragmentation reactions rather than radical fragmentation as in pyrolysis, and contributes thermally stable aromatic units to the hydrochar structure (Libra *et al.*, 2011). Together, these foundational studies show that HTC is governed by carbohydrate dehydration chemistry and lignin recondensation chemistry, producing structured carbonaceous materials under mild hydrothermal conditions.

Table 1: Properties of the initial feedstock and obtained hydrochar at different HTC temperatures ranged from 220˚C to 250˚C

Types of Feedstocks	Ultimate Analysis, HHV, Solid Yield (SY%), and Energy Yield (EY%)	Fresh Feedstock	Hydrochar			
			T = 220˚C	T = 230˚C	T = 240˚C	T = 250˚C
Quince	C%	47.51	64.64	67.10	69.55	70.20
	H%	3.83	2.99	3.00	2.89	2.89
	N%	0.83	0.85	0.88	0.87	0.91
	S%	0.20	0.41	0.34	0.32	0.32
	A%	2.4	1.28	1.10	1.34	1.30
	O%	45.23	29.83	27.58	25.03	24.38
	HHV (MJ/kg)	18.71	24.70	25.38	26.55	27.42
	SY%		56.91	54.30	53.01	49.87
	EY%		75.12	73.66	75.21	73.07
Apple	C%	47.69	66.64	68.74	70.09	71.77
	H%	4.26	3.20	3.25	3.35	3.12
	N%	1.39	1.01	1.08	1.06	1.13
	S%	0.17	0.25	0.23	0.21	0.23
	A%	3.40	0.98	0.81	1.16	1.10
	O%	43.09	27.92	25.89	24.13	22.65
	HHV (MJ/kg)	18.84	25.99	26.96	28.26	28.65
	SY%		53.90	52.34	49.20	47.66
	EY%		74.37	74.9	73.79	72.48
Pear	C%	47.68	64.75	66.16	69.40	71.77
	H%	5.07	3.41	3.33	3.29	3.41
	N%	0.51	0.79	0.80	0.86	0.93
	S%	0.14	0.40	0.26	0.21	0.19
	A%	4.86	1.25	0.97	0.82	1.02
	O%	41.74	29.40	28.48	25.42	22.68
	HHV (MJ/kg)	17.85	25.21	26.04	27.46	28.30
	SY%		44.62	42.56	40.39	38.52
	EY%		63.01	62.08	62.13	61.08
Beetroot	C%	45.16	62.97	65.23	70.01	70.21
	H%	4.19	3.06	3.04	3.05	3.30
	N%	2.12	2.61	2.73	2.98	3.08
	S%	0.20	0.26	0.28	0.28	0.26
	A%	8.63	4.63	5.20	3.19	5.39
	O%	39.71	26.47	23.52	20.49	17.76
	HHV (MJ/kg)	16.99	24.79	25.33	26.82	27.17
	SY%		43.92	41.42	37.01	36.86
	EY%		64.09	61.75	58.43	58.95

Carrot	C%	43.24	56.28	60.4	63.44	65.93
	H%	4.34	3.35	3.57	3.42	3.37
	N%	1.17	1.62	1.89	2.14	2.21
	S%	0.18	0.21	0.21	0.21	0.23
	A%	11.54	11.49	11.45	13.12	13.68
	O%	39.53	27.05	22.48	17.67	14.58
	HHV (MJ/kg)	16.07	22.29	23.85	25.39	27.00
	SY%		39.81	33.32	31.53	29.47
	EY%		55.20	49.43	49.81	49.51

In HTC, under mildly acidic conditions, limited amounts of alkaline additive allow the pH to drop early in the reaction. This shift promotes the conversion of sugars, mainly glucose from cellulose, into furan compounds and organic acids. These intermediates rapidly condense, forming a solid, carbon-rich material that visibly separates from the liquid phase. The resulting solid is dense and well-formed, while the remaining liquid is clear and contains low concentrations of dissolved organics. Spectral data indicate the presence of oxygenated aliphatic compounds in solution, while signals associated with unsaturated or aromatic structures are largely absent (Tkachenko *et al.*, 2023). These observations suggest that reactive furan derivatives are rapidly removed from the liquid phase by condensation reactions into the solid phase. The lignin component of the biomass remains unchanged primarily during this process, undergoing only slight chemical transformation. It contributes structurally to the solid product but does not produce significant quantities of dissolved aromatic compounds. As mentioned previously (Kang *et al.*, 2012), lignin yielded the highest hydrochar yield compared to wood meal, cellulose, and D-xylose because it remained in the solid phase under HTC conditions. In general, elemental analysis of HTC products confirms a shift toward carbon-enriched material with reduced oxygen content, consistent with dehydration as the dominant transformation pathway (Tkachenko *et al.*, 2023).

