

Review

Hydrothermal Carbonisation of Waste Biomass: A Review of Combustion Behavior, Kinetics, Thermodynamics and Reaction Mechanisms

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Abstract

The increasing generation of organic waste and the growing demand for sustainable solid fuels have intensified interest in hydrothermal carbonisation (HTC) as a pathway for biomass valorization within circular bioeconomy systems. HTC uses subcritical water to upgrade moist biomass into hydrochar with improved fuel properties and combustion behavior. This review correlates key HTC parameters, including temperature, residence time, pH, and the nature of feedstock, with the chemical evolution and thermal reactivity of different hydrochars. Data synthesis identifies a typical ‘kinetic optimization’ range between 180 and 220 °C for conventional lignocellulosic feedstocks. Within this thermal interval, activation energy (E_a) decreases from 180–260 kJ/mol for raw biomass to 70–180 kJ/mol for hydrochars, while the high heating value (HHV) reaches up to ~28 MJ/kg. The results further demonstrate that feedstock composition strongly influences combustion reactivity and kinetic behavior under similar HTC conditions. The integration of isoconversional methods with thermodynamic parameters (ΔH , ΔG , ΔS) confirms a transition toward more ordered and thermally stable carbon structures. Additionally, Criado’s master plots indicate a shift from diffusion-controlled to reaction-controlled combustion mechanisms with increasing HTC severity. These findings provide valuable insights into the optimizing of HTC conditions for balance energy densification and combustion reactivity, offering a comprehensive understanding to guide future hydrochar-based energy applications and scale-up studies.

Keywords: hydrothermal carbonisation; hydrochar; combustion; fuel; isoconversional kinetic; activation energy; thermodynamic

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1. Introduction

The increasing generation of organic waste and the growing demand for sustainable energy carriers have intensified interest in thermochemical conversion technologies capable of transforming wet biomass into stable carbonaceous materials. Biomass is currently recognized as the world’s fourth-largest primary energy resource and represents a renew-

able alternative for reducing dependence on fossil fuels and mitigating greenhouse gas emissions [1,2]. However, the direct thermal conversion of raw biomass remains challenging due to its high moisture content, low bulk density, heterogeneous structure, and elevated concentrations of inorganic species, particularly alkali and alkaline earth metals, which contribute to slagging, fouling, and corrosion during combustion processes [3,4]. In addition, the disposal of untreated organic residues via landfilling generates substantial CH₄ emissions, underscoring the need for efficient waste-valorization pathways that produce stable, energy-dense solid fuels within a circular bioeconomy framework.

Hydrothermal carbonisation (HTC) has emerged as an efficient thermochemical pathway for upgrading wet biomass into carbon-rich solid fuels. Operating under subcritical water conditions, typically between 180 and 260 °C under autogenous pressure, HTC avoids the need for energy-intensive pre-drying, as water simultaneously acts as the reaction medium and participates in the transformation reactions [5,6]. The process involves a sequence of hydrolysis, dehydration, decarboxylation, and aromatization reactions, leading to progressive structural reorganization and the formation of hydrochar with enhanced carbon content and reduced oxygen functionality [6]. These transformations significantly influence combustion behavior by altering the release of volatile matter (VM), the fixed carbon (FC) content, aromaticity, and thermal stability. Consequently, hydrochars produced under different HTC severities often exhibit distinct ignition characteristics, combustion reactivity, and kinetic behavior compared to their raw biomass precursors [7–9].

Despite extensive reporting on the physicochemical transformations occurring during HTC, the direct relationship between process severity and the subsequent combustion behavior of hydrochars is not yet fully quantified. Recent reviews [10–13] have primarily focused on broad comparisons of HTC conversion pathways, hydrochar production, physicochemical characterization, and general fuel quality indicators, while the specific correlations between combustion kinetics, thermodynamic parameters, and reaction mechanisms have received less attention. Over the past several years, research on HTC has escalated, driven by the valorization of wet biomass and the production of sustainable solid fuels. Recent studies have emphasized HTC process optimization, hydrochar yields, elemental evolution, and improvements in fuel properties [14,15]. Concurrently, research has focused on combustion performance and kinetic evaluation using thermogravimetric approaches and isoconversional models. However, these aspects are frequently evaluated separately, and a comprehensive framework integrating combustion behavior, kinetic parameters, thermodynamic interpretation, and reaction mechanism analysis across different biomass feedstocks remains limited [16,17]. In particular, the significant variability in activation energy (E_a) and combustion profiles reported even under similar HTC conditions indicates that feedstock composition, inorganic constituents, and structural evolution directly determine hydrochar reactivity. Furthermore, systematic correlations integrating kinetic triplets with thermodynamic parameters (ΔH , ΔG , and ΔS) and reaction mechanism models are still limited, obstructing the establishment of consistent trends in hydrochar combustion behavior.

2. Hydrothermal Carbonisation

HTC (Figure 1) is a thermochemical conversion technology operating at moderate temperatures (180–260 °C) and autogenous pressures, specifically designed for the valorization of high-moisture biomass [6,7]. A defining feature of HTC is the multifunctional role of water; it serves as a reaction medium while simultaneously participating as a reactant and catalyst [7]. At elevated temperatures, the enhanced self-ionization of water facilitates the hydrolytic cleavage of lignocellulosic bonds, thereby promoting hydrothermal conversion and reducing the energy barrier for bond breakage [4]. Through a se-

quence of hydrolysis, dehydration, decarboxylation, and aromatization reactions, the feedstock is transformed into a carbon-rich solid known as hydrochar, while a liquid phase rich in dissolved organics is simultaneously formed [18,19]. Concurrently, subsequent reactions (such as further decarboxylation) lead to the degradation of carboxyl–carbonyl groups, releasing the bulk of the final flue gas, which consists primarily of CO₂ [5].



Figure 1. Hydrothermal carbonisation of waste biomass.

Compared to its precursor biomass, hydrochar exhibits enhanced fuel properties, such as increased hydrophobicity and higher energy density (ED) [20]. Typically, hydrochar exhibits an HHV in the range of 20–28 MJ/kg, depending on the feedstock and process severity (Table 1). These changes are primarily associated with the progressive removal of oxygen-containing functional groups (OFG) and the restructuring of the lignocellulosic matrix [2]. However, despite these advantages, the relationship between structural evolution and combustion kinetics is still not fully understood. These changes also improve handling and storage properties due to increased hydrophobicity and bulk density. Unlike biochars produced via dry pyrolysis, hydrochar typically retains a more cohesive morphology, often characterized by the formation of carbon microspheres [9,21,22]. These physicochemical transformations directly affect the thermal degradation behavior of hydrochars, particularly by modifying E_a , diffusion pathways, and dominant reaction mechanisms during combustion. As a result, HTC severity plays a key role in defining the transition from diffusion-controlled to reaction-controlled regimes, which is further discussed in the following sections [23].

Table 1. Elemental analysis and fuel properties of different waste biomass and hydrochars.

