

Integration of Hydrothermal Carbonization and Anaerobic Digestion for Energy Recovery of Biomass Waste: An Overview

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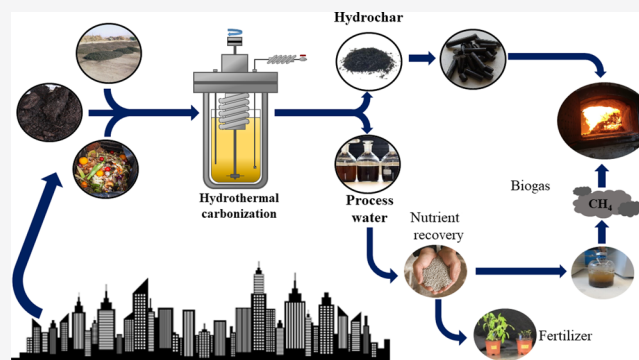
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ABSTRACT: Hydrothermal carbonization is emerging as a promising eco-friendly technology for the management of wet biomass wastes through energy recovery. It avoids drying of the feedstock and operates at a much lower temperature than conventional thermal conversion technologies, giving rise to a carbonaceous solid, hydrochar, of improved fuel quality with respect to the starting biomass. However, the aqueous fraction resulting from this process, the so-called process water, represents a troublesome secondary waste requiring effective treatment because of the high chemical oxygen demand and the presence of varying amounts of nutrients. Anaerobic digestion appears as a potential solution allowing significant reduction of the organic load while producing methane-rich biogas, thus contributing to energy recovery. Integrating hydrothermal carbonization and anaerobic digestion is gaining interest in the literature. This review compiles the reported studies on the application of hydrothermal carbonization coupled with anaerobic digestion for energy recovery of different biomass wastes, analyzing the energy balances. The main characteristics of the resulting HC and the methanogenic potential of the process waters are reviewed in connection with the operating conditions, as well as the possibility of nutrient recovery. Life cycle assessment and economic studies are included.



1. INTRODUCTION

The rising energy demand, the dependence on fossil fuels, and the growing concern for the environment, as well as the political commitment adopted in the Paris climate agreement,¹ encourage the search for new sources of energy that are more sustainable and compatible with environment protection. Worldwide, energy consumption represents the major source of greenhouse gases (GHG) emissions. Two thirds of those emissions (≈ 22.4 Mt CO₂equiv.) are caused by burning fossil fuels, and in the European Union (EU), up to 78% (≈ 2.6 Mt CO₂equiv.) of total emissions are linked to energy production,² leading in 2020 to historical CO₂ concentrations in the atmosphere (>425 ppm). Meanwhile, another significant problem is the increasing generation and accumulation of waste in the environment. In the EU, 86 Mt of biowaste (food and garden waste), 50 Mt sewage sludge, 2.7 Mt animal manure, and 220 Mt of forest and agricultural residues were generated^{3–7} in 2018. All these residues, called biomass, have been considered potentially problematic and difficult to manage. Landfills received 46% of the EU organic fraction of municipal waste (OFMW) generated, with 24% composted or recycled and only 30% used to energy recovery.⁸ Worldwide power generation from biomass accounts for about 6% of total renewable sources.² In many cases, raw biomass suffers important drawbacks to be directly used as fuel, due to high

wetness, high ash content, and low energy density.^{5,9,10} However, studies on biomass wastes and their potential as a fossil fuels substitute have gained growing attention.^{11–14}

Besides the traditional combustion of biomass for energy recovery, there are new and eco-friendly processes such as physicochemical, biochemical, and thermochemical processes. Physicochemical conversion consists in the esterification of oilseeds for the production of bio-oil. Biochemical processes, like anaerobic digestion (AD) and fermentation, are two of the most used ways to convert biomass into biofuel (biogas and ethanol, respectively). AD is a mature technology converting organic matter into methane-rich biogas. It has received considerable attention due to energy and nutrient recovery.¹⁵ Today, there are about 18,000 AD plants in the EU with a yearly overall production around 11,000 MW of equivalent energy.¹⁶ AD is a well-known biological process carried out by anaerobic microorganisms involving four main stages that are

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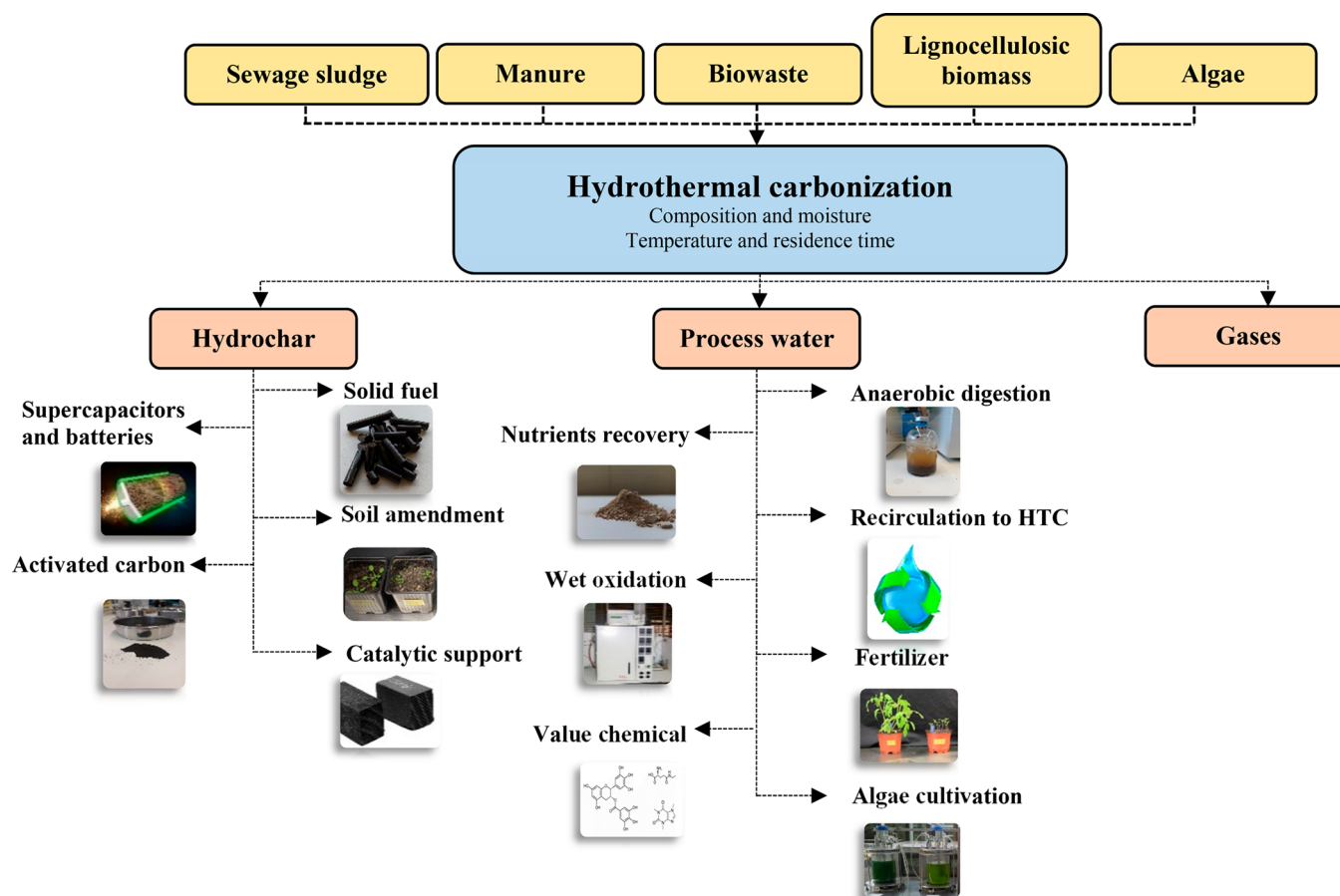


Figure 1. Hydrothermal carbonization, products, and applications.

hydrolysis, acidogenesis, acetogenesis and methanogenesis, with the former being recognized as the rate-limiting one. Key factors affecting digestion efficiency are the nature of the feedstock, the pretreatment steps, the design of the digester, and the operating conditions, including pH, temperature, carbon to nitrogen ratio (C:N), organic loading rate, and hydraulic retention time.¹⁵

Thermochemical processes, such as pyrolysis, gasification, and hydrothermal carbonization (HTC), have been gaining special interest for the transformation of biomass into char + bio-oil, syngas, and hydrochar, respectively, as the main products.^{14,17–19} Previous studies revealed that gasification and pyrolysis are not feasible or sustainable for wetness contents higher than around 30%,^{20–22} a quite frequent feature of biomass wastes. HTC represents an attractive and eco-friendly technology for thermochemical processing of high wetness biomass. HTC was first studied by Nobel laureate Friedrich Bergius (1913), who described the process of carbonization in a few hours by means of high temperature and self-generated pressure.²³ In recent years, HTC technology has received growing attention at lab and pilot-plant scale, and a number of full-scale projects have been developed with different biomass wastes, such as sewage sludge,^{24–26} animal manure,^{14,27,28} biowaste,^{29,30} lignocellulosic biomass^{31–33} and mixed residues.^{34–36} Some pilot-scale HTC plants have been constructed (Ingelia, HTCcycle, Terranova Energy, Ava CO₂), but thus far, the detailed structure of such plants and their efficiencies are still unknown to most researchers involved in HTC.