Hydrothermal Humification (HTH)

HTH emerges when moderate alkali concentrations, typically less than two equivalents relative to the carbohydrate content, maintain the solution in a neutral or slightly alkaline range throughout most of the reaction (Marzban, 2024). Under these conditions, carbohydrates do not immediately dehydrate to furans. Instead, they undergo retro-aldol cleavage (Tkachenko *et al.*, 2023). Glucose reacts through cleavage of the carbon-carbon bond between carbon three and carbon four to form glyceraldehyde and dihydroxyacetone. These intermediates undergo further rearrangement to pyruvaldehyde and lactic acid. Alkali also accelerates cellulose hydrolysis by weakening hydrogen bonding between chains and by direct nucleophilic attack at the glycosidic oxygen (H. Xu *et al.*, 2025). As a result, cellulose conversion is more extensive under HTH than under HTC. Lignin undergoes significantly greater transformation in this regime. The phenolic oxygen is deprotonated to form phenolate ions,

which are more reactive toward cleavage of the beta oxygen-four and alpha oxygen-four linkages. Deprotonated phenolic units undergo oxidative coupling through carbon–carbon bond formation or carbon–oxygen coupling to form larger aromatic clusters. Quinone and semiquinone intermediates appear during this process and drive further condensation by redox cycling (Ischia *et al.*, 2024; Marzban *et al.*, 2024b).

This shift in reaction chemistry is also accompanied by significant changes in the product composition. Increasing the concentration of KOH during hydrothermal treatment results in a marked decrease in furfural, hydroxymethylfurfural (HMF), and phenolic derivatives in both solid and liquid phases. Specifically, furfural concentrations in the liquid phase drop from approximately 32 mg/L under acidic conditions to nearly zero at KOH concentrations above 30% [Figure 2 (b)] (Ischia *et al.*, 2026). This reduction is most prominent at the highest KOH level, where the concentration of dissolved aromatics is far lower than in treatments without alkali (Marzban *et al.*, 2024b). In the solid products, aromatic content remains relatively consistent but lower than typical HTC outputs, indicating that new aromatic structures are less likely to form under these conditions (Marzban *et al.*, 2024b). On the other hand, as shown in Figures 2(a) and 2(c), the concentrations of sugars and organic acids increase with higher alkali levels, indicating enhanced deconstruction of cellulose and hemicellulose. Lactic acid, which is nearly absent under acidic conditions, rises to over 0.3 g/L, while formic acid increases from zero to approximately 0.6 g/L. Notably, the lactic acid concentration reaches several times the levels observed in conventional treatments (Ischia *et al.*, 2026). Fructose and arabinose also appear more readily, suggesting a more profound conversion of saccharides. The production of alcohols remains mostly unchanged, implying that KOH has a limited effect on alcohol generation pathways. While increased levels of organic acids and soluble sugars can be beneficial for downstream applications, their elevated levels may require further treatment to ensure suitability for use in soil or environmental systems (Marzban *et al.*, 2024b).

Aldehydes formed from retro-aldol fragmentation participate in aldol condensation. For example, glyceraldehyde can form enolate ions under alkaline conditions, which attack carbonyl groups of other aldehydes to yield alpha-beta unsaturated carbonyl compounds. These are classical precursors for aromatic ring formation. Repeated condensation and cyclisation produce aromatic structures that closely resemble the phenolic and arenic domains of natural humic acids (Sarlaki *et al.*, 2024a).