Sample	Conditions	Elemental Analysis (wt.%)				Fuel Properties		
		C	H	N	S	ED	HHV	Ref.
<i>Paulownia leaves</i>	-	-	5.71	76.70	8.90	-	18.99	[24]
	1 h, 180 °C	57.20	5.17	75.31	15.61	1.25	23.65	
	1 h, 200 °C	55.23	5.56	74.76	16.58	1.32	25.14	
	1 h, 220 °C	43.79	6.48	71.15	20.32	1.38	26.13	
	1 h, 240 °C	41.98	7.56	64.41	26.75	1.44	27.28	
	1 h, 260 °C	38.32	8.88	62.10	27.94	1.48	28.06	

Food waste	-	-	8.30	82.60	9.10	-	16.13	[25]
	6 h, 180 °C	53.86	5.90	70.20	23.90	1.35	21.72	
	6 h, 210 °C	51.41	6.70	60.80	32.50	1.63	26.24	
	6 h, 240 °C	44.65	7.50	56.30	36.20	1.79	28.86	
Grape pomace	-	-	6.48	75.49	17.29	-	21.64	[9]
	1 h, 180 °C	86.00	3.67	67.76	25.84	1.13	24.43	
	1 h, 200 °C	78.00	3.55	66.60	25.73	1.19	25.72	
	1 h, 220 °C	66.00	6.75	63.38	26.65	1.21	26.13	
Spent mushroom substrate	-	-	37.50	49.02	7.26	-	10.83	[8]
	1 h, 180 °C	57.20	34.69	48.72	11.16	1.38	14.9	
	1 h, 200 °C	55.23	35.60	48.61	10.42	1.42	15.40	
	1 h, 220 °C	43.79	36.43	46.82	12.25	1.46	15.82	
	1 h, 240 °C	41.98	37.58	44.88	13.44	1.55	16.82	
	1 h, 260 °C	38.32	39.01	43.82	13.50	1.58	17.06	
Digestate from agricultural waste	-	-	15.70	63.20	21.10	-	11.63	[26]
	2 h, 200 °C	-	21.30	55.30	23.40	-	13.95	
	2 h, 220 °C	-	24.00	45.70	30.30	-	14.82	
	2 h, 240 °C	-	31.40	33.00	35.60	-	16.24	
	2 h, 260 °C	-	31.60	32.40	37.80	-	16.93	

3. Influence of HTC Operational Parameters

The transformation of raw biomass into a high-quality solid biofuel is strictly governed by the severity of the HTC conditions. However, these parameters are often investigated independently in the literature, which limits a comprehensive understanding of their combined effect on hydrochar reactivity. The interaction between temperature, residence time, and the chemical nature of the aqueous medium dictates the extent of carbonisation and the final fuel quality.

3.1. Influence of Temperature

Temperature is the decisive factor in HTC, governing both thermodynamic equilibrium and reaction kinetics [27]. Within the 180–260 °C range, the increased ionization of water and its reduced dielectric constant initiate the hydrolytic cleavage of lignocellulosic bonds [28]. The resulting structural transformation follows a well-defined degradation sequence: hemicellulose begins to decompose near 180 °C, while cellulose requires temperatures exceeding 200 °C for significant degradation [8,29]. However, this temperature threshold is primarily applicable to lignocellulosic biomass. Significant deviations frequently occur in non-lignocellulosic feedstocks such as food waste and anaerobic digestates. In food waste, the presence of readily degradable carbohydrates, proteins, and lipids fundamentally modifies the hydrothermal reaction pathways [30,31]. Specifically, easily hydrolyzable polysaccharides (such as starch and sucrose) decompose into basic monosaccharide units like glucose and fructose at much lower temperatures (100–175 °C), which initiates early structural transformations before the classical hemicellulose degradation onset [32]. Simultaneously, the residual lignocellulosic fractions within the waste matrix undergo depolymerization and liquefaction into water-soluble compounds across a broader temperature range (160–280 °C). Similarly, anaerobic digestates exhibit divergent conversion behavior due to prior biological degradation and their complex organic–mineral matrix [33]. As a result, the onset and progression of hydrothermal reactions in these alternative feedstocks do not follow the classical, sequential hemicellulose–cellulose degradation pathways commonly reported for pure lignocellulosic biomass.

Data compiled in Table 1 confirm that higher temperatures promote C enrichment and O removal, although the extent of these changes depends on the type of biomass. For

example, several studies report a steady increase in C content with temperature, reflecting progressive carbonisation of the biomass matrix (Table 1). A parallel effect is seen in grape pomace, where elevated temperatures accelerate the degradation of sugars and polyphenols, yielding a more mature carbon structure [9]. A nearly universal trend is the inverse relationship between mass yield and HHV. Intensified decomposition of organic matter transfers soluble intermediates into the liquid phase, thereby increasing ED. This behavior is particularly pronounced in food waste-derived hydrochars, where HHV can reach values close to 28 MJ/kg at higher temperatures (Table 1). However, feedstock composition can alter this trajectory. In high-ash materials like spent mushroom substrate, HTC initiates the leaching of certain inorganics, but the substantial loss of VM can concentrate the remaining ash, reaching ~38% (Table 2) at higher temperatures. Ultimately, while temperature dictates the severity of carbonisation, the final fuel properties result from the combined effect of process conditions and the inherent biomass matrix. These variations are critical for interpreting combustion kinetics, as identical HTC temperatures can produce hydrochars with vastly different reactivities.

Table 2. Mass yield and proximate analysis of different biomass and hydrochars.

Sample	Conditions	Yield (wt.%)	Proximate Analysis (wt%)			Ref.
			Ash	VM	FC	
<i>Paulownia leaves</i>	-	-	5.71	76.70	8.90	[24]
	1 h, 180 °C	57.20	5.17	75.31	15.61	
	1 h, 200 °C	55.23	5.56	74.76	16.58	
	1 h, 220 °C	43.79	6.48	71.15	20.32	
	1 h, 240 °C	41.98	7.56	64.41	26.75	
	1 h, 260 °C	38.32	8.88	62.10	27.94	
Food waste	-	-	8.30	82.60	9.10	[25]
	6 h, 180 °C	53.86	5.90	70.20	23.90	
	6 h, 210 °C	51.41	6.70	60.80	32.50	
	6 h, 240 °C	44.65	7.50	56.30	36.20	
Grape pomace	-	-	6.48	75.49	17.29	[9]
	1 h, 180 °C	86.00	3.67	67.76	25.84	
	1 h, 200 °C	78.00	3.55	66.60	25.73	
	1 h, 220 °C	66.00	6.75	63.38	26.65	
Spent mushroom substrate	-	-	37.50	49.02	7.26	[8]
	1 h, 180 °C	57.20	34.69	48.72	11.16	
	1 h, 200 °C	55.23	35.60	48.61	10.42	
	1 h, 220 °C	43.79	36.43	46.82	12.25	
	1 h, 240 °C	41.98	37.58	44.88	13.44	
	1 h, 260 °C	38.32	39.01	43.82	13.50	
Digestate from agricultural waste	-	-	15.70	63.20	21.10	[26]
	2 h, 200 °C	-	21.30	55.30	23.40	
	2 h, 220 °C	-	24.00	45.70	30.30	
	2 h, 240 °C	-	31.40	33.00	35.60	
	2 h, 260 °C	-	31.60	32.40	37.80	

3.2. Residence Time

Residence time directly governs the degree of biomass conversion and the resulting product distribution [34]. Consistent with temperature-induced effects, mass yield typically declines as residence time increases, driven by the sustained decomposition of the organic matrix and the progression of secondary reactions [35].