Thus, far, the ability of HTC to produce clean solid biofuel from wet biomass wastes has been reported in the already wide literature on the topic. However, a major challenge of this technology is the effective treatment of the resulting aqueous residue, so-called process water (PW). At the commonly used temperature (180–250 °C), some significant amount of matter from the starting feedstock is transferred in the form of soluble organic compounds, salts, and nutrients to the aqueous phase, which must be conveniently treated before discharge. Recent studies have been conducted on the integration of HTC, AD, and nutrient recovery to provide a sustainable way to manage high-moisture biomass wastes with improved energy recovery.

In summary, the potential advantages of integrating HTC, AD, and nutrient recovery are the following: (i) contribution to mitigate the problems of organic waste disposal and GHG generation, (ii) no biomass drying required, (iii) hydrochar production of expected growing applications in the short term, (iv) obtaining a clean fuel gas, and (v) HTC, AD, and nutrient recovery fitting well in the concept of circular economy.

This review examines the existing literature on HTC coupled with AD applied to different biomass wastes, focusing the attention on the energy balances and considering the potential recovery of nutrients from the PW. The operating conditions are associated with the main characteristics of the resulting HC as well as the methanogenic potential of the PW. Life cycle assessment (LCA) and economic studies are included.

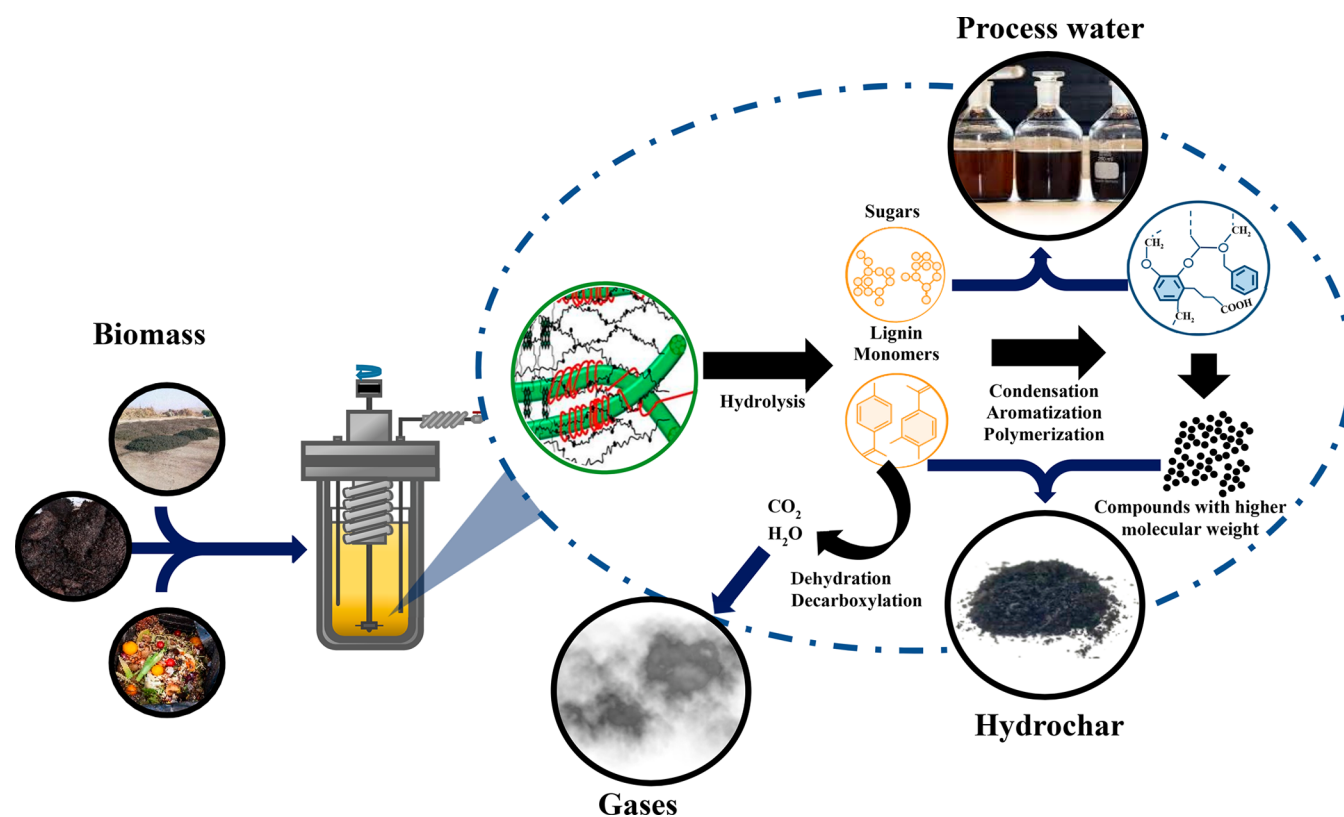


Figure 2. Main reaction pathways in HTC.

Table 1. Distribution of Main HTC Fractions from Different Biomass Wastes under Conditions Indicated in Literature

Biomass waste	Temperature (°C)	Time (min)	Biomass:water ratio	HC (%)	PW (%)	Non-condensable gases (%)	ref
Primary sewage sludge	180–220	30–240	10:90	61–71	29–39	—	56
	150–250	30	15:85	37–50	84–85	—	57
Secondary sewage sludge	150–250	30	20:80	40–56	≈ 84	3	57
Mixed sewage sludge	150–250	30	12.5:87.5	40–55	84–85	4–5	57
Digestate	250	30	15:85	64–88	12–36	—	24
	200–300	30–120	10:90	49–73	27–51	—	26
	180–240	60	2.5–30:70–97.5	52–74	26–53	—	58
	160–220	30	15:85	62–70	32–34	—	59
OFMW ^a	180–250	60–360	12.5:87.5	40–67	29–55	—	29
Wheat straw	220	40	20:80	65	32	—	60
Orange pomace	175–260	30–120	10:90	39–54	46–61	—	61
Chaff	200	240	5–9:91–95	51–53	22–30	—	62
Water hyacinth	150–250	60	10:90	38–80	20–62	—	63
Macroalgae	150–250	60	10:90	22–48	78–52	—	64
Microalgae	180–240	60	10:90	37	63	—	65
Cattle manure	170–230	60	15:85	54–65	35–46	—	14

^aOFMW is the organic fraction of municipal waste.

Table 2. Representative Characteristics (Dry Basis) of Biomass Wastes Used in HTC Experiments of Table 1

Biomass waste	C (%)	N (%)	S (%)	FC ^a (%)	VM ^a (%)	Ash (%)	HHV (MJ/kg)	ref
Primary sewage sludge	36.6	5.3	—	3.9	68.6	27.4	16.2	56
	31.1	3.0	0.6	—	—	36.2	13.7	57
Secondary sewage sludge	32.2	3.4	0.6	—	—	36.4	14.2	57
Mixed sewage sludge	30.9	3.0	0.7	—	—	36.3	13.5	57
Digestate	33.3	4.0	1.2	9.3	51.8	36.7	14.2	24
	40.2	4.7	—	—	70.2	29.9	18.0	26
	32.7	5.1	1.0	4.4	54.7	40.9	14.9	58
	34.8	5.0	1.2	7.7	55.8	31.8	14.0	59
OFMW	42.9	2.8	—	10.9	71.3	17.9	19.1	29
Wheat straw	49.2	<0.1	0	17.8	82.1	0.1	17.8	60
Orange pomace	45.4	1.6	1.2	—	—	5.5	20.3	61
Chaff	45.4	0.1	—	—	—	6.2	18.6	62
Water hyacinth	38.7	2.7	0.1	0.0	85.4	14.6	11.0	63
Macroalgae	33.0	1.9	0	13.3	75.8	10.9	12.4	64
	35.6	2.0	0	11.8	70.8	17.4	14.2	64
Microalgae	38.4	5.8	0.5	12.1	48.3	29.7	16.9	65
Cattle manure	39.9	2.7	0.5	15.7	68.8	15.5	16.0	14

^aFC and VM is referred to fixed carbon and volatile matter, respectively.