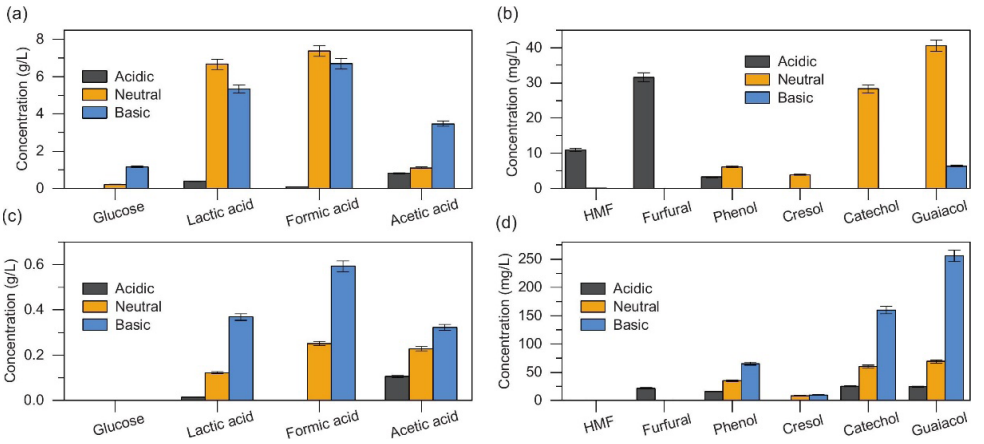


Figure 2: HPLC analysis of the aqueous phase following hydrothermal treatment, showing the effect of final pH on the composition. (a) and (b) represent products derived from cellulose, while (c) and (d) correspond to compounds derived from lignin

Hydrothermal Fulvification (HTF)

HTF refers to the transformation pathway that occurs under strongly alkaline hydrothermal conditions, typically when the molar ratio of base to carbohydrate exceeds two (Kohzadi *et al.*, 2023; Marzban, 2024; Marzban *et al.*, 2024b). Under these conditions, the reaction medium remains stably alkaline throughout the process, which fundamentally alters the reaction mechanisms compared to HTC and HTH. In HTF, the chemistry is dominated by base-catalysed reactions, particularly retro-aldol cleavage and aldol condensation, leading to the accumulation of short-chain organic acids and highly functionalised soluble organic matter. The alkaline environment suppresses acid-catalysed dehydration and aromatisation reactions, thereby inhibiting the formation of furans and phenolic condensation products. Instead, carbohydrates such as glucose undergo cleavage at specific carbon–carbon bonds, yielding intermediates such aslyceraldehyde and dihydroxyacetone (Marzban, 2024). These are rapidly converted to lactic acid and other carboxylic acids via further rearrangement and oxidation steps. As a result, the concentration of lactic acid increases significantly, while formic acid and other aliphatic acids also rise. The formation of furan derivatives is effectively halted, and any potential aromatic structures are instead diverted toward oxidation and fragmentation (Tkachenko *et al.*, 2023).

The chemical profile of the HTF process is characterised by the near-complete conversion of carbohydrates to soluble products. This includes a broad range of organic acids, many of which are detected in both monocarboxylic and polycarboxylic forms. Aromatic content in the liquid and solid fractions is minimal, and any aromatic compounds that remain are typically highly oxidised and functionalised, rather than condensed (Marzban, 2024). These are likely stabilised in the aqueous phase through deprotonation of phenolic groups and formation of phenolate ions. The final product is a mixture rich in fulvic-like substances: Low-molecular-weight, water-soluble organic compounds bearing multiple functional group such as carboxylic acids, hydroxyls, and residual carbonyls (Tkachenko *et al.*, 2023). In terms of physical outcomes, the HTF pathway yields almost no solid hydrochar. The bulk of the biomass carbon is solubilised, forming

either true solutions or highly stable colloidal dispersions. The stability of these systems is due to the presence of ionised functional groups that prevent aggregation or precipitation, even upon cooling or storage. This high solubility is one of the defining features of HTF, distinguishing it from HTC and HTH, where more carbon remains sequestered in the solid phase (Tkachenko *et al.*, 2023).

From a chemical standpoint, HTF represents a shift away from condensation and polymerisation, favouring fragmentation and functionalisation. It offers a promising route for the production of bio-derived chemicals, particularly organic acids and fulvic substances, but may require downstream processing to remove excess alkalinity and reduce phytotoxicity before environmental application. The selectivity and solubilisation efficiency of HTF make it attractive for applications in biorefinery, wastewater treatment, or carbon recycling processes focused on dissolved organic matter (Tkachenko *et al.*, 2023).