Under isothermal conditions, prolonged exposure intensifies reaction severity, which facilitates the secondary polymerization of intermediates originally dissolved in the liquid phase [22]. This mechanism results in ‘secondary char,’ characterized by a more condensed polyaromatic structure and the formation of characteristic carbon microspheres [35]. For example, extended residence times promote more complete conversion, enabling the recombination of intermediates into a more ED solid fuel (Table 1). The impact of residence time, however, plateaus beyond a specific threshold. Lucian et al. [36] demonstrate that extending the process past 6 h yields diminishing returns, with no significant further reduction in mass yield or gains in carbon stability. Within optimal ranges, longer thermal exposure reduces VM in favor of FC, producing a more chemically resilient solid fuel [37]. This increased structural ordering is typically associated with enhanced thermal stability, which may result in higher E_a and a shift toward reaction-controlled combustion mechanisms.

3.3. Influence of Medium pH

The initial pH of the process water is a primary factor in directing reaction pathways [38]. As HTC progresses, the degradation of organic matter generates in situ organic acids (such as acetic and formic acid), which decrease the pH of the medium [12,16,39]. However, deliberate pH regulation prior to HTC is often employed to modify product characteristics. Acidic environments are typically established by adding either mineral acids, such as H_2SO_4 , HCl, or H_3PO_4 , or organic acids like citric and acetic acid [12,23]. These solutions create an acid-catalyzed environment that accelerates the hydrolytic cleavage of structural polysaccharides, favoring xylan breakdown and subsequent furfural formation via dehydration [16,21,23]. In contrast, alkaline additives such as NaOH, KOH, and $Ca(OH)_2$ promote cellulose degradation, modify ash chemistry, and alter the distribution of OFG within the hydrochar structure [12,21,40,41].

These chemical additions strongly interact with the feedstock’s inherent composition. Forest residues typically generate more acidic process water, whereas agricultural residues and manures often result in alkaline conditions due to their higher ash content and the leaching of alkali and alkaline earth metals into the subcritical water [12]. The choice of the specific acid or alkaline agent determines the inorganic profile of the final product. For instance, using mineral acids like HCl or H_2SO_4 is highly effective for demineralization, as these solutions facilitate the leaching of inorganic components [12,23]. For high-ash feedstocks like spent mushroom substrate, this acid-induced washing effect is important for improving fuel quality and reducing the risk of slagging and fouling during combustion [8,9,12]. Consequently, pH regulation represents both a carbonization parameter and a strategic method for modifying hydrochar combustion behavior, ash characteristics, and thermal reactivity [12,16].

3.4. Influence of Pressure

Pressure is an important yet frequently overlooked parameter in HTC compared to temperature and residence time. Under HTC conditions, pressure is generated autogenously via water vapor formation and typically ranges between 2 and 10 MPa, depending on the process temperature, biomass loading, and reactor configuration [42,43]. This elevated pressure maintains water in the liquid state under subcritical conditions, altering its density and ionic product, which accelerates the hydrolytic cleavage of lignocellulosic

structures [14]. Consequently, pressure enhances carbon recovery in the solid phase and dictates hydrochar morphology, porosity, and pore development [44–46]. Although temperature remains the dominant factor controlling hydrothermal pathways, autogenous pressure influences both hydrochar yield and structural evolution under isothermal conditions [2]. Specifically, elevated pressures stimulate secondary char formation through the condensation and polymerization of liquid-phase intermediates [2]. However, excessive pressure can restrict pore accessibility, subsequently obstructing oxygen transport and diffusion pathways during hydrochar combustion.

3.5. Influence of Biomass Type

The progressive transformation during hydrothermal treatment is heavily dictated by the inherent composition of the biomass. Different biomass categories exhibit distinct transformation pathways during HTC due to variations in cellulose, hemicellulose, lignin, moisture, and ash content [2]. Lignocellulosic biomass and agricultural residues generally produce hydrochars with improved fuel properties and HHV owing to effective carbon densification [2,14]. Feedstocks rich in cellulose tend to exhibit greater devolatilization and improved energy content, whereas lignin-rich materials usually generate hydrochars with higher aromaticity and enhanced thermal stability [4]. In contrast, food waste, digestate, manure, and sewage sludge often contain elevated inorganic fractions that may increase ash accumulation and reduce combustion reactivity [47]. High ash content may limit oxygen diffusion, increase thermal resistance, and promote slagging and fouling tendencies during combustion [4]. Therefore, biomass selection represents a critical factor in determining hydrochar quality and combustion performance, and should be considered together with HTC operating conditions.

To provide a comprehensive overview, the individual and interactive effects of key HTC parameters, including temperature, residence time, autogenous pressure, pH, and feedstock composition, on the physicochemical modifications of hydrochars and their subsequent combustion performance are systematically summarized in Table 3.

Table 3. Summary of the effects of key HTC process parameters on hydrochar properties and combustion performance.

HTC Parameter	Operational Range	Main effects on Hydrochar Properties	Impact on Combustion Behavior
Temperature	180–260 °C	Reduces VM content Increases FC and carbon densification Promotes aromatic condensation Lowers hydrochar mass yield	Shifts combustion toward higher temperature zones Generally elevates E_a for lignocellulose Enhances fuel stability and reduces ignition risks
Residence time	5–240 min	Accelerates initial hydrolysis and dehydration Minor impact on carbon density after extended intervals Slightly reduces mass retention	Promotes uniform oxidation profiles Secondary effect compared to temperature severity
Pressure	2–10 MPa	Maintains water in the subcritical liquid state Increases water density and ionic product Promotes secondary char formation via polymerization	Excessive pressure can reduce pore accessibility Alters internal oxygen transport during oxidation
pH	2–10	Acidic media accelerate organic matrix hydrolysis	Modifies the ignition profile via ash mineral alterations

		Alters liquid–solid equilibrium and functional groups Influences the retention or leaching of alkali metals	Lower pH can mitigate high-temperature slagging tendencies
Feedstock composition	Variable (Biomass, Wastes)	High-lignin materials retain higher mass yields	High-ash feedstocks restrict oxygen diffusion pathways
		Cellulose-rich fractions enhance devolatilization	Alkali metals can act as inherent catalysts
		Mineral-rich wastes drive inorganic ash concentration	Governs multi-modal kinetic oxidation profiles

4. Fuel Properties of Hydrochars

The thermochemical transformations occurring during HTC are directly reflected in the elemental and proximate composition of hydrochars, which represent the primary indicators of fuel quality. As shown in Table 1, increasing HTC severity generally promotes carbon enrichment and oxygen removal, although the extent of these changes strongly depends on feedstock composition and inorganic content. The progressive elimination of oxygen-containing functional groups shifts the hydrochar composition toward the lignite and sub-bituminous coal regions, as confirmed by the Van Krevelen diagram obtained for the spent mushroom substrate hydrochars (Figure 2). This structural evolution is accompanied by improved fuel characteristics, including higher HHV and ED, resulting from carbon densification and increasing aromaticity [48]. In food waste-derived hydrochars, these effects are particularly pronounced, with HHV values approaching 28.86 MJ/kg under more severe HTC [25]. Similar trends are observed for lignocellulosic feedstocks such as Paulownia leaves and grape pomace, although the magnitude of carbonisation differs due to variations in biochemical composition and degradation pathways [9,24]. Regarding N and S, these elements generally remain stable or decrease slightly during HTC, reflecting the partial transfer of nitrogen- and sulfur-containing compounds into the liquid phase [8]. This “washing effect” can improve the environmental performance of hydrochars by reducing potential NO_x and SO_x precursor species during combustion.