2. HYDROTHERMAL CARBONIZATION

HTC is a thermochemical process for the treatment of biomass with high wetness performed under mild temperature (180–250 °C), low residence times (5–240 min), and autogenerated pressure. The main product of HTC is a carbonaceous solid named hydrochar (HC), but a liquid fraction called process water and a gas phase are also produced.^{37–40} Although the natural direct application of the HC is like a solid fuel alone^{41,42} or blended with coal or biomass,^{43,44} several authors have proposed some other potential uses after more or less intense transformation, such as for soil amendment,^{45,46} supercapacitors,^{47,48} active carbon,^{49–51} anaerobic digestion (of the slurry),^{52,53} and catalysts support.^{54,55} Figure 1 shows a representative scheme of HTC products (fractions) and their potential applications.

The PW from HTC has been regarded as a difficult-to-manage residue and has been the main drawback for full-scale implementation of this technology. However, in recent years, PW has been considered by some researchers as an interesting byproduct rather than a problem. Several potential solutions have been proposed, such as anaerobic digestion,^{24,66} nutrient recovery,^{58,67} PW recirculation to the HTC,^{32,59} wet oxidation,^{68,69} liquid fertilizer,^{70,71} and chemical recovery.^{72,73} The literature has also reported a small fraction of oil molecules generated in the HTC.⁷¹ Bio-oil species were obtained in the HTC from biomass rich in fatty acids (such as oleaginous plants), sewage sludge, and animal manure,^{7,74} although at fairly low yields. This bio-oil has shown a high heating value (HHV) and low ash content. This process also produces relatively small amounts of gases (1–5 wt % of the

initial feedstock), consisting mainly of CO₂, CO, CH₄, and H₂,⁷⁵ and a series of volatile organic compounds in smaller proportions, such as alcohols and alkylated naphthalenes.⁷⁶ The presence of CO₂ is indicative of the decarboxylation process taking place, although the amount generated is lower than that emitted in landfills or by composting.⁷⁷

The presence of water in HTC reduces the activation energy of the hydrolytic breakdown of biomass, resulting in less energy required for the process to take place.⁷⁸ The main reactions in HTC are hydrolysis, dehydration, decarboxylation, polymerization, recondensation, aromatization, and Maillards reactions. Reactions like hydrolysis, decarboxylation, and dehydration, typical of charring processes, break ester and ether bonds removing H and O from the biosolid as water and CO₂ and increasing the relative carbon content and the heating value of the solid product. The hydrolyzed organic molecules undergo polymerization, recondensation, aromatization, and Maillard reactions, giving rise to high molecular weight species that precipitate in the HC,^{32,79} while the rest remain in the PW. Figure 2 depicts the main reaction pathways in HTC.

2.1. Distribution of HTC Fractions. The relative distribution of the three main HTC fractions (HC, PW, and gas) depends on the nature of the biomass feedstock, relative amount of water (biomass:water ratio, b:w), reaction time, and operating temperature (with the corresponding associated pressure). Table 1 collects the results reported in the literature from different types of biomass (see characteristics in Table 2) under the given conditions. Temperature and reaction time are the factors determining the extent of carbonization of a given feedstock. Increasing both operating variables leads to a more

Table 3. Main Characteristics of Hydrochars and Energy Recovery in This Solid Product

Biomass waste	Temperature (°C)	Time (min)	C (%)	N (%)	S (%)	FC (%)	VM (%)	Ash (%)	HHV (MJ/kg)	Carbon yield (%)	Energy recovery (%)	ref
Primary sewage sludge	160	60	37.7	4.50	—	3.30	63.7	33.0	17.2	83.5	84.9	56
	160	30	40.3	2.1	0.1	—	—	28.7	18.5	65.3	68.7	57
Secondary sewage sludge	160	30	33.1	3.3	0.7	—	—	35.9	14.8	56.5	57.4	57
Mixed sewage sludge	160	30	29.9	2.5	0.6	—	—	—	14.5	67.6	59.8	57
Digestate	250	30	33.8	2.4	1.3	8.4	41.5	48.6	15.0	77.1	76.7	24
	200	60	42.4	1.9	—	0	54.5	45.5	21.5	64.3	66.0	26
	180	60	30.8	4.2	1.0	6.2	50.9	42.9	14.7	70.0	73.2	58
	160	30	35.5	5.1	1.1	9.2	49.7	38.6	15.0	70.2	75.0	59
OFMW	180	60	43.5	2.0	—	10.0	76.3	13.8	22.6	67.9	79.2	29
Wheat straw	220	40	63.5	0.1	—	31.2	68.7	0.1	24.6	83.8	—	60
Orange pomace	175	120	55.8	2.1	0.2	—	—	4.1	23.2	53.5	53.0	61
Chaff	200	240	58.6	1.7	0	—	—	4.6	23.8	66.7	66.7	62
Water hyacinth	200	60	45.6	3.7	0	—	70.6	15.9	12.0	81.1	84.0	63
Macroalgae	150	60	46.8	3.0	0	16.1	73.1	10.8	16.9	46.7	51.0	64
	150	60	41.1	2.8	0	16.9	71.4	11.7	18.1	40.0	56.8	64
Microalgae	180	60	38.8	2.3	0.2	10.9	45.9	34.7	16.7	39.3	40.8	65
Cattle manure	200	60	44.8	2.1	0.1	17.9	59.7	23.3	19.0	64.0	67.8	14

carbon-concentrated solid product but at lower mass yield, so that the results of the process with respect to hydrochar production must be evaluated in terms of energy.

Aragón-Briceño et al.²⁴ analyzed the influence of b:w ratio on the HC mass yield. The results showed that increasing that ratio increased the HC mass yield because a lower relative amount of water implies less solubilization from the biosolid. Lu and Berge⁸⁰ arrived at a similar conclusion. A direct relation was found between the carbon content of the raw biomasses and the HC mass yield, so that the higher the carbon content of the starting biomass is, the higher the mass yields of HCs are and the higher the heating value, which improves the energy recovery. The decrease in HC mass yield due to the high water content in the feedstock is probably due in part to the fact that water under subcritical conditions is richer in H⁺ ions that act as catalysts in hydrolysis reactions and, consequently, in the following steps involved in this process.⁸¹ These H⁺ ions promote the breaking of ester and ether bonds in the waste and tend to form a large amount of low molecular weight organic compounds that are transferred to the PW, resulting in lower HC mass yield. According to Antero et al.,⁷⁸ the water content in the biowaste reduces the activation energy of feedstock hydrolysis, leading to lower energy consumption for carbonization reactions, although there is still no consensus on the optimum amount of water. Heidari et al.⁶⁰ observed that waste recovery by HTC is an efficient and cost-effective alternative when the moisture content of the biomass is above 40%. This study only considered the energy associated with HC and the biogas generated in AD versus direct combustion (with predrying) of the biomass but without including nutrient

recovery, which would make this HTC technology much more attractive and cost effective. Moreover, it is important to consider that water implies energy needs in the reactor, which at some point can negatively affect the overall energy balance. Therefore, it is quite important to optimize the b:w ratio.

