

Review

An Overview of the Thermochemical Valorization of Sewage Sludge: Principles and Current Challenges

Bruna Rijo, Catarina Nobre , Paulo Brito  and Paulo Ferreira * 

VALORIZA—Research Center for Endogenous Resource Valorization, Portalegre Polytechnic University, Campus Politécnico 10, 7300-555 Portalegre, Portugal; bruna.rijo@ipportalegre.pt (B.R.); catarina.nobre@ipportalegre.pt (C.N.); pbrito@ipportalegre.pt (P.B.)

* Correspondence: pferreira@ipportalegre.pt

Abstract: With the increase in the world population and economic activity, the production of sewage sludge has grown, and its management has become an environmental problem. The most traditional method of managing sewage sludge is to dispose of it in landfills and on farmland. One way to valorize sewage sludge is to use thermochemical conversion processes to produce added-value products such as biochar, biofuels, and renewable gases. However, due to the high moisture content, thermochemical conversion using processes such as pyrolysis and traditional gasification involves multiple pre-treatment processes such as material drying. Hydrothermal thermochemical processes usually require high pressures, which pose many challenges to their application on a large scale. In this work, the advantages and disadvantages of the different existing thermochemical processes for the recovery of sewage sludge were analyzed, as well as the resulting industrial and environmental challenges. A SWOT analysis was carried out to assess the different thermochemical processes in terms of technical feasibility, economic viability, and broader market considerations.

Keywords: sewage sludge; biofuels; pyrolysis; gasification; hydrothermal conversion



Citation: Rijo, B.; Nobre, C.; Brito, P.; Ferreira, P. An Overview of the Thermochemical Valorization of Sewage Sludge: Principles and Current Challenges. *Energies* **2024**, *17*, 2417. <https://doi.org/10.3390/en17102417>

Academic Editors: Sumit Roy, Shivaprasad Kumar Vijayalakshmi and Alessandro Giampieri

Received: 27 March 2024

Revised: 9 May 2024

Accepted: 16 May 2024

Published: 17 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Sewage sludge, a nutrient-rich byproduct of wastewater treatment processes, poses significant challenges for environmental sustainability and resource management. With the rapid expansion of the global population and economic activities, sewage sludge production is expected to escalate, intensifying concerns regarding its management and disposal. In the European Union (EU), more than 2370 thousand tons of sewage sludge were produced in 2021 from urban wastewater treatment plants (WWTPs). From this total, 10.7% was landfilled and 27.9% was used for agriculture applications [1]. Similarly, in the United States, 4.75 million dry metric tons of sewage sludge were generated in the same year, with only 51% utilized for agricultural and non-agricultural purposes, while the remainder was disposed of through incineration, landfilling, and other management practices [2].

The escalating production of sewage sludge underscores the urgency of optimizing its management strategies. Conventional methods such as landfilling and land-farming are increasingly criticized for their negative environmental impacts and economic inefficiencies. The disposal of sewage sludge not only poses risks to soil and water quality but also leads to significant energy consumption and greenhouse gas (GHG) emissions. Approximately 25–40% of operating costs in conventional wastewater treatment plants are attributed to energy consumption, highlighting the need for sustainable alternatives [3,4]. Fortunately, sewage sludge represents a valuable resource with untapped potential for energy and materials recovery. More than 60% of the organic matter in wastewater is concentrated as sewage sludge, offering significant opportunities for energy production through various technologies [5].

Thermochemical conversion processes, such as incineration, pyrolysis, gasification, and hydrothermal treatment, have emerged as promising approaches for sewage sludge management due to their ability to recover energy and materials, reduce volume, and effectively destroy pathogens [6]. These processes involve the decomposition of almost all organic parts of the sludge by applying controlled heating and/or oxidation. This allows the conversion of sewage sludge to energy or fuels in short periods of time, which represents a crucial advantage when compared to biochemical processes like anaerobic digestion (AD) [7]. Furthermore, these thermochemical processes allow for a multitude of products: incineration will yield heat and/or electricity; pyrolysis results in bio-oil, biochar, and gas; gasification results in syngas (with biochar and ash as byproducts); and hydrothermal processes can yield hydrochar, biocrude, and gas.