In HTF, most reaction products remain dissolved in the liquid phase as organic acids, whose concentrations can be further enriched, while furanic compounds are essentially absent. The fulvification pathway proceeds primarily through base-catalysed aldol condensation, generating linear, highly soluble biopolymeric structures commonly described as fulvic-like acids (Figure 3). When excess alkali is supplied, nearly all carbohydrates are converted via retro-aldol reactions, even after complete consumption of these carbohydrates, residual alkali maintains a persistently high pH. Under such alkaline conditions, ketones and aldehydes become particularly reactive and can participate in secondary transformations, yielding intermediates such as pyruvaldehyde, levulinic acid, and glyceraldehyde (Kohzadi *et al.*, 2023).

HTF is further evidenced by the progressive transformation of aromatic compounds into humic- and fulvic-type structures. A relatively higher abundance of lactic acid, compared with formic and acetic acids, within the hydrochar also signals a dominant fulvification tendency. Under HTF conditions, the resulting hydrochar typically exhibits reduced carbon content (≈ 35.14%), lower higher heating value (≈ 16.08 MJ/kg), and limited porosity (BET ≈ 4.80 m²/g) relative to raw wheat straw (Kohzadi *et al.*, 2023). Compared with HTC, which performed at neutral or acidic pH, the solid product shows lower carbon content and higher ash levels, due to the retention of organic–inorganic constituents. Accordingly, the reduced HHV is directly linked to a decrease in carbon content, while decreases in H/C and O/C ratios indicate the removal of hydrogen and oxygen and the formation of a more condensed carbon matrix (Kohzadi *et al.*, 2023). At a KOH-to-carbohydrate ratio of 4.2 and reaction conditions of 200°C for 12 hours, the HTF generated hydrochar at a yield of 43.5%, with a mean particle size of approximately 18.5 μm (Kohzadi *et al.*, 2023).

Regarding alkali dosage, increasing KOH markedly decreased concentrations of furfural, HMF, and phenolic derivatives, especially catechol, suggesting that either acidic environments are required for phenol liberation or that alkaline conditions promote their subsequent consumption. Meanwhile, concentrations of soluble sugars (glucose and fructose) and several organic acids (lactic, succinic, and formic acids) rose substantially, reaching up to 65 g/L in the liquid phase and 28 g/kg in the hydrochar. In contrast, acetic acid remained near 1 wt% due to cleavage of acetyl groups from hemicellulose and lignin (Tkachenko *et al.*, 2023). Importantly, the elevated organic acid content produced during HTF represents a value-added stream with potential application in white biotechnology, including biogas production (Marzban *et al.*, 2024b).

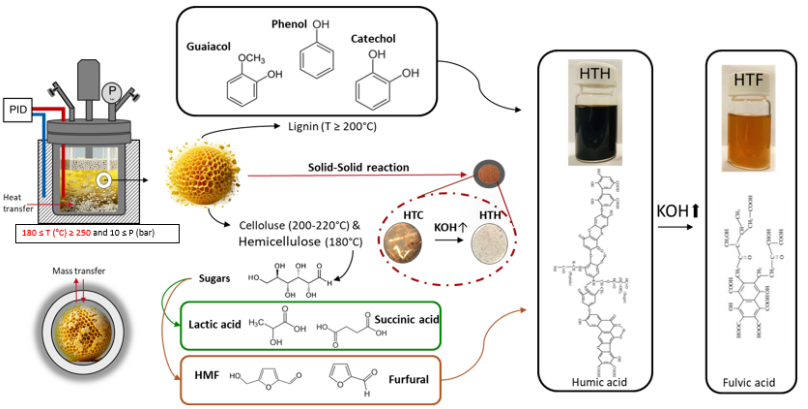


Figure 3: Transformation mechanisms of humification and fulvification pathways in the hydrothermal conversion of biomass and the production of artificial humic acids and artificial fulvic acids
Source: Marzban *et al*. (2024) under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0). © The Author(s) 2024. Published by Biochar (Springer Nature); Ischia *et al*. (2026); Bioresource Technology (2026); CC BY license