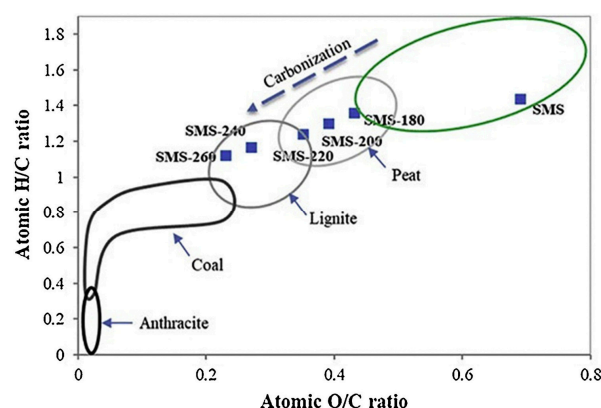


Figure 2. Van Krevelen diagram of waste biomass and hydrochars. Reprinted with permission from Kojić et al. [8]. Copyright (2021) Elsevier.

Proximate analysis further confirms the transition from volatile-rich biomass to a more stable carbonaceous material during HTC. In most feedstocks, increasing process severity reduces VM while promoting FC formation, indicating progressive structural condensation of the carbon matrix. For example, in digestate-derived hydrochars, the VM decreases from 63.20 to 32.40% at 260 °C, accompanied by a proportional increase in FC [26]. The most pronounced improvement in energy-related properties is observed for food

waste-derived hydrochars, where the ED reaches 1.79 [25]. However, the evolution of fuel properties differs considerably for high-ash feedstocks. In spent mushroom substrate, the ash content increases from 37.50 to 39.01% at 260 °C due to degradation of the organic fraction and the relative concentration of inorganic species [8]. Unlike lignocellulosic residues, these materials tend to accumulate mineral components during HTC, which represents a significant limitation for fuel applications because elevated ash contents increase the risk of slagging and fouling during combustion [2]. Therefore, the evolution of fuel properties during HTC reflects a trade-off between carbon densification and inorganic accumulation, governed by both process severity and the inherent characteristics of the biomass matrix. These variations are particularly important for interpreting combustion behavior, as hydrochars produced under similar HTC conditions may exhibit substantially different thermal reactivities and kinetic responses [49].

5. Combustion Behavior and Thermal Stability of Hydrochars

Thermogravimetric analysis (TGA) provides the data to assess hydrochar viability as a solid fuel. From the TG and DTG profiles, key combustion indices, including ignition temperature (T_i), burnout temperature (T_b), and the maximum weight loss rate (DTG_{max}), are derived to correlate structural changes with thermal reactivity [50]. To quantify these oxidation dynamics and provide a comparative basis for different hydrochars, several combustion indices are used to evaluate overall performance, as summarized in Table 4.

Table 4. Main combustion indicators used for evaluation of hydrochar combustion.

Property	Interpretation	Ref.
T_i	Ignition temperature; lower values indicate easier ignition	[51,52]
T_b	Burnout temperature; lower values indicate more complete combustion	[52,53]
DTG_{max}	Maximum weight loss rate; indicator of combustion intensity and combustion reactivity	[51,52]
D_i	Ignition index; indicator of fuel ignitability and combustion initiation	[52]
S	Comprehensive combustion index; indicator of overall combustion performance	[52,54]
E_a	Thermal stability and resistance toward oxidation	[54]

Oxidative degradation proceeds through two main stages: the release and ignition of VM, followed by the combustion of the FC fraction [55]. Hydrochars exhibit more separated combustion stages than raw biomass due to structural reorganization during HTC [4]. At moderate process temperatures, DTG curves often show a dual-peak distribution (Figure 3). The first peak (250–370 °C) corresponds to the decomposition of residual low-molecular-weight components and hemicellulose-derived fragments [56]. As HTC severity increases, polycondensation reactions promote the development of stable aromatic structures, shifting the thermal intensity toward the second DTG peak (370–530 °C), which represents the oxidation of the carbon-rich matrix [57].

A direct consequence of HTC is the systematic rise in T_i compared to raw feedstocks [29,58]. This elevation is caused by the reduction in VM and the formation of a more ordered carbon structure. A higher T_i enhances fuel stability, reducing the risks of spontaneous ignition during storage and handling [59]. Despite higher ignition temperatures, hydrochars retain high reactivity due to residual OFG and accessible active sites that facilitate oxygen adsorption [2,60]. Combustion efficiency is reflected in T_b , which indicates the completion of oxidation. Hydrochars produced under moderate conditions frequently exhibit lower T_b values than raw biomass, indicating efficient burnout. This behavior is associated with the thermal interaction between volatile release and FC oxidation, where the heat from the initial stage promotes the subsequent combustion phase [61]. However,

severe HTC conditions can induce pore collapse or the formation of overly condensed aromatic structures, which restrict oxygen diffusion. Furthermore, in high-ash materials like spent mushroom substrate, the inorganic fraction acts as a physical barrier, shielding reactive sites from oxygen access [8]. Therefore, the thermal stability and E_a profiles of hydrochars reflect a balance between carbon densification, structural cross-linking, and oxygen transport characteristics within the solid matrix [58].

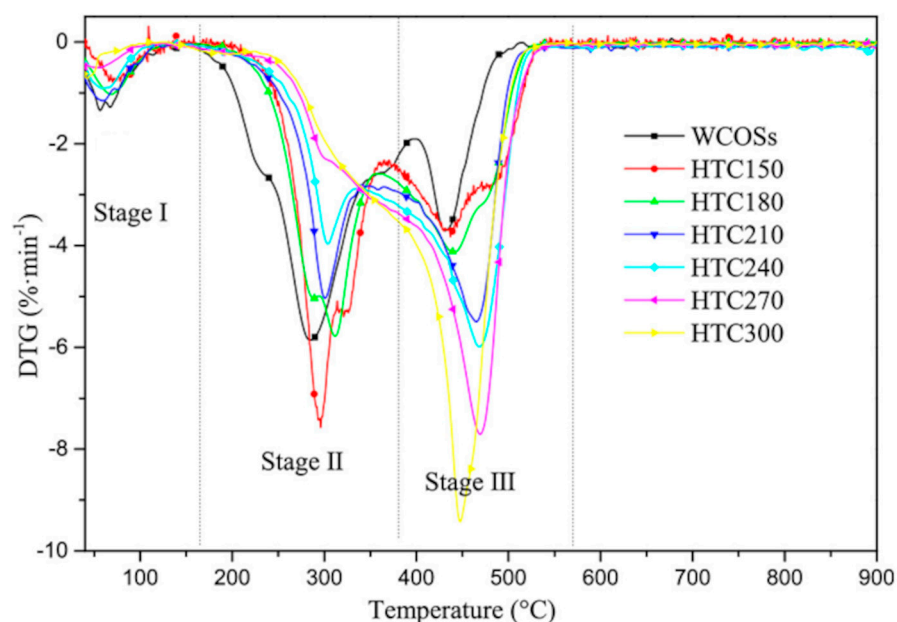


Figure 3. DTG curves of waste biomass and hydrochar. Reproduced from Chen et al. [56], licensed under CC BY 4.0.