Operating conditions, such as temperature, residence time, and b:w ratio, are of determining importance for the quality of the solid fuel obtained. In addition, the characteristics of the starting waste are also crucial to obtain a good HC, with a high heating value and low ash and S and N contents. These characteristics were analyzed by Lu and Berge⁸⁰ in the HTC of different single and mixed substrates, confirming that the feedstock properties strongly influence the characteristics of carbonization products. In general, higher contents of cellulose, hemicellulose, sugars, starch, and proteins produce lower HC yield due to the high reactivity of these components under subcritical water conditions.^{82,83} The opposite occurs with lignin given its higher thermochemical stability. Feedstocks like sewage sludge and animal manure give higher HC mass yield, but vary greatly due to their high ash content, which determines a poorer energy-density solid product. It has been reported in the literature that metals, such as Fe, Al, P, and Ca, produce highly stable compounds of low water solubility prone to remain in the HC.^{84–86} This is much more noticeable in the case of sewage sludge, when different Fe- and Al-based polyelectrolytes are used in the flocculation–coagulation stage in wastewater treatment. On the other hand, it has been reported that metals such as Na and K, which are highly soluble in water, are transferred to the PW, thus improving the combustion behavior of HC, avoiding problems

Table 4. Limits for Industrial Use of Hydrochars^a

Feedstock	Normative							Informative					
	N (%)	S (%)	Cl (%)	Ash (%)	VM (%)	HHV (MJ/kg)	As (ppm)	Cd (ppm)	Cr (ppm)	Pb (ppm)	Ni (ppm)	Zn (ppm)	Ash fusion temperature (°C)
Lignocellulosic biomass and digestate	1.5	0.2	0.15	10	<75	>18	10	10	50	100	100	300	1150
Biowaste and sewage sludge	3	0.5	0.2	Value to be stated	<75	>17							Values to be stated

^aStandard ISO/TS 17225-8.⁹⁰

Table 5. Main Characteristics of Process Water from Hydrothermal Carbonization of Biomass Waste

Biomass waste	Temperature (°C)	Time (min)	pH	COD (g/L)	TOC (g/L)	TVFA (g/L)	TN (g/L)	TP (mg/L)	Carbon yield (%)	ref
Primary sewage sludge	160	60	—	21	10	6.5	1.1	—	16.5	56
	160	30		51	—	—	3.8	30	34.7	57
Secondary sewage sludge	160	30	—	16	—	—	5.8	70	43.5	57
Mixed sewage sludge	160	30	—	19	—	—	4.8	40	32.4	57
Digestate	250	30	8.3	72.3	29.8	4.6	8.1	167.6	22.9	24
	200	60	7.1	52.5	11.4	—	—	—	26	26
	180	60	7.4	56.2	28.8	3.5	8.1	18.2	30.1	58
	160	30	9.2	12.6	4.7	0.2	2.1	53.9	30.5	59
OFMW	180	60	4.9	43.9	—	1.2	1.1	—	32.1	29
Wheat straw	220	40	—	—	—	—	—	—	16.7	60
Orange pomace	175	120	3.9	65	25	1.7	—	—	28.5	61
Chaff	200	240	3.4	44.3	19.2	4.1	1.1	423	18.2	62
Water hyacinth	200	60	4.4	27.5	11.1	1.4	—	—	18.9	63
Macroalgae	150	60	4.4	39	15.6	0.3	—	—	52	64
	150	60	4.8	41.4	16.6	0.1	—	—	50	64
Microalgae	180	60	6.1	26.8	12.8	1.4	—	—	60.7	65
Cattle manure	200	60	6.9	12.8	6.6	2.9	2.4	—	35.8	14

such as fouling and slagging.^{43,87} According to Zhu et al.,⁸⁸ increasing the water content of the HTC feeding increases the leaching of alkali metals (Na and K) and Mg to the PW, while heavy metals were barely affected because the formation of low-solubility species at increasing temperature favored immobilization in the HC.

2.2. Hydrochar Characteristics. Table 3 summarizes the main characteristics of hydrochars reported in the literature from the HTC of the biomass feedstocks of Table 2 under different conditions of temperature and reaction time (see Table 1 for the b:w ratio). As a main feature, the hydrochar from HTC is an upgraded solid fuel with respect to the starting biomass feedstock. It has a more homogeneous chemical composition, with higher mass density and, in general, decreased sulfur, nitrogen, and ash contents,^{32,89} thus entailing improved energy density and quality. Therefore, as a general trend, HTC increases the C content and heating value with respect to the feedstock. In some cases, increases in C content around 25% and up to 30% in HHV have been observed. However, the reactions involved in HTC imply a more or less

significant transfer of carbon-containing species to the aqueous and gas phases, so that the C and energy retained in the hydrochar varied within a wide range, about 40%–85%, depending on the starting biomass and the operating conditions. Table 3 also shows the proximate analysis and the N and S contents of the hydrochars.

2.2.1. Use of Hydrochar for Energy Production. The ISO 17225-8⁹⁰ Standard defines the requirements for industrial use of HC as a solid fuel (Table 4). These limits were established to prevent the emissions of NO_x, SO_x, and chlorinated species (like HCl, PCBs, and PCDD/F) and minimize corrosion and slagging problems, as well as the risk of explosions (volatile matter) in the combustion chambers⁹¹ in order to obtain a carbonaceous material ideal for combustion with low environmental impact.

In general, the S, N, and VM of the feedstock are transferred to the PW in great part.^{92,93} Deamination is the main reaction reducing the N content of the final HC, which in most cases represents no more than 10%–30% of the existing in the raw biomass.^{59,93,94} A similar effect occurs with S and VM.

Table 6. COD Removal and Methane Production in Anaerobic Digestion of Process Water

Biomass waste	Temperature (°C)	Time (min)	AD of PW from HTC			AD feedstock		ref
			COD removal (%)	Methane yield (mL CH ₄ /g COD _{added})	Energy recovery (%)	Methane yield (mL CH ₄ /g COD)	Energy recovery (%)	
Primary sewage sludge	160	60	—	219	6.7	—	—	56
	160	30	61	259	13.4	137	13.2	57
Secondary sewage sludge	160	30	51	258	15.3	120	4.3	57
Mixed sewage sludge	160	30	66	280	20.1	253	8.1	57
Digestate	250	30	57	288	16.6	135	42.6	24
	200	60	50	297	9.1	—	—	26
	180	60	46	325	23.5	150	36.4	58
	160	30	80	276	7.7	174	42.6	59
OFMW	180	60	57	205	11.5	150	24.3	29
Wheat straw	220	40	—	165	26.4	—	—	60
Orange pomace	175	120	—	213	25.6	—	—	61
Chaff	200	240	—	196	4.9	141	24.1	62
Water hyacinth	200	60	61	213	13.9	103	28.0	63
Macroalgae	150	60	—	230	18.8	200	34.2	64
	180	60	—	225	12.0	175	12.9	64
Microalgae	200	60	55	356	48.5	120	20.0	65
Cattle manure	160	60	49	294	18.8	111	25.6	14

However, a large mass loss from the solid feedstock may compensate that transfer to the liquid phase entailing in some cases concentrations of those components in the HC exceeding the ISO 17225-8 limits. The nature of the starting biomass is a determining issue in that respect, and commonly, lignocellulosic biomasses are much better precursors for good-quality fuel hydrochars than other biomass wastes like, for instance, sewage sludge, manure, or algae. A potential solution investigated by several authors has been blending these last few with lignocellulosic residues for co-HTC.^{34,35,44,95}

Co-HTC appears as an alternative with the objective of improving the properties of the HC obtained, especially in the case of lower quality wastes, such as sewage sludge or animal manure.⁹⁶ Lignocellulosic biomass has been the richest feedstock studied in co-HTC. The hydrochar obtained from co-HTC of sewage sludge and pinewood sawdust showed 80% less ash and 40% higher carbon content compared to the raw sewage sludge. In addition, the higher the ratio of pinewood sawdust to sewage sludge is, the higher the HC yield is, resulting in higher energy recovery in the hydrochar from HTC.³⁵ Similar results were obtained in co-HTC of sewage sludge with fruit and agricultural wastes.³⁴ The mixture of low-quality biomass with lignocellulosic material presents a great synergy, high yields of HC, and better physicochemical characteristics such as high HHV and low ash, N, and S contents; plus, they are products that can be valorized together without the need for prior separation. Additionally, it could help in the extraction of nutrients from PW since it has been

reported that PW from lignocellulosic biomass HTC present acid pH,^{33,36,97} unlike the pH of sewage sludge, algae, and animal manure that present basic values,^{14,24,65,71} and as it is already known, basic pH nutrients such as phosphorus tend to precipitate as insoluble salts^{98,99} and are retained in the HC, which would hinder their extraction for use as fertilizers. Co-combustion of hydrochars with different types of coals has been also studied^{100–102} and could be other alternative to fulfill the requirement establish in the ISO/TS 17225-8 guideline.