However, despite the growing interest in thermochemical valorization, numerous challenges persist. The physicochemical properties of sewage sludge vary widely, complicating the development and implementation of thermochemical conversion technologies [8,9]. The physicochemical properties of sewage sludge, including moisture content, organic content, ash content, elemental composition, heating value, and the presence of contaminants, exhibit significant variability, thereby complicating the development and implementation of thermochemical conversion technologies [10,11]. Sewage sludge typically possesses a high moisture content ranging from around 70% to 90% or higher, needing energy-intensive drying processes prior to thermochemical conversion [12]. Its organic content varies broadly depending on the wastewater composition and treatment efficiency, impacting the energy potential and emission profiles during conversion. Additionally, sewage sludge contains inorganic materials contributing to its ash content, which varies based on factors such as industrial discharge presence and treatment effectiveness [13]. Variations in the elemental composition, including carbon, nitrogen, phosphorus, sulfur, and heavy metals, influence the kinetics and environmental impacts of thermochemical conversion processes. Furthermore, differences in heating value, influenced by organic content, moisture content, and elemental composition, affect the energy efficiency and economic viability of conversion technologies [10]. The presence of contaminants, such as heavy metals, pathogens, pharmaceuticals, and organic pollutants, adds complexity to thermochemical conversion, requiring supplementary treatment or mitigation measures for environmental compliance [10,14]. Additionally, many thermochemical processes, namely hydrothermal processes, are still in the exploratory stage, with limited scalability for large-scale applications [15]. The environmental and economic sustainability of these processes must be carefully evaluated to ensure their viability as long-term solutions.

The aim of this paper is to provide a comprehensive review of the principles, current challenges, and future strategies for the thermochemical valorization of sewage sludge. By synthesizing the existing literature and analyzing key research findings, this review seeks to elucidate the potential of thermochemical conversion processes in addressing the complex issues surrounding sewage sludge management.

2. Sewage Sludge Composition

Sewage sludge is generated in the wastewater treatment process, including primary (physical and/or chemical), secondary (biological), and tertiary (which complements secondary treatment, often involving nutrient removal) treatments (Figure 1).

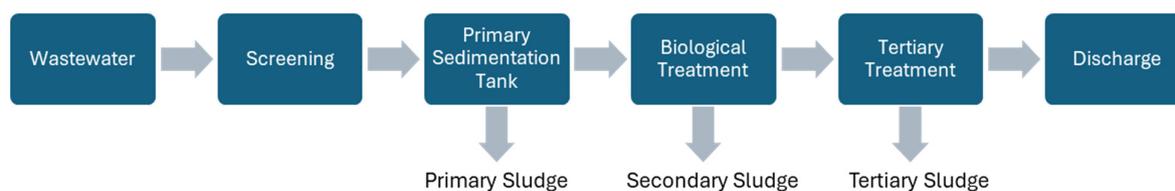


Figure 1. General scheme of wastewater treatment plants.

In general, dewatered sewage sludge has a high water content, about 70–85%; it is usually very greasy, making it difficult to handle and transport, and gives off a pungent odor due to the presence of biologically active substances [7,16,17].

The composition and characteristics of sewage sludge are heterogeneous and depend on several factors, ranging from the characteristics of the wastewater and the pollutant load entering the WWTP unit, the treatment method, the processing stage, the duration and conditions of storage, and the coagulating agents used in the WWTP. Seasonal variations can also cause variability in sludge properties [7,16,17]. Due to the great heterogeneity of sewage sludge, it is essential to determine its physical and chemical characteristics to assess its usefulness in thermochemical processes. Table 1 shows the composition of different sewage sludge samples according to different authors.

Table 1. Composition of different sewage sludge samples.