6. Kinetic Analysis

The determination of E_a is fundamental to assessing the thermal reactivity and energy barriers of hydrochar combustion [3]. Due to the multi-component nature and complex degradation pathways of these materials, isoconversional methods (Table 5), primarily Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) (Figure 4), are applied [62]. These models allow for the evaluation of E_a across the entire conversion range ($\alpha = 0.1$ – 0.9) without the constraints of a predefined reaction mechanism, providing a robust description of heterogeneous solid fuels.

Table 5. Isoconversional models.

Models		Ref.
Flynn–Wall–Ozawa (FWO)	$\ln(\beta) = \ln\left(\frac{AE_a}{Rf(\alpha)}\right) - \frac{E_a}{RT}$	[62]
Kissinger–Akahira–Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_af(\alpha)}\right)$	[62]
Starink (STK)	$\ln\left(\frac{\beta}{T^{1.92}}\right) = -1.0008 \frac{E_a}{RT} + Const$	[63]
Coats–Redfern (CR)	$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{AR}{E_a\beta}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}$	[64]
Friedman (FD)	$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln[Af(\alpha)] - \frac{E_a}{RT}$	[26]
Vyazovkin (VZK)	$\varphi = \sum_i^n \sum_{j \neq i}^n \frac{I(E_a, T_i)\beta_j}{I(E_a, T_j)\beta_i} = minimum$	[65]

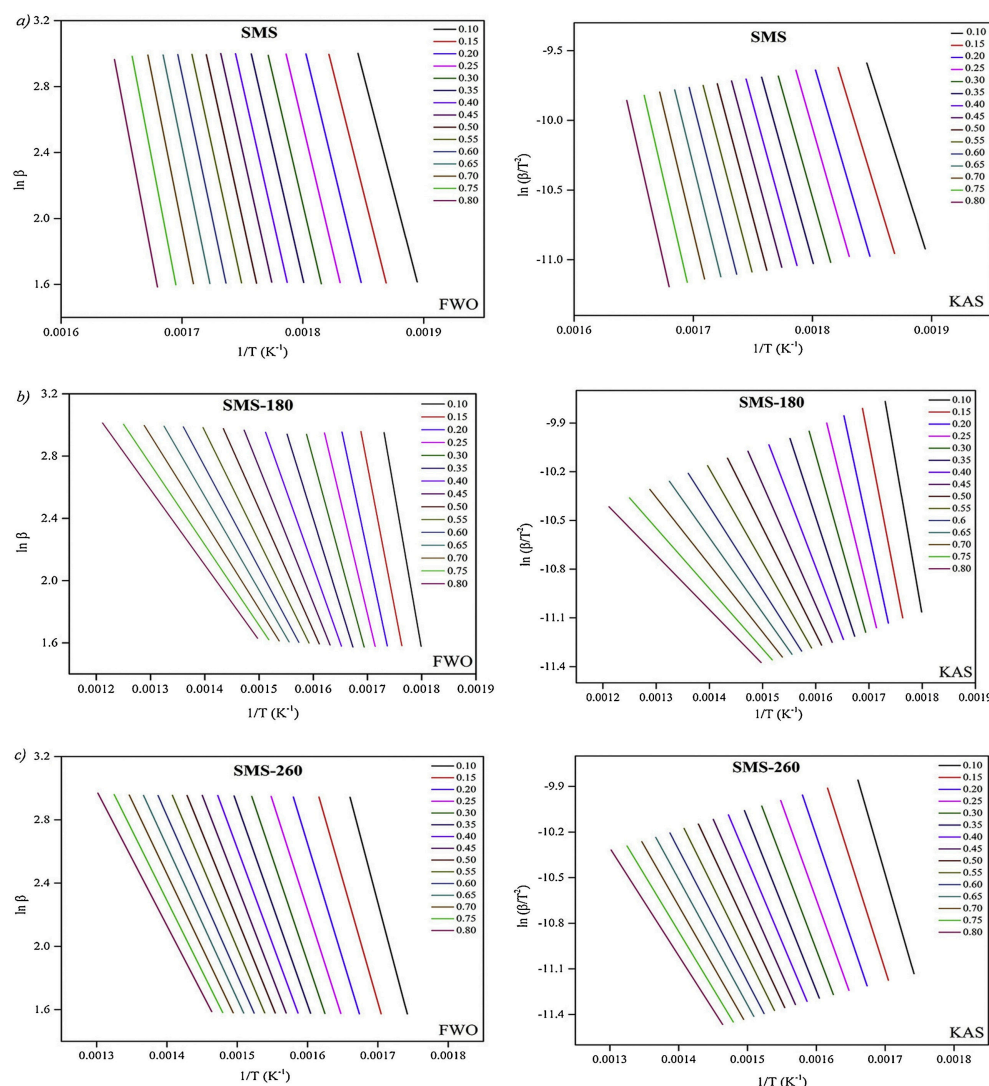


Figure 4. FWO and KAS of (a) waste biomass, (b) hydrochar prepared at 180 °C and (c) hydrochar prepared at 260 °C. Reprinted with permission from Kojić et al. [8]. Copyright (2021) Elsevier.

The variation of E_a throughout conversion is closely related to the sequential decomposition of biomass constituents. Lower α values are associated with the degradation of hemicellulose-derived structures and light volatile compounds, while intermediate α values are dominated by cellulose decomposition [8]. At higher conversion stages, lignin-derived structures and char oxidation become increasingly dominant, resulting in greater thermal resistance and higher E_a values [8]. Raw biomass typically exhibits elevated E_a due to its OFG-rich and structurally heterogeneous composition [3]. HTC under moderate temperatures (180–220 °C) generally reduces E_a , signaling lower energy barriers and enhanced combustion reactivity. In this lower temperature range, the shift in fuel properties is accompanied by high thermal reactivity. However, as process severity increases, this trend gradually reverses. Despite continued increases in HHV (Table 1), E_a frequently rises (Table 6), signaling the formation of a more stable and condensed carbon matrix [11]. This shift stems from progressive dehydration, decarboxylation, and aromatic condensation, which strengthen C-C bonds and increase resistance to thermal degradation [66]. Consequently, hydrochars produced at higher HTC temperatures exhibit greater thermal stability and require more controlled oxidation conditions [4]. However, these thermal trends are strongly feedstock-dependent, as distinct structural and compositional variations occur across different waste matrices. For instance, the spent mushroom substrate exhibits lower E_a values at 260 °C than at 180 °C (Table 4), demonstrating an enhanced