2.3. Process Water. Table 5 shows representative analyses of the process water from HTC of different biomass feedstocks under the given conditions. Depending of the biomass and the operating conditions, the liquid fraction from HTC has been reported to retain within about 20–65 wt % of the carbon stored in the substrate (Table 5). The composition of PW is, in general, highly complex including mostly low molecular weight soluble organic compounds such as sugars, furfural, volatile fatty acids (VFA), recalcitrant compounds, and nutrients such as ammonia-N and P-containing species. Thus, far, a number of studies have been conducted to learn the analytical characterization of this HTC fraction.^{25,103,104} In terms of overall organic load COD and TOC values, within around 10–90 and 4–30 g/L, respectively, have been measured. Therefore, effective treatment of these liquid residues is needed to avoid severe environmental impacts. On the other hand, their own composition offers opportunities for energy recovery as well as of some components like nutrients or chemical precursors.

HTC temperature, reaction time, and feedstock nature are the factors determining the characteristics of the PW. Increasing the temperature increases the COD and TOC values of PW, because higher amounts of organic components are dissolved from the biomass substrate. However, beyond 220 °C (approximately), the organic load was found to decrease in most of the cases referenced in Tables 1 and 3, due to the increasing contribution of aromatization, condensation, polymerization, and Maillard reactions of dissolved compounds, giving rise to higher molecular weight species precipitating back as HC.^{30,104–106} The P content in the PW has been found to decrease by increasing the HTC temperature. Up to 50% reduction has been reported in some cases, in particular, with sewage sludge, due to the high contents of metals like Fe and Al from flocculants, which precipitate low-solubility phosphates.^{24,57} An opposite effect has been reported for ammonium-N, with up to a 185% increase in PW by increasing the temperature in the HTC of algae, due to higher protein hydrolysis.^{63–65} The increase of temperature provoked acidification of PW in the HTC of lignocellulosic biomass, whereas the opposite has been reported with sewage sludge, algae, and manure, due to the higher protein content of these last few.^{82,94,106}

2.3.1. Potential Solutions for PW Management. The process waters from HTC are, in general, highly polluted and cannot be discharged to the environment without some previous treatment allowing effective reduction of COD and N and P species, the most representative components of those aqueous wastes. In fact, that is the main drawback affecting sustainability and hindering so far full-scale implementation of hydrothermal carbonization. However, the composition of PW offers, in principle, promising opportunities to design solutions fitting the circular economy concept, where treatment for pollution abatement can be integrated with energy and nutrient recoveries.

Several alternatives have been proposed in that respect. Recoveries of bio-oil, aromatic aldehydes, and fuel additives have been reported in the literature.^{107–109} Nutrient recovery (N, P, Mg, K) has been also studied by several authors in recent years.^{110–114} Anaerobic digestion has gained growing interest because of its adaptability to the high organic load of PW and the benefit of obtaining methane-rich biogas. In the following, the application of AD to PW treatment with energy recovery is revised and also the way nutrient recovery could substantially improve the overall process.

3. ANAEROBIC DIGESTION OF PROCESS WATER

AD appears a promising complement to HTC allowing energy recovery while reducing substantially the commonly high COD of the resulting process water.^{24,29,115} AD is a well-known technology widely applied to high organic load wastewaters and waste sludges. However, its effective feasibility depends on multiple factors such as substrate composition, temperature, pH, microbial community, and type and source of inoculum used, among others, and therefore, the AD of PW from HTC needs to be better understood for the sake of optimal integration.

Literature results on AD of PW have shown thus far some significant discrepancies in terms of COD removal and methane yield (Table 6). Process waters from higher HTC temperatures appear to show poorer behavior in anaerobic digestion, although a comprehensive general conclusion cannot be postulated thus far, and further studies are needed where

the nature of the feedstock and the operating variables in both HTC and AD should be more systematically considered. The available results seem to indicate that methane yield is favored in process waters from HTC carried out below 200 °C and are comparable or better in many cases to the obtained upon direct AD of the starting biomass. The energy recovery is lower, as expected since a great part of the energy value of the feedstock remains stored in the hydrochar. Increasing the HTC temperature within the range of 200–300 °C dramatically decreases the efficiency of further AD of the resulting PW. Gaur et al.²⁶ reported that a severity factor higher than 6 in HTC (>200 °C and 60 min) leads to a substantial decrease of methane production, rapid inhibition, and acidification in the AD step.

The direct AD of some raw feedstock in Table 6 without previous HTC proved to be quite uninteresting for energy recovery compared to the integrated HTC-AD. The poor results obtained with those feedstocks can be attributed mainly to the poor anaerobic biodegradability of the raw waste due to slow hydrolysis, which is the rate-limiting step of AD. In those cases, the HTC-AD approach significantly improves the energy recovery because the PW resulting from HTC is more prone to AD because of the hydrolytic breakdown undergone by the waste components upon the hydrothermal treatment, so that the COD removal from PW reaches up to 80% in some cases.

Values of the first-order rate constant for methane production (referred to the transformation of acetate to methane) ranging within 0.04–0.13 d^{−1} have been reported for the anaerobic digestion of PW. Those values are below the commonly considered ideal for rapid methane production (0.2–0.7 d^{−1}),⁴⁰ mainly due to the lag time for microorganism adaptation, poor biodegradability, presence of inhibiting species, or high ammonium concentrations in the PW. Particularly, low values of *k* (0.03–0.05 d^{−1}) have been reported in the AD of PW from sewage sludge HTC.²⁵ However, anaerobic codigestion (AcoD) of that PW with other residues improved substantially the kinetics as shown by de la Rubia et al.¹⁰³ The AcoD of PW from sewage sludge with biowaste yielded *k* values around 0.44–0.56 d^{−1}. In addition, to improve the rate of methane production and COD removal, different inoculum to substrate ratios (ISR) have been tested,^{25,29,60,116,117} with the general conclusion that ISR < 2 inhibited methanogenic activity by acidification, excess of recalcitrant compounds, and higher ammonium concentrations in the reaction medium. According to de la Rubia et al.,¹¹⁶ selecting the inoculum with appropriate characteristics and structure could improve methane production yields in AD of HTC process water. Three different types of inocula were compared, two granulars obtained from anaerobic digestion of brewery and sugar manufacture wastewaters and a flocculant inoculum from a municipal wastewater treatment plant. With the granular inocula, lag phase was not observed in the AD of PW from HTC of sewage sludge, while with the flocculant inoculum, a 5-day lag phase occurred. Similar results were reported by Villamil et al.,¹¹⁸ in AcoD of PW from HTC of primary sewage sludge.

3.1. Recalcitrant Compounds in Anaerobic Digestion.

A wide variety of compounds that are inhibitory or toxic to the AD process have been reported in the literature, such as recalcitrant nitrogen compounds, heavy metals, and N-NH₃, among others. The presence of recalcitrant and toxic compounds (produced in HTC) has been detected in the PW and are the main causes of the low methane yield by

Table 7. Energy Recovery from Hydrothermal Carbonization and Anaerobic Digestion

Biomass waste	Temperature (°C)	Time (min)	Energy recovery from HC (%)	Energy recovery from AD of PW (%)	Overall energy recovery (%)	Energy recovery in direct AD of feedstock (%)	ref
Primary sewage sludge	160	60	84.9	6.7	91.6	—	56
	160	30	68.7	13.4	82.1	13.2	57
Secondary sewage sludge	160	30	57.4	15.3	72.7	4.3	57
Mixed sewage sludge	160	30	59.8	20.1	79.9	8.1	57
Digestate	250	30	76.7	16.6	93.3	42.6	24
	200	60	66.0	9.1	75.1	—	26
	180	60	73.2	23.5	96.7	36.4	58
	160	30	75.0	7.7	82.7	42.6	59
OFMW	175	120	53.0	11.5	90.7	24.3	29
Wheat straw	200	240	66.7	26.4	93.1	—	60
Orange pomace	200	60	84.0	25.6	78.6	—	61
Chaff	150	60	51.0	4.9	71.6	24.1	62
Water hyacinth	180	60	56.8	13.9	97.9	28.0	63
Macroalgae	200	60	40.8	18.8	69.8	34.2	64
	160	60	67.8	23.0	68.8	12.9	64
Microalgae	160	60	84.9	48.5	89.3	20.0	65
Cattle manure	160	30	68.7	28.8	86.6	25.6	14

inhibition of methanogenesis.^{25,118,119} Hydrolytic degradation of lignin and reactions of sugars with amino acids, from carbohydrates and proteins, gives rise to a wide diversity of heterocyclic nitrogen-bearing and oxygenated compounds, which are water soluble, toxic, and barely prone to anaerobic biodegradation.⁹⁴ Other compounds resulting from sugar breakdown, like furans, have been also identified as recalcitrant and AD inhibitors.^{117,120,121} Several studies have reported partial or complete removal of phenols, benzaldehydes, and pyrroles in AD of HTC process waters.^{65,118,121} In general, lower HTC temperatures reduce the presence of recalcitrant species in the PW,^{26,43,82,120} and below 200 °C seems to be ideal for a better performing AD. However, obviously, the optimum temperature must be regarded in the overall context of the HTC-AD combined strategy. Several methods have been proposed in the literature to remove those recalcitrant and toxic compounds, like adsorption previous to AD with different materials such as active carbons, polyurethane, or zeolites.¹⁰⁴ The ion-exchange capacity of zeolites favors the retention of molecules with free electrons, such as nitrogen- and oxygen-bearing molecules,¹²² which have been reported recalcitrant and toxic to AD.^{39,65,118}

Another toxic species is N-NH₃ from the degradation of proteins and amino acids due to deamination reactions. According to several authors, concentrations above 1700 mg N-NH₃/L are inhibitory for anaerobic microorganisms,^{22,116} although in other studies 2500–5000 mg N-NH₃/L were reached before inhibition was observed.^{123–125} These discrep-

ancies can be due to proper acclimation that alleviates stress from N-NH₃ accumulation.