Ultimate Analysis (wt.%)					Proximate Analysis (wt.%)					References
C	H	N	S	O	Moisture	Ash	Volatile Matter	Fixed Carbon	HHV (MJ/kg)	
26–69	4–9	2–9	0.2–2	22–56	71–89	11–76	22–82	1–22	11–16	[7,16–19]
Protein		Lignin		Biochemical composition (wt.%)						
22–42		18		Lipid	Hemicellulose		Cellulose		Others	[18,20]
				1–14			4		0.3	-
Heavy metal composition (ppm)										
Zn	Ni	Cr	Cd	As	Cu	Hg	Pb			
603–744	20–24	42–229	1	5	0–338	3–4	67–80		[18,19]	

As previously described and reported in Table 1, sewage sludge has high moisture content which varies between 71 and 89 wt.%. In most experiments, dried sludges are normally used as feedstock for thermochemical processes to avoid high energy consumption. The volatile matter has a range of approximately 22–82 wt.% on a dry basis, which makes it useful for producing bio-oil and gas with a higher energy content. It can also be observed that the ash content of the samples varies between 11 and 76 wt.%. High ash content in sewage sludge results in a lower calorific value, which can result in less effective fuel and can cause agglomeration and corrosion problems in thermal conversion equipment [10]. The samples contain a small fraction of fixed carbon, between 1 and 22 wt.% on a dry basis.

The heavy metal concentrations reported in the sewage sludge samples (Zn: 603–744 ppm, Ni: 20–24 ppm, Cd: 1 ppm, As: 5 ppm, Cu: 0–338 ppm, Pb: 67–80 ppm) highlight potential environmental and health risks. Considering that the major applications of sewage sludge are in agriculture, heavy metals are important because of their detrimental effects. Elevated levels of zinc and copper, essential for plant growth, may disrupt soil microbial communities and pose toxicity risks to plants. Nickel and cadmium, even at low concentrations, can adversely impact soil health and crop productivity, while arsenic and lead, known for their carcinogenic properties, pose severe health risks to humans. Furthermore, the Hazard Quotient (HQ) of the heavy metals' values (3–4 ppm) suggest potential adverse health effects, particularly for vulnerable populations. Proper management of sewage sludge, considering its heavy metal content, is imperative to mitigate contamination risks and safeguard human health and ecosystems [21,22].

3. Thermochemical Conversion of Sewage Sludge

In recent years, the thermochemical conversion of sewage sludge, driven by technologies such as pyrolysis, gasification, and hydrothermal processes, has emerged as a focal point in research and development efforts aimed at addressing the pressing challenges of efficient waste management and sustainable energy production [23]. These thermochemical

processes offer the capability to decompose the complex organic compounds present in sewage sludge under controlled conditions of temperature and pressure, yielding valuable energy-rich products such as biochar, syngas, and bio-oil. Through the precise control of process parameters, including residence time, heating rate, and reactor design, these technologies enable the transformation of sewage sludge into usable energy forms while minimizing the environmental impacts associated with conventional disposal methods. Moreover, the potential for the simultaneous valorization of byproducts and reduction in GHG emissions further underscores the significance of thermochemical conversion as a viable pathway towards achieving circular economy objectives within the wastewater treatment sector.

3.1. Gasification

Gasification is a process that converts sewage sludge under limited O₂ concentrations to avoid the complete combustion of the feedstock and produce combustible gases such as CO, H₂, and methane (CH₄) and some oxidation compounds like CO₂. This mixture of gases is called producer gas (after leaving the gasifier) and synthesis gas or syngas (after gas cleaning). In the gasifier, there are four zones where the processes of drying, pyrolysis/devolatilization, gasification (oxidation), and combustion (reduction) take place. The sequence of these zones depends on the flow direction of the solid and gas phases [24]. Different technologies of sewage sludge gasification have been studied, such as the types of gasification agents (air, steam, oxygen, or their mixtures) to be introduced or the type of catalysts to be introduced in the beds to improve the quality and quantity of the produced gas. Table 2 reports a literature survey on sewage sludge gasification.