combustion reactivity at elevated treatment temperatures. This divergent behavior highlights the influence of the feedstock matrix, particularly its native mineral fraction, in modifying subsequent combustion kinetics, where inorganic alkali species can exert an inherent catalytic effect on char oxidation. Nevertheless, these kinetic parameters must be evaluated alongside mass and energy balances to determine overall process efficacy. Although a processing temperature of 260 °C yields the lowest E_a for specific biomass types, it simultaneously induces severe primary matrix degradation, resulting in a drastically reduced hydrochar mass yield compared to mild treatment at 180 °C. Furthermore, elevated temperatures accelerate the devolatilization of the organic matter while leaving the inorganic fraction intact, thereby driving a significant concentration of ash in the final solid fuel. This accumulation of mineral matter can impede oxygen diffusion and shield reactive sites, an effect that becomes more pronounced at higher temperatures [67,68]. Consequently, this cumulative effect of diminished mass retention and elevated ash content reduces the overall solid energy yield and introduces severe operational risks, such as slagging or fouling, during combustion. Ultimately, hydrochar kinetics is governed by the combined influence of HTC severity and feedstock-specific transformations. Identifying the intermediate temperature range in which E_a and fuel properties reach an optimal equilibrium is essential for optimizing hydrochars toward specific industrial combustion applications.

Table 6. Activation energy of different feedstock and hydrochars.

Sample	Temperature (°C)	Models	α	E_a (kJ/mol)	Ref.
Spent mushroom substrate	-	FWO	0.1–0.8	223.79–306.76	[8]
	180	KAS		226.49–312.64	
		FWO		158.83–38.25	
	260	KAS		157.64–27.89	
		FWO		133.06–67.40	
		KAS		130.18–58.87	
Food waste	-	FWO	0.1–0.9	58.21–312.39	[25]
	180	KAS		54.04–316.93	
		FD		61.23–328.58	
		FWO		79.54–255.27	
	210	KAS		60.09–213.93	
		FD		67.94–225.96	
		FWO		64.59–214.83	
		KAS		60.09–213.93	
		FD		67.94–225.96	
Sunflower stalks	-	FWO	0.1–0.8	91.49–342.01	[67]
	180	KAS		87.82–347.32	
		VZK		81.71–323.97	
		FWO		139.09–270.96	
	280	KAS		137.01–273.22	
		VZK		128.74–252.65	
		FWO		207.08–505.54	
		KAS		208.89–518.4	
		VZK		195.21–483.43	
Olive Tree Pruning	-	FWO	0.1–0.7	106.83–174.48	[49]
	250	VZK		104.27–172.65	
		FD		108.32–178.10	
		FWO		163.74–175.21	
		VZK		162.56–171.90	
		FD		167.40–178.11	

7. Thermodynamic Parameters

In addition to kinetic parameters, thermodynamic analysis provides insight into the energy changes and structural evolution of hydrochars during combustion. While E_a defines the energy barrier required to initiate the process, the pre-exponential factor (A) reflects the frequency of effective molecular collisions and the accessibility of reactive sites. Together with thermodynamic parameters, enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), these values provide a more complete description of the degradation process.

The pre-exponential factor may be determined by the following expression:

$$A = \frac{\beta E_a \exp(\frac{E_a}{RT_{\max}})}{RT_{\max}^2} \quad (1)$$

Based on the E_a and A , the following thermodynamic parameters can be determined: enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) can be calculated using the following equations:

$$\Delta H = E_a - RT \quad (2)$$

$$\Delta G = E_a + RT_{\max} \ln\left(\frac{k_b T_{\max}}{hA}\right) \quad (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_{\max}} \quad (4)$$

where k_b is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), h_A is the Planck constant ($6.626 \times 10^{-34} \text{ J s}$), $T_{\max}$ is the peak temperature corresponding to the peak devolatilization rate.

The thermodynamic parameters summarized in Table 7 further confirm that HTC significantly alters the structural stability and combustion behavior of biomass-derived fuels. In most studies, the ΔH values remain close to the corresponding E_a values, indicating that only a limited additional energy input is required for the formation of the activated complex once the activation barrier has been overcome [3,69]. This behavior is consistently observed across different feedstocks, including food waste, sunflower stalks, and spent mushroom substrate, suggesting that the combustion process is primarily governed by the structural rearrangements induced during HTC.

The evolution of the A reflects substantial differences in the structural organization of hydrochars. Lower A values are generally associated with less condensed and more reactive structures, whereas higher values indicate the formation of thermally stable aromatic domains with reduced accessibility of reactive sites [70,71]. In several hydrochars produced under severe HTC conditions, A increases by multiple orders of magnitude, confirming the progressive transition toward more ordered carbon matrices [66]. This trend is particularly evident for sunflower stalk and spent mushroom substrate hydrochars, where increasing HTC severity promotes structural condensation and reduced combustion reactivity.

The ΔG values remain predominantly positive for all investigated feedstocks, confirming that hydrochar combustion requires continuous external energy input, which is characteristic of solid-state oxidation processes [69]. At the same time, increasing ΔG values with HTC severity indicate the development of more thermally resistant carbon structures.

In contrast, the behavior of ΔS strongly depends on both feedstock composition and treatment severity. Negative ΔS values, frequently observed for hydrochars produced at elevated temperatures, suggest a reduction in structural randomness and the formation of more ordered aromatic systems during HTC [72]. Positive ΔS values, on the other hand, are generally associated with the release of volatile compounds and the decomposition of less stable biomass fractions [72].

Overall, the thermodynamic analysis demonstrates that hydrothermal carbonisation promotes a gradual transition from highly reactive and heterogeneous biomass structures toward more ordered and thermally stable hydrochars. These findings are consistent with the kinetic analysis, confirming that increasing HTC severity enhances structural stability while simultaneously reducing combustion reactivity.

Table 7. Thermodynamic parameters of different feedstock.