Other species that can cause inhibition of methanogenic microorganisms are heavy metals. To our best knowledge, there are no specific studies relative to the presence of heavy metals in the PW of HTC and their inhibitory effect on AD. However, it has been described how these metals have an inhibitory effect on the anaerobic digestion of different types of feedstocks. Some metals have been observed to have a positive effect on the activation of enzymes and coenzymes in AD at lower concentrations.^{123,126} Also, it is known that certain heavy metals, such as Zn (>40 ppm), Cr (>80 ppm), Cd (>32 ppm), Ni (>32 ppm), and Pb (>60 ppm), among others, cause inhibition of methanogenic microorganisms and impede the use of the digestate in soils.^{88,127,128} According to Nguyen et al.,¹²⁷ the presence of Cu²⁺, Zn²⁺, Cr⁶⁺, and Pb²⁺ decreases microbial activity, reduces COD removal by around 7%–10%, and reduces methane yield by 27%–36%.

3.2. Improved Anaerobic Digestion of Process Water.

Nowadays, different methods have been detailed to improve and provide greater stability to the AD process such as AcoD and use of biochar, among others. The use of hydrochar in the anaerobic digestion of HTC process water has been investigated, and enhanced methane production as well as better process stability were found. The HC improves hydrogenotrophic methanogenesis due to its ability to facilitate the electron transfer (DIET: direct interspecies electron transfer) and promotes the reduction of CO₂ to CH₄ by a higher amount of H⁺ intermediates.¹²⁹ Enhancements of the

Table 8. Energy Balance for the Integration of Hydrothermal Carbonization and Anaerobic Digestion

Biomass waste	Temperature (°C)	Energy Input (kWh/t _{feedstock} ^a)		Energy Output (kWh/t _{feedstock} ^a)			ref
		Feedstock	External input	HC	CH ₄	Total output	
Primary sewage sludge	160	3806	385	997	442	1439	57
	250	3806	492	549	1135	1685	57
Secondary sewage sludge	160	3800	385	1131	215	1346	57
	250	3800	492	603	372	976	57
	180	5220	429	529	165	694	136
	200	5220	316	458	244	702	136
	220	5220	288	442	245	687	136
	240	5220	272	411	253	664	136
Mixed sewage sludge	160	3806	385	1176	261	1437	57
	250	3806	492	598	497	1095	57
Digestate	210	4528	2071	1860	133	2363	137
Water hyacinth	150	3056	1388	2556	329	2885	63
	200	3056	1945	2335	397	2772	63
	250	3056	2499	2107	519	2626	63
OFMW	180	4833	2248	3629	556	4185	29
	220	4833	2756	4073	516	4589	29
	250	4833	3018	2847	444	3290	29

^aFeedstock dry basis.

methane yields in the range of 32%–52% have been reported.^{119,129,130} On the basis of the study conducted by Lim et al.,¹³¹ the addition of biochar could promote the growth of electroactive *Clostridia* and *Methanosarcina*, which favor the degradation of volatile fatty acids into acetate, increasing the methane yield.

In addition, the use of HC resulted in enhanced degradation of N- and O-containing heterocyclic, phenolic, and aromatic compounds,¹¹⁹ thus improving COD removal. In general, HC has shown some significant advantages in AD, such as providing microbial support promoting DIET, reducing the inhibition by high ammonium concentrations,⁵² decreasing the lag phase, increasing alkalinity and the production of intermediates (such as acetic acid and hydrogen), supplying nutrients, and purifying the biogas by retaining part of the CO₂ generated.^{130,132,133} Furthermore, HC retains high amounts of macro- and micronutrients (P, K, Ca, Mg, Fe), which makes it of some interest for soil amendment. However, HC is the most valuable HTC fraction concentrating most of the energy, and therefore, its eventual application to improve somewhat the AD performance must be limited to minor relative amounts.

3.3. Anaerobic Digestion in Continuous Mode. All the studies on AD of process waters from HTC referenced thus far in this review have been conducted in batch, and only few recent works were found reporting experiments in continuous mode. The PWs from corn¹¹⁵ and sewage sludge¹³⁴ HTC performed at 220 and 200 °C, respectively, were treated by AD in an anaerobic filter (AF) and a continuous stirred tank reactor (CSTR) in mesophilic and thermophilic conditions. The PW from the first substrate was fed at an organic load rate (OLR) of 1 g COD/L·d in 90-day experiments to AF and CSTR. Similar results were obtained with both reactors in terms of COD removal and methane production, with achieved values up to 75% and 250 N mL/g COD_{added}·d, respectively. During the early days, acidification was observed

due to the fast acidogenic phase, which was evidenced by an AGV/alkalinity ratio higher than 0.4 (acidogenic inhibition). After about 40 days of operation, a drastic drop of methane production (up to 50%) occurred, which was associated with a lack of essential nutrients. Further restoration of the above-mentioned value of methane production was achieved by nutrients addition.

In the AD of PW from sewage sludge HTC, different OLRs were tested in both mesophilic and thermophilic conditions in 175-day experiments in AF. Methane production was somewhat lower (150–200 N mL/g COD_{added}) at the same OLR than for corn PW. Both processes reached their highest methane production rate, around 900 and 1100 N mL/g COD_{added}·d, with an OLR of 5 g COD/L·d, while at higher organic loading rate, inhibition occurred.

The nature and complexity of the PW demand us to learn more on the evolution and adaptation of the microbial community in the AD process. Different studies have reported an enhanced growth of hydrolytic and acidogenic bacteria (*Clostridium* and *Bacteroidia*) and reduced growth of methanogenic archaea (*Methanomassiliicoccus* and *Methanosarcina*).^{117,119} An increased presence of microorganisms like *Bacteroidia* can improve the production of VFA as well as the degradation of phenolic and aromatic compounds.¹³⁵ This change in the acidogenic community was more pronounced with PWs obtained at high HTC temperatures. Furthermore, the addition of hydrochar also enhanced the development of acidogenic bacteria (up to 12%).¹¹⁹

4. ENERGY BALANCE AND SUSTAINABILITY OF HTC AND AD INTEGRAL APPROACHES

Table 7 summarizes the results reported on energy recovery in the HTC + AD integral treatment of the different biomass feedstocks previously considered. The highest energy recovery rates in most cases were obtained at HTC temperatures below