The Hydrothermal Carbon Evolution

The Van Krevelen diagram maps the progression from biomass (high O/C, H/C) through peat, lignite, subbituminous, bituminous, to anthracite (low O/C, H/C) (Figure 4). It provides a framework for interpreting how the elemental composition of biomass evolves during hydrothermal processing and how these trajectories parallel early geological carbon maturation (Palacio Lozano *et al.*, 2021). The diagram visualises this transformation by plotting atomic H/C versus O/C ratios, revealing the dominant chemical reactions driving compositional shifts (Figure 4). Dehydration removes water, leading to a downward movement due to the simultaneous loss of hydrogen and oxygen. Decarboxylation eliminates carbon dioxide, leading to a diagonal shift with a sharp decrease in O/C and a moderate change in H/C. Decarbonylation causes a similar but milder diagonal shift due to the removal of CO. In oxygen-rich substrates, retro-aldol cleavage breaks C–C bonds, generating smaller aldehydes and acids that may undergo aldol condensation, thereby increasing molecular complexity and carbon density. These condensation reactions, along with partial oxidation and limited aromatic ring formation, move the material toward the lower left of the diagram, indicating reduced polarity and increased structural stability. Overall, these pathways mirror the geochemical routes of early carbon maturation in nature (Palacio Lozano *et al.*, 2021).

Biomass transformations under HTC, HTH, and HTF follow distinct chemical pathways that are influenced by pH and alkali concentration. In HTC, which takes place under acidic conditions without added alkali, glucose and cellulose undergo dehydration reactions that generate intermediates like HMF and furfural. These quickly condense into insoluble, carbon-rich solids dominated by aromatic structures. Lignin remains mostly intact, and the resulting hydrochar exhibits a low O/C ratio. The trajectory in Van Krevelen space shows a steep decline in the O/C ratio with little change in H/C (Figure 4), characteristic of dehydration and aromatic condensation reactions (Marzban *et al.*, 2024a).

In contrast, HTH occurs when moderate alkali is present, allowing the pH to remain in a neutral or weakly basic range. Under these conditions, glucose undergoes retro-

aldol cleavage to form dihydroxyacetone and glyceraldehyde, which are converted into organic acids such as lactic acid. Cellulose is more extensively hydrolysed due to base activation, and lignin is transformed into reactive phenolates that further condense into artificial humic structures. Aromatic condensation is significantly suppressed, and instead, larger oxygenated molecules form. In Van Krevelen terms (Figure 4), this results in a moderate decrease in O/C ratio and a relatively higher H/C ratio compared to HTC (Tkachenko *et al.*, 2023). HTF represents the most alkaline regime, where nearly all carbon is shifted into the liquid phase. Furan formation is completely avoided, and instead, soluble products such as formic acid, acetic acid, lactic acid, and fulvic-like colloids dominate. Lignin is almost fully depolymerised into small soluble phenolic fragments. The resulting dark process liquid is highly stable and rich in dissolved organic matter. The Van Krevelen position reflects oxidative fragmentation with increased oxygen content and minimal carbon condensation (Tkachenko *et al.*, 2023).

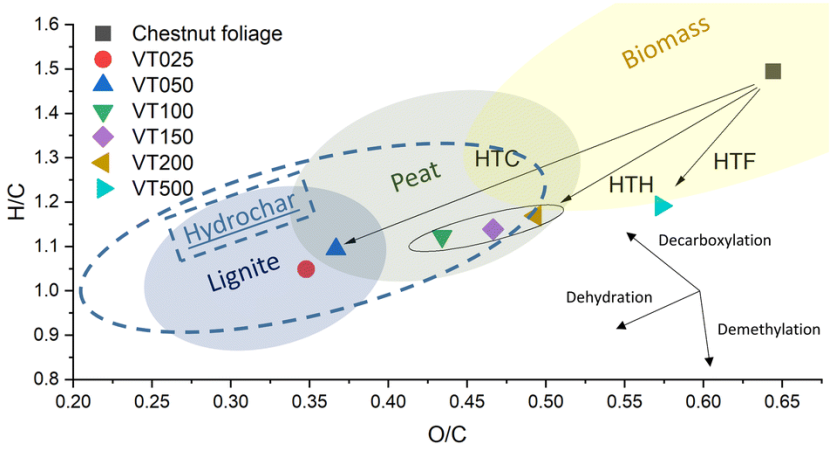


Figure 4: The Van Krevelen diagram among the three thermochemical humification mechanisms of HTC (no KOH, VT025, and VT050), HTH (mild KOH, VT100, VT150, and VT200), and HTF (excessive KOH and VT500) based on the dose of alkali used in the hydrothermal system.