Table 2. Gasification of sewage sludge with different technologies, types of gasification agents (air, steam, oxygen, or their mixtures), and catalysts.

Raw Material	Type of Reactor	Catalyst	Temperature (°C)	Gasification Agents	HHV (MJ/Nm ³)	LHV (MJ/Nm ³)	H ₂ /CO Ratio	H ₂ Yield (%)	Reference
Sewage sludge	Updraft fixed bed	---	900	Air	12.2	---	1.4	42.0	[25]
				Oxygen	14	---	1.4	40.0	
	Downdraft fixed bed		Air	12.8	---	1.6	46.0		
			Oxygen	12.7	---	1.1	45.0		
Sewage sludge	Fluidized bed	NiO/modified dolomite	800	Steam	---	9.7	≈1.2	≈26.0	[26]
800			---		12.4	≈1.5	≈37.0		
600			---		12.3	≈1.4	≈36.0		
700			---		11.8	≈1.5	≈39.0		
800			---		11.3	≈1.7	≈46.0		
900			---		10.6	≈1.7	≈48.0		
Sewage sludge	Fixed bed	---	800	Steam	---	---	≈2.9	35.3	[27]
		Ni/HZSM-5			---	---	≈3.1	40.9	
		Ni/Al-MCM48			---	---	≈3.2	44.8	
		Ni-Fe/Al-MCM48			---	---	≈3.2	47.9	
		Ni-Co/Al-MCM48			---	---	≈3.1	51.9	

Table 2. Cont.

Raw Material	Type of Reactor	Catalyst	Temperature (°C)	Gasification Agents	HHV (MJ/Nm ³)	LHV (MJ/Nm ³)	H ₂ /CO Ratio	H ₂ Yield (%)	Reference	
Sewage sludge	Bubbling fluidized bed	Olivine	809	Air	---	4.1	1.4	16.8	[28]	
		Olivine	799	Air	---	4.7	1.6	18.8		
		Olivine	796	Steam/O ₂	---	8.8	2.1	37.7		
		Dolomite	803	Steam/O ₂	---	9.2	1.9	37.9		
		Limestone	816	Steam/O ₂	---	9.3	2.2	38.8		
Sewage sludge (SS)	Fixed bed	---	550	Steam	---	---	4.7	27.0	[29]	
		CaO/SS (1:1)			---	---	1.3	81.6		
		CaO/SS (1:2)			---	---	2.5	40.0		
Sewage sludge	Fixed bed	-	800	Air	---	---	0.2	4.3	[30]	
		Activated Carbon			---	---	1.0	15.1		
		Biochar		---	---	0.7	11.4			
		Activated Carbon		---	Steam/Air	---	---	0.9		15.1
		Biochar		---	---	2.0	22.5			
Sewage Sludge	Bubbling fluidized bed	---	750	Air	3.0	2.8	1.1	7.6	[31]	
			800		3.6	3.3	1.3	10.4		
			850		4.2	3.9	1.2	12.1		
		750	Steam/Air	3.5	3.2	1.3	10.0			
		800		3.8	3.5	1.4	12.0			
		850		4.6	4.2	1.6	16.1			
		Alumina	750	Air	3.0	2.7	1.1	8.0		
			800		3.8	3.5	1.4	12.3		
			850		4.7	4.3	1.2	15.0		
			800		Steam/Air	4.0	3.7	1.9		15.2

One way to reduce the high moisture content of sewage sludge is to combine it with biomass with a low moisture content. The co-gasification of wet sewage sludge and pine sawdust for syngas production was investigated and showed that the addition of pine sawdust to wet sewage sludge decreased the moisture content and improved the volatile matter content in the mixtures. Moreover, co-gasification was favorable for syngas production with an increase in H₂ content due to the self-generated steam production from the wet sewage sludge favoring water–gas reactions [26].