Sample	Temperature (°C)	α	A (1/s)	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)	Ref.
Winemaking industry wastes	246	0.1–0.9	3.58×10^7 – 4.76×10^6	117.23–105.19	−115.52–−137.07	161.34–157.44	[63]
Spent mushroom substrate	-		5.63×10^{18} – 4.18×10^{26}	221.98–307.59	101.37–251.10	162.97–161.41	[8]
	180	0.1–0.8	1.54×10^{12} – 9.32×10^0	152.83–21.03	−24.01–−262.17	167.50–176.01	
	260		3.90×10^7 – 1.00×10^2	125.18–52.48	−113.24–−222.2	205.59–210.18	
Sunflower stalks	-		2.27×10^6 – 2.50×10^{28}	77.62–317.81	−135.82–282.62	157.78–151.02	[65]
	180	0.1–0.8	1.51×10^7 – 1.14×10^{20}	124.18–246.81	−63.47–−19.56	163.35–159.89	
	230		1.9×10^7 – 8.33×10^{34}	126.83–413.11	−61.22–407.83	164.99–158.98	
Food waste	-		2.90×10^2 – 15.8×10^{19}	50.54–311.17	−209.25–107.04	166.01–252.10	[25]
	180	0.1–0.9	6.13×10^3 – 2.21×10^{11}	71.42–250.80	−184.92–14.10	181.96–242.36	
	210		3.62×10^2 – 8.84×10^{10}	56.24–207.99	−208.11–−51.04	183.15–239.10	
	240		2.71×10^2 – 4.67×10^{18}	57.25–330.26	−210.77–96.28	185.28–271.78	

8. The Criado Master-Plot Methods

The evaluation of reaction mechanisms represents the final step in understanding hydrochar combustion, as it links the calculated kinetic parameters with the physical processes occurring during thermal degradation. Although isoconversional methods provide reliable E_a values without assuming a predefined reaction model, they do not directly identify the controlling mechanism. For this reason, the Criado master-plot method is commonly applied to compare experimental conversion data with theoretical solid-state reaction models, including diffusion (D), reaction order (F), nucleation (A), geometrical contraction (R), and power-law (P) models [62] (Table 8).

As a representative example from the literature, the Criado master plots for raw lignin-rich hydrolysis residue (LRR) and HTC-derived hydrochars are presented in Figure 5 to illustrate the evolution of combustion mechanisms with HTC severity. The experimental curves show a comparable trend for all samples at low conversion levels, indicating similar initial degradation behavior dominated by moisture removal and the release of easily volatilized compounds. With increasing conversion, deviations between samples become more pronounced, reflecting the structural modifications induced by HTC. The raw residue and hydrochars produced at lower HTC severity show a closer correspondence with diffusion-related models, suggesting that internal heat and mass transfer limitations contribute to the early combustion stages. In contrast, samples obtained at higher HTC temperatures exhibit improved agreement with reaction-order and geometrical contraction models, particularly in the intermediate and high conversion regions. This behavior suggests that increased carbonization, aromatic condensation, and structural reorganization during HTC reduce diffusion limitations and enhance the contribution of chemical reaction control during hydrochar oxidation [73].

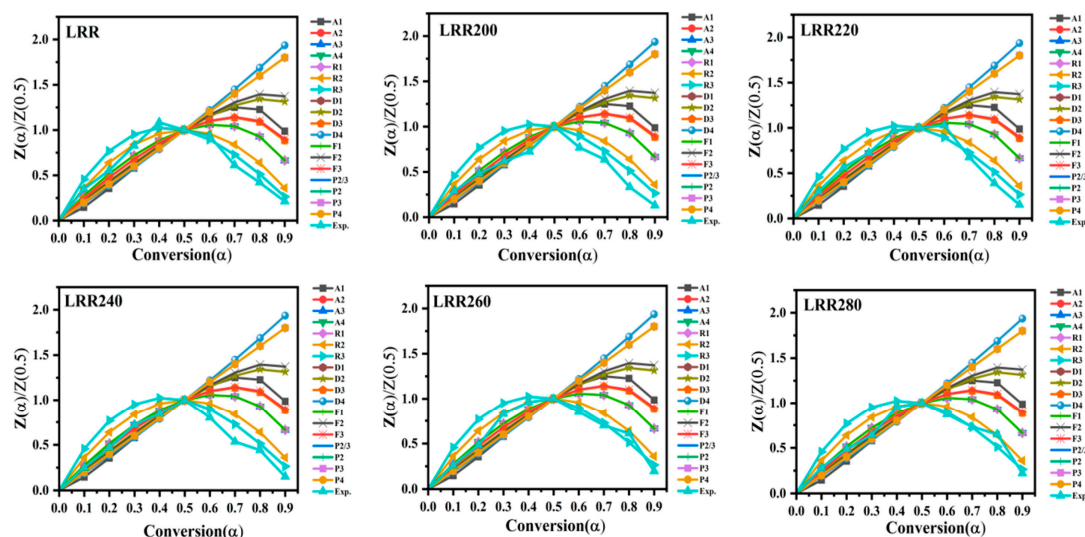


Figure 5. Criado's master plots comparing theoretical solid-state degradation models with experimental conversion data for LRR and HTC-derived hydrochars produced at different temperatures. Reproduced from Kumar et al. [73] under the terms of the license under CC BY 4.0.

In hydrochar combustion, the dominant reaction mechanism is strongly influenced by HTC severity and the resulting structural evolution. Under mild HTC conditions, experimental curves frequently follow diffusion-type models, indicating that heat and mass transfer limitations partially control the combustion process. This behavior is associated with the preservation of less-condensed lignocellulosic structures and limited oxygen diffusion through the hydrochar matrix [56]. As HTC severity increases, dehydration, decarboxylation, and polycondensation reactions progressively promote the formation of aromatic carbon structures with higher thermal stability [66]. Consequently, combustion behavior gradually shifts toward reaction-controlled models, reflecting the increasing contribution of chemical reaction kinetics relative to diffusion limitations.

The transition from diffusion-controlled to reaction-controlled mechanisms is particularly evident in hydrochars produced at elevated HTC temperatures, where structural ordering and carbon densification become more pronounced. In contrast, high-ash feedstocks may retain diffusion-related limitations due to the accumulation of inorganic species that restrict oxygen accessibility and shield reactive sites during combustion [67]. Overall, the Criado master-plot analysis supports the kinetic and thermodynamic observations, confirming that hydrothermal carbonisation modifies not only E_a values but also the dominant combustion pathways governing hydrochar oxidation [74].

Table 8. Theoretical model functions for solid-state reaction mechanisms [65].

Mechanisms		Symbol	$f(\alpha)$	$g(\alpha)$
Reaction order	First-order	F1	$1 - \alpha$	$-\ln(1 - \alpha)$
	Second-order	F2	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
	Third-order	F3	$(1 - \alpha)^3$	$((1 - \alpha)^{-2} - 1)/2$
	nth-order	F _n	$(1 - \alpha)^n$	$((1 - \alpha)^{-(n-1)} - 1)/(n - 1)$
Diffusion	One-way transport	D1	$1/2\alpha$	α^2
	Two-way transport	D2	$(-\ln(1 - \alpha)) - 1$	$\alpha + (1 - \alpha)\ln(1 - \alpha)$
	Three-way transport	D3	$3/2 (1 - \alpha)^{2/3} (1 - (1 - \alpha^{1/3})^{-1})$	$(1 - (1 - \alpha)^{1/3})^2$
	Ginstling–Brounshtein equation	D4	$3/2((1 - \alpha)^{1/3} - 1)^{-1}$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
Geometrical contraction	Cylinder contraction	R2	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$

Random nuclea- tion and nuclei growth	Sphere contraction	R3	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
	Two-dimensional	A2	$2(1 - \alpha)(-\ln(1 - \alpha))^{1/2}$	$(-\ln(1 - \alpha))^{1/2}$
	Three-dimensional	A3	$3(1 - \alpha)(-\ln(1 - \alpha))^{2/3}$	$(-\ln(1 - \alpha))^{1/3}$
Exponential nucle- ation	2-Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
	3-Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
	4-Power law	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$

9. Challenges and Future Perspectives

Despite the advancements in utilizing HTC for waste valorization, compiling and scaling these multi-component datasets reveals distinct research gaps that must be addressed to transition from laboratory evaluations to industrial solid fuel production. A primary challenge is the strong dependence of hydrochar fuel properties on the initial feedstock matrix and carbonization severity. Under identical operational conditions, different biomass streams exhibit highly divergent combustion profiles, thermodynamic stability, and kinetic footprints. This heterogeneous response complicates the establishment of universal process parameters or standardized combustion models for industrial boilers.