The H/C and O/C ratios of hydrochar, humin, and artificial humic substances derived from glucose, cellulose, and lignin vary notably across acidic, neutral, and alkaline hydrothermal conditions. For glucose, hydrochars formed under acidic conditions and humins under neutral conditions display similar elemental composition, while artificial humic substances formed under alkaline conditions show an apparent decrease in both H/C and O/C ratios due to increased condensation and deoxygenation. In the case of cellulose, hydrochars formed under acidic conditions have the lowest H/C and O/C ratios, reflecting strong aromatisation and dehydration. Under neutral and alkaline conditions, humins and humic acids retain more oxygenated functionalities, leading to higher H/C and O/C ratios, especially in the neutral regime. With increasing alkalinity, cellulose-derived humic acids become more condensed, lowering both ratios. Lignin shows relatively stable H/C ratios between acidic and

neutral conditions, but a substantial drop in O/C under alkaline treatment indicates enhanced removal of oxygen functionalities and aromatic condensation. Overall, acidic conditions promote carbonisation and the loss of heteroatoms, while neutral and, especially, alkaline conditions retain more functional groups or drive selective condensation depending on the substrate and the product type (Ischia *et al.*, 2026).

In summary, while the Van Krevelen diagram offers a powerful tool to track the chemical evolution of biomass during thermal processing, the final position of each product on this diagram reflects not only intrinsic reaction pathways but also key operational parameters. Among these, temperature is the most influential factor, driving dehydration and condensation reactions that increase aromaticity and carbon content in the solid phase. Higher temperatures can shift the composition of hydrochar toward that of coal-like materials (Marzban *et al.*, 2022), particularly when coupled with alkaline conditions that enhance solubilisation and the formation of artificial humic and fulvic substances in the liquid phase (Ischia *et al.*, 2026). The composition of the original biomass, especially its cellulose, hemicellulose, lignin, and inorganic fractions, further determines the extent of these transformations. Although reaction time plays a smaller role, the biomass-to-water ratio can still significantly influence both yield and elemental distribution. Understanding how these variables shape reaction trajectories within the Van Krevelen space is essential not only for interpreting experimental data but also for engineering tailored processes and carbon products. These insights form the foundation for the next section, which explores how this knowledge can guide the development of practical applications in soil management, material design, and sustainable bioeconomy systems.

Implications for Carbon Management and Climate Mitigation

The acceleration of carbon maturation achieved through hydrothermal processing offers several promising pathways for climate mitigation, soil restoration, and the development of a circular bioeconomy. Because biomass acquires carbon directly from the atmosphere through photosynthesis, stabilising that carbon through hydrothermal conversion creates opportunities for medium- to long-duration carbon storage. Hydrochar, AHAs, and fulvic-like dissolved organics each contribute differently to carbon cycling depending on their chemical structures and environmental behaviours (Yang *et al.*, 2024).

AHAs are increasingly recognised as multifunctional biostimulants and soil amendments that improve soil fertility, nutrient cycling, and plant performance while contributing to soil carbon sequestration and GHG mitigation (Figure 5) (Sarlaki *et al.*, 2024b; Antu *et al.*, 2025). Their application enhances dissolved and total organic carbon, nutrient availability, and pH buffering, particularly in degraded soils (Ji *et al.*, 2024; Yuan *et al.*, 2025a, 2025b). AHAs also enhance phosphorus retention through electrostatic interactions and complexation, thereby limiting leaching under fluctuating environmental conditions (Zhao *et al.*, 2024). By stimulating microbial metabolism and enzyme activities, AHAs increase microbial biomass and necromass formation, thereby stabilising long-term soil carbon pools (Tang *et al.*, 2021; Meng *et al.*, 2025). Spectroscopic analyses reveal structurally complex AHA matrices with aromatic and aliphatic domains that resist rapid mineralisation while continuing to influence rhizosphere processes (Meng *et al.*, 2025).

Operating at the soil–microbe–plant interface, AHAs consistently promote root development, biomass accumulation, and

yield formation through improved rhizosphere nutrient dynamics and photosynthetic efficiency (Yuan *et al.*, 2025a, 2025b). They enrich functional microbial groups involved in carbon sequestration and nitrogen cycling, and AHA-based fertiliser formulations markedly enhance nitrogen-use efficiency by synchronising nitrogen release with crop demand (Jin *et al.*, 2023; Zeng Liu *et al.*, 2025). AHAs also increase stress tolerance to salinity, alkalinity, and contaminant exposure by modulating hormone signalng and antioxidant pathways (Yang *et al.*, 2023). In contaminated soils, combinations of AHAs with biochar or functional microbes immobilise Cd and Cr (VI), improve nutrient status, and substantially increase plant growth and root development (Peng *et al.*, 2025; Qin *et al.*, 2025).