Tezer et al. [25] studied the gasification of sewage sludge in two different types of fixed-bed gasifiers with different technologies, updraft, and downdraft. It was reported that the volumetric percentages of H₂, CO, and CH₄ gases were the highest in the downdraft gasifier, not varying with the gasifying agent used (air or pure O₂), while the higher heating value (HHV) obtained was between 12.7 and 12.8 MJ/Nm³. This was also reported by Quan et al. [24], who studied the gasification of sewage sludge using downdraft gasifiers, obtaining a synthesis gas with a moderately high lower heating value (LHV) of 9–11 MJ/Nm³. However, the gasification of sludge with pure O₂ leads to an increase in the calorific value of the syngas obtained in both types of gasifiers [25].

Jeong et al. [28] studied sewage sludge gasification in a bubbling fluidized bed gasifier with steam/O₂ using olivine, dolomite, and limestone as the bed materials. The authors observed that the use of catalyst and steam/O₂ mixtures promoted an increase in the produced gases, with H₂ contents in the range of 38–39 vol.%. Moreover, the use of olivine as the catalyst significantly reduced the NH₃ and tar contents in the gas. Schmid et al. [32] showed similar results in the gasification of sewage sludge, as the use of CaO as the

catalyst was effective for tar cracking, and also significantly reduced the tar, H₂S, and COS contents. Reductions in these compounds in the gaseous product is a positive outcome, as cleaning systems can become less complex and expensive. Moreover, most impurities can be removed by activated carbon placed after the tar cracking reaction. Since activated carbon has properties such as a high surface area and is a porous material, it promotes a high adsorption capacity for the removal of impurities [28]. The activated carbon filter can also be placed after the gasifier, and in this case, it can adsorb tar molecules, as well as NH₃ and H₂S, which are thermally or catalytically decomposed into H₂ and N₂ and S, respectively [28].

3.2. Pyrolysis

High moisture and metal content are challenges for the pyrolysis process converting sewage sludge into value-added products. There are several studies on sewage sludge drying as a pre-treatment for the pyrolysis process. Most of the works described and referenced pyrolyzed sewage sludge with a maximum moisture content of 10%, using drying methods from the exposure of the raw material to the outside and the use of dryers with temperatures between 103 and 120 °C [19,30,33,34]. Table 3 presents different works on sewage sludge pyrolysis and the relevant results.

Table 3. Pyrolysis of different types of sewage sludge under various experimental conditions.

Raw Material	Type of Pyrolysis	Type of Reactor	Catalyst	Temperature (°C)	Bio-Oil (wt.%)	Biochar (wt.%)	Gas (wt.%)	Ref.	
Sewage sludge	Fast	Fixed-bed reactor	---	300	33.3–36.3	65.3–68.9	3.9–4.1	[35]	
				600	14.5–18.2	17.3–19.9	31.5–33.4		
Sewage sludge	Fast	Tubular reactor	---	450	43.1	47.1	9.8	[36]	
				650	37.5	30.0	32.5		
	450			38.2	53.6	14.2			
	650			32.2	33.2	28.6			
Sewage sludge (SS) and rice husk (RH)	Fast	Tubular/Fixed-bed reactor	-	-	17.2	53.5	29.3	[37]	
				Biochar from SS pyrolysis	11.3	53.4	35.3		
				Biochar from co-pyrolysis of SS and RH	650	10.7	53.7		35.6
				Biochar from RH pyrolysis	9.5	53.2	37.3		
				Ash from the RH pyrolysis biochar	12.0	53.1	34.9		
Sewage sludge	Slow	Tubular reactor	---	600	33.0	≈48.0	≈19.0	[38]	
				700	26.0	≈45.0	≈29.0		
Sewage sludge	Fast	Conical spouted-bed reactor	---	450	44.8	52.2	3.0	[39]	
				500	48.5	46.3	5.2		
				600	45.4	43.2	11.4		
Sewage sludge	Slow	Rotating cylinder reactor	---	500	22.1	61.9	16.0	[33]	
				600	24.5	54.0	21.5		
Sewage sludge	Fast	Fluidized-bed reactor	---	450	31.3	51.5	17.2	[40]	
				550	32.3	53.2	14.5		
				650	25.0	47.2	27.9		

Table 3. Cont.