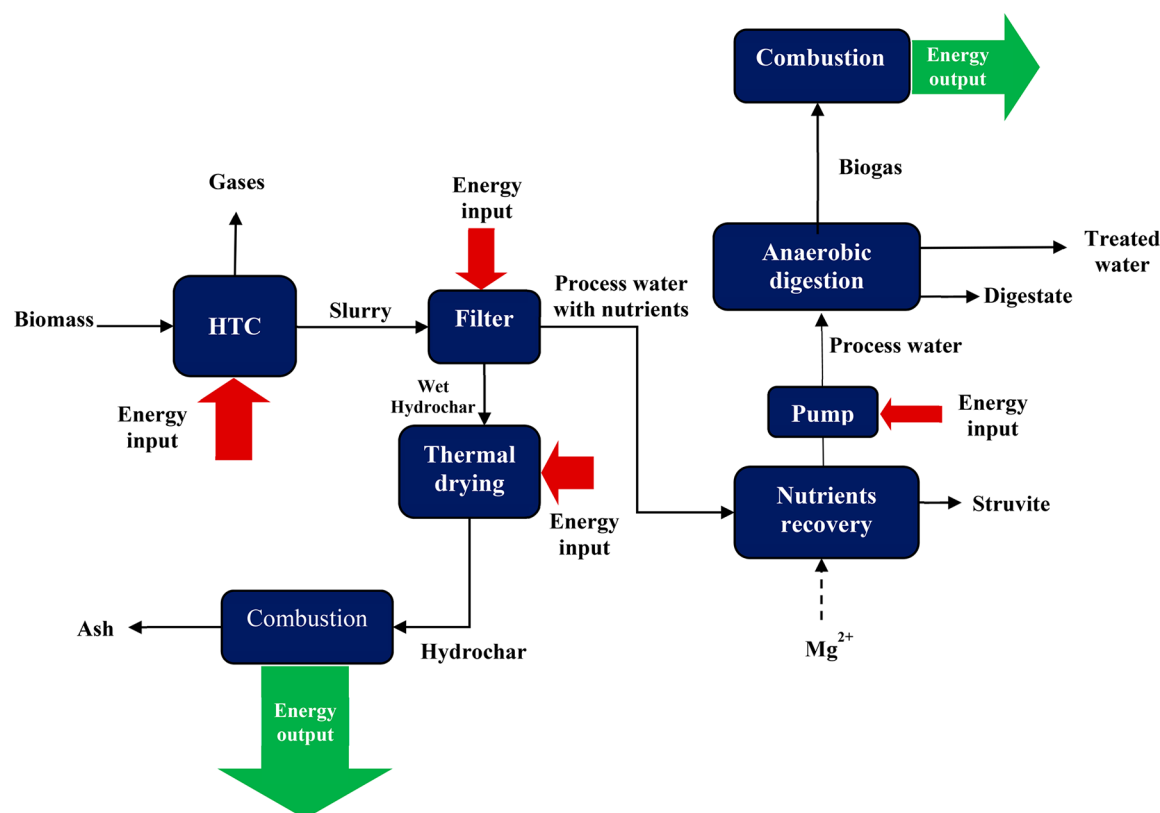


Figure 3. Schematic flow diagram of wet biomass valorization through hydrothermal carbonization, anaerobic digestion, and nutrient recovery.

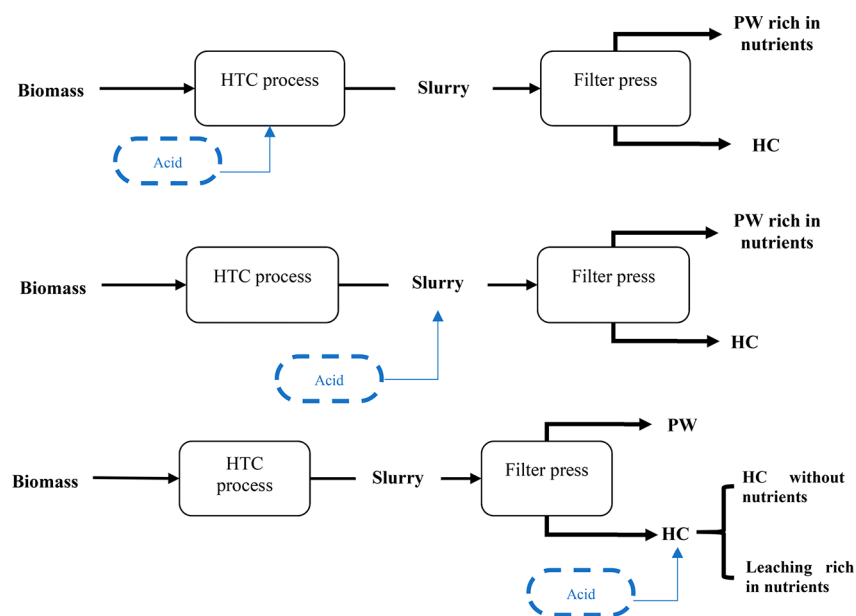


Figure 4. Strategies used for nutrient recovery from HTC.

200 °C. However, lowering the HTC temperatures affects the quality of the resulting hydrochar, by far the main product from the process in terms of energy recovery, as can be seen from Table 3. AD represents, in some cases, a significant contribution and, anyway, provides a potential solution to reduce the negative environmental impact associated with the high organic load of PW. The energy recovery from direct AD of the starting feedstocks is much lower than that achieved by the integral approach considered in this review.

The data of Table 7 refer only to the relative amount of energy that can be recovered with respect to the stored energy in the starting substrate. Assessment of the sustainability of this integral approach as a potential way for biomass wastes management must include the external energy inputs and, of course, economic analysis. Those issues are needed to complete LCA for a better understanding of this technology as a circular economy concept. Table 8 summarizes the energy balances in the referenced studies after inclusion of the

operational energy inputs. Figure 3 shows a conceptual diagram with materials and energy flows where nutrient recovery has been also included. The green arrows represent the energy released in the combustion of HC and biogas, while the red arrows are the energy requirements of each of the stages involved. According to the energy balances analyzed, the energy recovery is greater than the external input to the process, therefore the energetic sustainability of the system can be postulated.

Only in few cases of those reported in Table 8 is the energy associated to the methane produced from AD of the process water higher than the external energy input needed for the integrated process. In general, for this process to be self-sustained, a significant amount of the energy stored in the hydrochar would be needed. In general, it can be said that the integrated HTC + AD is a self-sustained process but requiring a significant contribution of the hydrochar obtained. Notice that eventual energy recovery by, for instance, heat exchange, has not been included. Cao et al.¹³⁷ demonstrated that heat recovery could represent almost 20% of the thermal needs, while Heidari et al.⁶⁰ showed that the integration of HTC and AD is a more efficient and cost-effective approach than direct combustion when the biomass has a wetness content above 40%. With respect to direct AD of the raw biomass, Villamil et al.²³ concluded that integration of HTC and AD is much more efficient in terms of energy recovery.

5. NUTRIENT RECOVERY

Recovery of nutrients from the PW is an additional possibility of HTC. Several studies have been conducted in that respect.^{58,67,111,113,120} Up to 95% of P in the PW has been recovered as high value-added struvite upon Mg^{2+} addition.¹²⁰ Recovery of fertilizer nutrients has been also reported from algae HTC.⁸² However, it has been demonstrated that in HTC nutrients are commonly retained in great part in the HC. Acid addition enhances the transfer of phosphorus to PW,⁹⁹ although further neutralization would be needed before AD.

Several authors have detailed different strategies for nutrient recovery from biomass wastes such as sewage sludge, animal manure, and algae. Figure 4 provides an schematic description of such strategies consisting of (i) acid washing of the HC,^{99,138} (ii) direct acid washing of the slurry exiting the HTC reactor,¹³⁸ and (iii) HTC under acidic conditions to mobilize most of the nutrients into the process water.^{139,140} Gerner et al.¹³⁸ recovered up to almost 85% P and 55% N of the starting biomass by the first approach, while with HTC a low pH allowed Shi et al.¹³⁹ to recover up to 85% of P and 95% of N in the PW. This strategy leads also to a low-ash HC with an improved heating value,¹¹³ although at the expense of a more contaminated PW, which, moreover, would need further neutralization before anaerobic digestion. On the other hand, expensive materials would be needed for the HTC reactor and associated components of the plant.

6. ECONOMIC EVALUATION AND FEASIBILITY

The economic feasibility of HTC has been analyzed by some authors. Lucian and Fiori¹⁴¹ reported the design of a HTC plant for 9300 t/year of grape pomace waste, without PW treatment and/or nutrient recovery. The investment was estimated to approach 1.8 M€, and a market price of 200 €/t was calculated for the hydrochar to have acceptable profitability, which could not compete with coal. A much more

promising estimate was reported by Ischia et al.,¹⁴² who calculated a profitable price of 37 €/ton for the hydrochar produced in a solar-heated HTC reactor. Benavente et al.¹⁴⁸ also analyzed the possibilities of HTC at industrial scale. Saba et al.⁹⁵ presented a techno-economic assessment (TEA) on the use of miscanthus HC and a coal blend. They reported an estimated cost around 10.8 M€ for a HTC plant of 43 t HC/h capacity, including subsequent blending with coal, and concluded a selling price of 100 €/t for the HC.