Beyond immediate agronomic benefits, AHAs make strategic contributions to climate-smart agriculture by strengthening soil carbon pools and reducing CO_2 losses. They accelerate humification, enhance microbial carbon assimilation, and promote aggregate formation and iron–carbon interactions that physically and chemically protect organic matter (Lan *et al.*, 2024; Peng *et al.*, 2024). Their chemically stable structures support long-term carbon storage, helping mitigate greenhouse-gas emissions (Wei *et al.*, 2022; Almendros & González-Pérez, 2025). Moreover, AHAs can increase photosynthetic carbon fixation and improve soil carbon sequestration indicators such as TOC, DOC, and MBC, particularly when combined with complementary amendments (Tang *et al.*, 2022; Zeyu Zhang *et al.*, 2024; Zhang *et al.*, 2024). Together, these AHA products create a spectrum of carbon-based materials with applications ranging from sustainable agriculture to water remediation (Figure 5) (Yang *et al.*, 2021; Marzban *et al.*, 2024b).

Figure 5: Functional contributions of artificial humic acids to sustainable, climate-smart agriculture encompass improvements in soil structure and conditioning, enhancement of organic carbon sequestration with associated reductions in greenhouse gas emissions, stimulation of microbial diversity and enzymatic functioning, remediation of contaminated soils, and promotion of crop growth and productivity

From a circular bioeconomy perspective, hydrothermal processes add value to agricultural residues, forest waste, food processing byproducts, and municipal biowaste streams. Converting these materials into hydrochar, humic analogues, or fulvic acids reduces waste and supports nutrient cycling. The aqueous phase produced during hydrothermal reactions can contain organic acids, sugars, and phenolics, which may be further processed for biogas production, as fermentation substrates, or for biochemical extraction. Thus, hydrothermal conversion supports integrated biorefinery concepts where carbon, nutrients, and energy are co-recovered (Marzban *et al.*, 2025).

From a planetary boundaries perspective, replacing fossil-derived materials with hydrothermal carbon products helps reduce anthropogenic carbon emissions. Although hydrothermal products are less recalcitrant than high-temperature pyrolytic char, they still retain meaningful carbon. Their moderate stability makes them particularly important for near-term carbon sequestration strategies that prioritise soil function and agricultural productivity. At the same time, hydrothermal carbon materials can substitute for peat in horticulture, reducing pressure on fragile peatland ecosystems and avoiding associated carbon emissions (Marzban *et al.*, 2025).

Technological Challenges in Hydrothermal Processing and Future Suggestions

Hydrothermal processing offers a promising route to accelerate the conversion of biomass into mature carbon forms, including artificial humic substances and coal-like materials, often referred to as hydrochar or artificial coal. However, the operational window between 180°C and 250°C introduces significant engineering and economic challenges, particularly when harsh chemical conditions are required. Processes that rely on highly alkaline solutions, such as potassium hydroxide (as in HTH and HTF), or that result in strongly acidic environments (as in HTC), demand reactors capable of withstanding both elevated temperatures and high pressures, often above 30 bar. These corrosive and high-stress conditions significantly increase the cost, complexity, and safety demands of reactor design and operation, thereby limiting the scalability and broader application of current hydrothermal technologies. Recent advances in low-pressure hydrothermal operation, semi-batch and continuous reactor designs, and staged or extrusion-assisted processing indicate that key humification reactions can be promoted without relying solely on high autogenic pressure, offering pathways to mitigate corrosion, lower capital costs, and improve scalability. This limitation becomes even more pronounced when the intended product is not for fuel applications, where energy recovery could offset production costs, but for soil improvement or environmental use. In such cases, the resulting materials become too expensive to compete in markets where fossil-based products are still preferred due to their lower cost.

To address current limitations, future innovations and research should focus on optimising hydrothermal reactions at lower temperatures and pressures. Research should investigate how high alkalinity, even with reduced thermal input, can selectively decompose biomass, particularly with the assistance of catalysts, to release soluble compounds such as artificial humic and fulvic acids. Simultaneously, a portion of the biomass may remain partially degraded yet more chemically stable, preserving its fibrous structure in a form more resistant to decomposition than the original feedstock. This pathway closely mimics natural peat formation and offers a promising approach for producing sustainable peat alternatives for horticultural applications. By emphasising milder but efficient processing conditions, it becomes possible to design systems that are safer, more cost-effective, and

easier to scale. This strategic direction could support the development of next-generation technologies capable of delivering high-quality carbon materials without dependence on energy-intensive processes. Ultimately, in the context of the bioeconomy, ensuring both technological and economic scalability must remain a central objective.