Raw Material	Type of Pyrolysis	Type of Reactor	Catalyst	Temperature (°C)	Bio-Oil (wt.%)	Biochar (wt.%)	Gas (wt.%)	Ref.				
Sewage sludge and humic acid	Slow	Fixed-bed reactor	---	700	32.9	≈45.0	9.8	[34]				
Sewage sludge			---		38.7	≈43.0	7.7					
			Kaolin		33.0	50.3	6.7					
			CaO		26.8	55.3	6.8					
Sewage sludge	Slow	Fixed-bed reactor	---	500	47.3	35.1	17.6	[41]				
			Composite alumina	400	42.5	45.6	11.8					
				500	48.4	34.3	17.3					
				600	48.3	27.7	24.0					
			Sewage sludge	Slow	Fixed-bed reactor	---	450		43.1	---	---	[42]
						CaO	850		36.6	---	---	
450	37.1	---					---					
KCl	850	35.9				---	---					
	450	29.9				---	---					
Na ₂ CO ₃	850	41.7				---	---					
	450	30.4	---	---								
Fe ₂ O ₃	850	46.5	---	---								
	450	32.5	---	---								
Sewage sludge	Slow	Fixed-bed reactor	-	500	32.5	58.8	8.7	[43]				
			Fe ₂ O ₃		39.1	48.8	12.1					

From Table 3, it is possible to observe a common fact in all the tests: the increase in the gas yield with increasing temperature. This trend may be due to the secondary reactions of the tar, such as the breaking of organic bonds, which become active at temperatures above 550 °C [36]. The presence of the decarboxylation, decarbonylation, dehydration, and dehydrogenation reactions of volatiles in the main step of pyrolysis leads to the formation of the gas phase, which is mostly composed of CO₂, CO, CH₄, and H₂ [34,36].

Feng et al. [35] found that increasing the pyrolysis temperature changes the composition of the bio-oil formed. The increase in temperature promotes an increase in C and N contents, from 55.8–57.6 wt.% to 61.4–62.6 wt.% and from 2.9–3.9 wt.% to 7.7–8.2 wt.%, respectively, while the H contents decreased, from 9.4–9.7 wt.% to 8.2–8.3 wt.%, in the bio-oil. This increase in C and N contents occurred due to the presence of dehydrogenation reactions, condensation (aromatization), and secondary cracking reactions during pyrolysis at high temperatures.

Agar et al. [38] observed that less than half of the original nitrogen and sulfur are preserved in biochar after pyrolysis, while the remaining nitrogen is mainly lost by the volatilization of different nitrogen groups such as NH₄-N or NO₃-N at temperatures below 600 °C, and pyridine at temperatures above 600 °C. The loss of S is due to volatile organic compounds containing sulfur, mainly as carbonyl sulfide during pyrolysis [44].

As seen in Table 3, pyrolysis can occur in the absence or presence of a catalyst. The use of catalysts in pyrolysis, as in upgrading, aims to improve the quality of the bio-oil. The need to upgrade the bio-oil through the elimination of oxygenated and nitrogenous compounds by deoxygenation and denitrification is crucial to increase the HHV, the stability, and therefore the quality of the bio-oil. Some studies of the catalytic post-treatment of sewage sludge pyrolysis vapors by means of FCC, HZSM5, and γ-Al₂O₃ have been reported. This treatment in fixed-bed reactors filled with catalysts improved the characteristics of the treated bio-oil, leading to an increase in HHV. The treated bio-oil showed a higher