Aragon-Briceño et al.⁵⁷ studied the combination of HTC, AD, and P recovery as struvite from primary, secondary, and mixed sewage sludge and the scale-up of the process. Recovery of struvite would represent an income around 25 €/ton of treated sludge, which could reach more than 40 €/ton including the energy value of HC and biogas. Bevan et al.¹⁴³ analyzed the possible implementation of HTC and AD in a wastewater treatment plant. Capital and operating expenditures of the existing technologies for sewage sludge treatment were compared with the estimated for an alternative HTC, AD, and nutrient recovery plant and concluded that the latter would be a cost-effective, profitable, and eco-friendly approach. Medina-Martos et al.¹⁴⁴ concluded that the integration of HTC and AD is a more cost-effective solution than direct AD for sewage sludge treatment, with an income of 94 vs 66 €/ton of sludge. It has been estimated that an integrated HTC + AD plant for sewage sludge management would cost around 42% more than a conventional AD facility of similar capacity.¹⁴⁴ However, the energy recovery is in favor of the combined system.

7. LIFE CYCLE ASSESSMENT

Although LCA is known to be an essential tool to understand the potential environmental impacts and resource consumptions of any transformation process, it has been thus far scarcely used in HTC studies and even less in those dealing with the integrated HTC + AD approach, the subject of this review.

To our best knowledge, the only study in the literature dealing with LCA of the integrated HTC + AD approach has been reported by Medina-Martos et al.,¹⁴⁴ who compared this system with standalone AD for the treatment of sewage sludge. They concluded that the integrated approach has a lower environmental impact, increasing by almost 15% the overall energy recovery, but at 1.4-fold higher estimated cost.

Regarding standalone HTC, quite a number of works have mentioned that the use of the hydrochar from HTC as solid fuel is more eco-friendly than direct combustion of biomass wastes. However, only few studies have supported that statement through comprehensive LCA. Some authors have compared HTC with several traditional approaches, like AD, composting, gasification, and combustion.^{145–149} In general, these works concluded that HTC of biomass wastes offers a new, more efficient, and environmentally friendly way of recovery. In the case of olive mill wastes, HTC followed by hydrochar combustion results in net environmental savings, although the most environmentally friendly management option appears to be waste drying and incineration.¹⁴⁸ In the same way, the highest benefits were achieved by substituting coal by HTC char pellets for thermal energy production, followed by wood pellets and natural gas.¹⁴⁹ In the case of sewage sludge, management through agricultural use is, in general, not advantageous with respect to energy recovery.¹⁵⁰

In summary, there is still a severe lack of LCA studies which could comprehensively support full-scale implementation of

HTC combined with AD of the resulting PWs in the future for a wide diversity of biomass wastes.

8. CHALLENGES AND PERSPECTIVES

The information thus far reported in the literature highlights the HTC temperature as a key variable for the optimization of the integrated HTC + AD system. However, this needs to be refined, because the widely diverse nature of biomass substrates and the different operating conditions used in both HTC and AD steps in the reported studies make it difficult to extract generally accepted conclusions from the existing results, which in fact vary within quite wide ranges.

The composition of the feedstock itself is of great importance concerning the quality of the hydrochar, the main product from HTC. Undesirable components will affect its potential use as fuel. That is the case for S and N, whose relative amounts in the starting waste need to be carefully considered together with their fate during the HTC process to ensure that a clean solid fuel can be obtained, which is a main advantage of biomass-derived chars. On the other hand, the anaerobic biodegradability of the PW components determines the treatability of the aqueous waste from HTC and the methane yield, thus affecting the efficiency of the integrated system as a potential way of energy recovery from biomass wastes. Therefore, a main challenge, which should be addressed in the very next future, is accomplishing more systematic studies with a wide diversity of biomass wastes to establish comprehensive relations between the feedstock composition and the performance of HTC under different conditions (mainly temperature and b:w ratio) and how these conditions affect to further AD of the resulting process water.

Although AD is a well-known technology, its specific application to PWs needs to be investigated more in depth to stress the possibilities of enhancing the methane yield and the concurrent abatement of the high COD of these aqueous wastes. According to the results thus far reported in the literature, COD reductions within 60%–80% have been achieved, which need to be improved to reach a better position as an environmentally acceptable solution for those PWs. This is a main challenge demanding significant research efforts before AD can be effectively integrated with HTC. AcoD of PW with biodegradable raw wastes appears an interesting approach that must be investigated more in depth to learn its possibilities with different types of wastes. Ultimately, the potential application of AD to these PWs will have to compete with alternative technologies for high organic load aqueous wastes. In that respect, wet air oxidation has the advantage of a full-scale demonstrated technology in terms of highly effective COD abatement but with the counterpart that one energy-valuable product is obtained. However, aqueous phase reforming (APR) is emerging as a promising way for hydrogen production, investigated, in principle, with model organic compounds but more recently tested for some high organic load wastewaters from biomass-related industrial processes, like brewery effluents.¹⁵¹

Nutrient recovery from the PW is a relevant issue, which deserves much more attention than the thus far received. In general, significant relative amounts of N and P in the raw biomass are retained in the hydrochar. Performing HTC under acidic conditions can release most of those nutrients to the PW, so they can be recovered from this fraction. But the way that would affect to further AD needs to be well understood together with the actions to avoid any detrimental effect and

with the possible economic impact. Most of the studies carried out on acid-assisted HTC mention the benefits concerning the quality of the resulting HC and the recovery of nutrients from the liquid phase. However, there is a lack of research dealing with the effect on the treatability of the PW. Besides nutrients, some other components can be more easily transferred to the liquid phase under acidic conditions, including heavy metals and recalcitrant compounds that can seriously hinder anaerobic digestion. This is an important gap that needs further attention.

The economic feasibility of HTC and integrated HTC + AD has not been demonstrated thus far with conclusive studies. Therefore, full-scale implementation appears not likely yet, and resolute efforts must be done to learn more on this crucial aspect. Research on the design of novel HTC reactors as well as modeling and development of the integrated process for continuous operation are determining challenges for the future of this technology. In particular, performing HTC in continuous mode needs to be investigated. This requires significant efforts addressed to reactor design. Another important assistance must come from process simulation to allow optimization of the integrated HTC + AD system.

In principle, this combined approach appears a promising solution in terms of environmental sustainability and integration in the circular economy concept but that must be confirmed with more detailed studies as mentioned above. In addition, we must highlight the need of stressing life cycle analysis for the sake of comparison with other existing and emerging solutions for the effective integral management of biomass wastes. This is a crucial issue regarding potential full-scale implementation of integrated HTC + AD and therefore deserves much more attention than thus far received from the limited studies to date.

9. CONCLUSIONS

Hydrothermal carbonization represents a promising way of energy recovery from wet biomass waste, avoiding predrying and working at a much lower temperature than conventional thermal conversion technologies. The ability to transform wastes into value-added char and the potential for integration with other processes such as AD and nutrient recovery are main strengths of HTC for biomass management.

The main product, so-called hydrochar, is a solid of better fuel quality than the starting raw biomass, storing a great part of its energy content at improved energy density (higher heating value). The reduction of alkali metals (Na and K), a main cause of fouling and slagging problems, is a significant advantage of HC. In addition, S and N, when present in the starting substrate, are also partly removed from the solid product because of solubilization into the aqueous phase. The energy recovery in the hydrochar can reach up to 85%, although little more than 40% has been also reported in some cases in the literature, depending of the starting waste and the operating conditions.

However, the aqueous fraction resulting from the process is a troublesome secondary waste, named process water, requiring adequate treatment because of its high polluting load, which consists majorly of organic matter of a quite diverse nature entailing a high COD (13–97 g COD/L). Anaerobic digestion provides a potential solution to reduce that organic load allowing additional energy recovery. Somewhere around 200 °C appears to be the optimum HTC temperature leading to the highest energy recovery and the

best PW treatability. AD methane potential values in the range of around 200–350 N mL CH₄/g COD_{added} have been reported, associated to COD removal from 60% to more than 80%.

Therefore, integration of HTC and AD appears a promising approach whose interest has been reflected in the growth of available studies within the last years working with different biomass feedstocks. Those studies focus mainly on mass and energy yields, characterization of the hydrochar from HTC, and methane production in the subsequent AD of the resulting PW. The integrated HTC + AD allowed overall energy recovery ranging from around 50% to more than 90% in the literature. The energy balance shows the thermal self-sustainability of the system. Finally, some still scarce techno-economic studies and life cycle assessments show that integration of HTC and AD is a promising approach, although potential future implementations would require stressing those crucial issues and answering a number of important questions still demanding significant further research efforts.

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Notes

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