To address this descriptive gap and move the field toward predictive modeling, future research needs to shift from qualitative trial-and-error laboratory evaluations toward data-driven methods. Specifically, the development of machine learning (ML) models trained on integrated datasets, compiling feedstock proximate/ultimate analyses, HTC variables (temperature, residence time, water-to-biomass ratio), and thermogravimetric (TGA) kinetic triplets, is required. These models should target the multi-component forecasting of hydrochar characteristics and oxidation behavior, reducing the need for extensive laboratory screening.

Furthermore, to resolve the current fragmentation in the literature and connect model-free kinetics with solid-state reaction pathways, a standardized, four-step methodological protocol is proposed as a guideline for future HTC combustion studies:

1. **Kinetic Profiling:** Determining stable E_a trajectories across the entire conversion range using complementary isoconversional methods (FWO, KAS, and Starink) to eliminate method-specific artifacts.
2. **Thermodynamic Fingerprinting:** Utilizing these isolated E_a values to calculate the incremental shifts in ΔH , ΔG , and ΔS , thereby linking reaction rates directly to thermodynamic state functions.
3. **Mechanistic Mapping:** Feeding these established kinetic parameters into Criado master-plot geometric equations to identify the exact reaction mechanisms (such as diffusion regimes vs. reaction-order control) dominating specific conversion stages.
4. **Predictive Scaling:** Integrating these multi-layered kinetic matrices and feedstock profiles into data-driven ML setups to enable the simulation of combustion behavior across heterogeneous biomass streams.

Concurrently, the operational limitations imposed by the inorganic fraction of wet wastes must be rigorously confronted. Feedstocks characterized by high ash content, such as anaerobic digestates and spent mushroom substrates, yield hydrochars that introduce risks of slagging, fouling, and oxygen diffusion barriers within high-temperature zones. Under severe HTC configurations, carbon condensation and micro-pore collapse can further restrict reactive site accessibility, offsetting the benefits of energy densification. Therefore, optimizing the trade-off between carbon densification and volatile reactivity remains a vital target. Future research directions should deploy targeted experimental setups, including chemical looping or staged combustion configurations, to monitor the real-time

volatilization and transformation of specific ash-forming elements (K, Na, Ca, Mg, Si, P). Quantifying these specific inorganic pathways is important for understanding how mineral matter shields active carbon sites and alters local transport phenomena during large-scale oxidation.

Beyond fuel chemistry, the commercial viability of HTC is constrained by process economics and operational feasibility when compared to alternative thermochemical platforms. Table 9 outlines the key operational parameters, advantages, and limitations of HTC relative to conventional pyrolysis and gasification.

Table 9. Comparison of hydrothermal carbonisation with other thermochemical conversion technologies.

Technology	Temperature (°C)	Feedstock Moisture	Pretreatment	Main Product	Main Advantage	Main Limitation	Ref.
HTC	180–260	High	Not required	Hydrochar	Suitable for wet biomass; reduced drying demand	Pressurized reactor; higher CAPEX	[75,76]
Pyrolysis	350–700	Low	Drying required	Biochar	High carbon recovery	Additional energy for drying	[77,78]
Gasification	700–1200	Low	Drying required	Syngas	High energy conversion efficiency	Complex gas cleaning	[77,79]

As summarized in Table 9, HTC offers a major thermal and economic advantage when treating highly moist biomass fractions (e.g., food waste, sludges, and fresh agricultural residues) because it operates directly in an aqueous environment under subcritical autogenous pressure. This process eliminates the intensive thermal energy demand required for feedstock pre-drying, which typically reduces the thermal efficiency and increases operational expenditures (OPEX) of dry thermochemical systems like pyrolysis and gasification.

However, the requirement for continuous operation under pressurized conditions introduces economic challenges, primarily associated with high capital investment (CAPEX) for pressure-rated reactors, specialized feeding mechanisms, and corrosion-resistant auxiliary components. Additional costs arise from post-process water management, as the process generates a liquid phase containing organic fractions that require dedicated catalytic or biological treatment. Consequently, while high-temperature technologies (pyrolysis and gasification) remain more economically viable for rapid centralized energy recovery from dry woody biomass, HTC presents superior economic potential for the decentralized processing of wet organic wastes within localized circular networks.

To transition from bench-scale TGA assessments to actual commercial energy infrastructures, the priority for future studies must shift toward continuous pilot-scale fluidized bed or drop-tube furnace trials. Running these larger-scale experiments in parallel with comprehensive techno-economic assessments (TEA) and life-cycle analyses (LCA) represents the only reliable methodology to fully quantify the long-term economic scalability and net environmental trade-offs of integrating hydrochar into real-world energy matrices.

10. Conclusions

HTC represents an effective and versatile pathway for converting diverse waste biomass feedstocks into energy-dense solid fuels with tunable combustion properties. The process promotes progressive carbon enrichment, oxygen removal, and structural reorganization of the biomass matrix, leading to hydrochars with improved HHV, ED, and thermal stability. How-

ever, the extent of these transformations strongly depends on both HTC severity and feedstock composition, highlighting the importance of tailored process optimization.

This review demonstrates that moderate HTC conditions, typically between 180 and 220 °C, often provide the most favorable balance between combustion reactivity and fuel quality. Under these conditions, hydrochars generally exhibit reduced E_a and improved oxidation behavior while retaining sufficiently reactive structures. In contrast, more severe HTC conditions promote extensive dehydration, decarboxylation, and aromatic condensation, resulting in increasingly ordered and thermally stable carbon matrices with lower combustion reactivity. The transition from diffusion-controlled to reaction-controlled combustion mechanisms further confirms the progressive structural evolution induced by HTC.

The analysis also reveals that feedstock composition plays a decisive role in governing hydrochar behavior. Even under similar HTC conditions, substantial differences in activation energy, combustion profiles, ash accumulation, and thermodynamic parameters are observed due to variations in lignocellulosic composition and inorganic content. High-ash feedstocks, such as spent mushroom substrate and digestate, remain particularly challenging because mineral accumulation can limit oxygen diffusion and increase the risks of slagging and fouling during combustion.

Overall, the integration of fuel characterization, combustion analysis, isoconversional kinetics, thermodynamic interpretation, and reaction mechanism modeling provides a more comprehensive understanding of hydrochar combustion behavior. Future research should focus on strengthening the relationship between structural evolution, ash chemistry, and combustion reactivity while expanding pilot-scale investigations and process integration studies. Such approaches will be essential for advancing hydrothermal carbonisation toward large-scale applications within sustainable waste-to-energy and circular bioeconomy systems.

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