content of aliphatic and aromatic hydrocarbons compared to the bio-oil produced by pyrolysis only. Nitrogenous species were removed in the form of gaseous ammonia and in the biochar [45–47]. Still from Table 3, a notable range of yield fluctuations in bio-oil, biochar, and gas outputs is evident, contingent upon the distinctions of pyrolysis conditions, particularly temperature and reactor design. For example, when sewage sludge undergoes fast pyrolysis within a fixed-bed reactor at 300 °C, a higher proportion of biochar (65.3–68.9%) is observed compared to bio-oil (33.3–36.3%) and gases (3.9–4.1%). Conversely, under similar feedstock and pyrolysis conditions in a tubular reactor at 650 °C, the biochar yield markedly decreases, while bio-oil and gas yields increase significantly. The variations observed in Table 3 arise from complex thermal degradation mechanisms within the pyrolysis process. At lower temperatures, secondary reactions promoting biochar formation are enhanced, leading to higher biochar yields. On the other hand, at higher temperatures, thermolysis pathways favoring the production of volatile compounds such as bio-oil and gases predominate, resulting in reduced biochar yield while increasing those of bio-oil and gases.

Additionally, the impact of catalyst deployment is evident in pyrolysis products. For instance, introducing biochar derived from sewage sludge pyrolysis as a catalyst enhances bio-oil yields relative to pyrolysis without catalysts. Catalysts play a pivotal role in modulating reaction kinetics and altering reaction pathways.

Qiu et al. [37] reported that the content of N species in bio-oil obtained by catalytic co-pyrolysis (biochar as catalyst) of sewage sludge decreases compared to thermal co-pyrolysis. Additionally, an increase in the HHV of bio-oil from 25.8 to 34.7 MJ/kg was also observed in catalytic co-pyrolysis, showing an improvement in bio-oil quality. This means that N species were reduced when biochar-catalyzed pyrolysis occurred (except for rice husk biochar ash). This demonstrates that using biochar as a catalyst promotes denitrification reactions decomposing N species into NH_3 /HCN gases or hydrocarbons.

Meng et al. [48] studied the multiple effects of CaO on the evolution of nitrogen compounds at different pyrolysis temperatures of sewage sludge. These authors found that the effect of CaO on the pyrolysis process is different and depends specifically on the temperature. The presence of CaO can affect only the NH_3 component, which is mainly derived in the initial step of pyrolysis, devolatilization, while HCN is mainly generated from the secondary reaction of N functionals in biochar and tar. The authors also reported that at low temperatures (255–350 °C), CaO promotes the deamination of acid amide into NH_3 and inhibits the decomposition of N-nitrile in biochar into HCN, while at higher temperatures (490–750 °C), CaO inhibits NH_3 production and in turn promotes the hydrogenation and ring opening of N-heterocyclic in biochar and dehydrogenation of N-amine in tar, leading to HCN production [48]. Thus, the catalytic pyrolysis of sludge with CaO as the catalyst promotes the conversion of sludge into hydrogen- and carbon-rich fuel free of nitrogenous compounds. Udayanga et al. [34] observed the same, where CaO promoted deoxygenation and ring-opening reactions of the compounds present in bio-oil, while kaolin did not show any significant impact. The presence of CaO in sludge pyrolysis led to a decrease in the amount of CO_2 , reducing the volume of non-condensable gas by 18% compared to that of sludge pyrolysis. CaO had a great influence on CO_2 sequestration, but it also led to an increase in CO formation due to the Boudouard reaction. The presence of kaolin led to the formation of less CO in the gaseous composition because it promoted the water–gas shift reaction with the water that developed during its decomposition.

Furthermore, it has been reported that the pyrolysis temperature affects the ultimate and proximate composition, stability, aromaticity, and polarity of the biochar produced at different temperatures, as well as the concentration of the originally present metals such as Ca, Mg, Cu, Zn, Pb, and Cd. Pyrolysis temperature also has an important contribution in transforming metals from more toxic forms into more stable non-toxic forms. Based on this, it is necessary to evaluate the ecological risk index of biochar from sewage sludge as an additive for soil amendment; for example, in [44].