HTC/HTH/HTF systems are increasingly evaluated through integrated techno-economic analysis (TEA) and life-cycle assessment (LCA), revealing a nuanced balance between value creation and environmental burden. TEA results show that product yield is the primary economic lever: Sequential acidic HTC–alkaline HTH markedly improves AHA output and is the only pathway delivering positive net profit, despite higher reagent and energy inputs (Wang *et al.*, 2025). Hydrothermal products derived from waste streams can reach competitive minimum selling prices, benefiting from economies of scale, process intensification, and solution recycling, while outperforming conventional humified markets in several scenarios. Nevertheless, capital intensity, steam demand, and alkali consumption remain cost-dominant factors (Wang *et al.*, 2025). Comparisons across humification routes indicate that catalytic pyrolysis offers a favourable cost-performance compromise (Chen *et al.*, 2026), composting is cheapest but slow and carbon-inefficient, and conventional HTH, though producing high-quality AHAs, often struggles with economic feasibility without integration and recycling strategies (Chen *et al.*, 2026).

From an environmental perspective, LCA highlights the reaction stage as the most significant contributor to energy demand, GHG emissions, and wastewater generation, with impacts strongly conditioned by temperature-pressure regimes and the electricity mix (Ziyun Liu *et al.*, 2025). Innovations such as oxygen-assisted HTH and low-temperature oxidative–alkaline humification substantially reduce specific energy use while maintaining high AHA yields, lowering CO_2-equivalent emissions and mitigating ecotoxicity and resource depletion (Sarlaki *et al.*, 2024a; M. Xu *et al.*, 2025). However, several pathways still exhibit notable trade-offs, including alkaline wastewater, soil acidification risks from reagent use, and variable carbon losses influenced by catalysts, oxidants, and operating temperature (Chen *et al.*, 2024; Q. Zhao *et al.*, 2024; Sheng *et al.*, 2025; Kong *et al.*, 2026). Overall, HTH/HTF presents credible potential for circular biocarbon management. Still, its sustainability depends on targeted mitigation, reagent optimisation, solution recycling, heat integration, and coupling with renewable energy to reconcile economic competitiveness with environmental stewardship.

Conclusions

Hydrothermal biomass processing represents a scientifically robust and technologically flexible analogue to the early stages of natural carbon maturation. Through dehydration, condensation, and redox-driven reactions in aqueous environments, hydrothermal systems can transform fresh biomass into carbon-rich materials that align chemically with peat, humus, and low-rank coal. HTC captures the essence of early diagenetic condensation through the formation of furans and aromatics. HTH advances the formation of colloidal, functionalised macromolecules analogous to humic acids. HTF favours oxygen-rich, soluble compounds that parallel natural fulvic acids. Each pathway contributes uniquely to the development of sustainable carbon materials. The Van Krevelen diagram provides a mechanistic lens through which these transformations can be tracked, revealing that hydrothermal processes recapitulate the key chemical vectors, dehydration, decarboxylation, aromatisation, and condensation, found in nature. These accelerated conversions offer practical

avenues for stabilising atmospheric carbon in forms suitable for agriculture, soil restoration, and environmental remediation. Hydrothermal products not only emulate the chemistry of ancient organic matter but also address modern sustainability goals by valorising waste streams and reducing dependence on fossil inputs. With further optimisation of reaction conditions and scale-up strategies, hydrothermal engineering can emerge as a cornerstone technology for carbon management in the bioeconomy era. Key priorities for future research include elucidating the catalytic effects of minerals and feedstock-derived ash, establishing robust life-cycle benchmarks, advancing low-temperature alkaline pathways, and accelerating near-term applications in soil amendment, including peat replacement through partial conversion of biomass to artificial humic substances and residual fibres. All efforts should consider scalable, economically feasible strategies for peat substitution and circular, bio-based chemical production.

Data Availability Statement

The data presented in this study are available on request from the corresponding author.

Acknowledgments

The authors would like to thank the Editorial Board and the anonymous reviewers for their constructive comments and valuable suggestions, which helped improve the clarity and quality of this article.

Conflict of Interest Statement

The authors declare no conflict of interest.

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