3.3. Hydrothermal Methods

The utilization of hydrothermal methods in the context of sewage sludge disposal involves the conversion of wastes into value-added materials within an aqueous environment characterized by moderate temperatures and autogenic pressure generated in a closed system [49]. This system aims to modify the reaction environment by altering the physical–chemical properties of water in sludge under sub-critical conditions, and its main products include hydrochars (solid waste), hydrothermal fluid (also known as process water), a biocrude (similar to pyrolysis bio-oil), and various types of gases [50].

The specific hydrothermal conversion method is classified according to the range of temperatures and pressures that are applied. As such, hydrothermal processes can be grouped into hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) [17]. The primary distinction among these processes lies in the composition and quantity of the obtained products. As in dry processes, the physical–chemical properties of the reaction medium and, consequently, the degree of degradation of materials immersed in the medium, are strongly influenced by temperature, residence time, and pressure [50].

3.3.1. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) of sewage sludge commonly takes place in an aqueous setting with temperatures ranging from 180 to 250 °C, accompanied by autogenous pressure. Under these conditions, the substrate undergoes decarboxylation, dehydration, and a reduction in hydrogen and oxygen concentrations [51]. Throughout HTC, various simultaneous reactions transpire, including hydrolysis, dehydration, decarboxylation, polymerization, and carbonization, and the resulting hydrochar exhibits a structure akin to natural lignite, with its calorific value closely linked to its carbon content [52]. Interestingly, diverse feedstock compositions do not induce significant structural changes in the hydrochar, and morphological similarities have been observed. Nevertheless, the properties of sewage sludge can impact the yield of hydrochar [52–54]. Table 4 shows an overview of different works concerning sewage sludge HTC, main operating conditions, and product yields.

Table 4. HTC of sewage sludge with different operating conditions, presence of catalyst, and product distribution.

Feedstock	Type of Reactor (Volume)	Catalyst	Temperature (°C)	Moisture Content/Solid Content/Solid–Liquid Ratio	Pressure (MPa)	Residence Time (min)	Production Distribution (wt.%)			Ref.
							Hydrochar	Biocrude	Gas	
Sewage sludge	Batch (1000 mL)	Sulfuric acid (VI), 30%	200	89.9% (moisture content)	2.5	120	4.2–6.2	89.3–90.6	4.2–5.7	[55]
Fenton-oxidized sewage sludge	Batch (50 mL)	---	180	1:10 (Solid–Liquid)	---	240	50.7–65.2	---	---	[56]
Sewage sludge	Batch (200 mL)	---	200/210/220	1:0.25, 1:0.5, 1:1, and 1:3 (Solid–Liquid)	---	300	54.8–74.1 (200 °C, varying L/S); 57.3–98.5 (210 °C, varying L/S); 53.6–62.5 (220 °C, varying L/S)	---	---	[57]
Sewage sludge (co-treatment with spent coffee grounds and bagasse)	---	---	220	---	---	---	Spent coffee grounds: 50.1–64.6. Bagasse: 42.8–49.9.	---	---	---

Table 4. Cont.

Feedstock	Type of Reactor (Volume)	Catalyst	Temperature (°C)	Moisture Content/Solid Content/Solid-Liquid Ratio	Pressure (MPa)	Residence Time (min)	Production Distribution (wt.%)			Ref.
							Hydrochar	Biocrude	Gas	
Sewage sludge	Batch (300 mL)	---	200/250	1:6	---	120/300	73.0 (200 °C, 120 min); 61.3 (200 °C, 300 min); 63.2 (250 °C, 120 min); 57.1 (250 °C, 300 min)	---	---	[54]
Sewage sludge co-treated with cheese whey	Batch (300 mL)	---	250	---	---	300	64.1 (250 °C, 300 min)	---	---	---
Sewage sludge	Batch (200 mL)	Acetic acid (AA) (0.4, 0.8, 1.24 M)	220	1:0.025/1:0.5/1:1/1:3	---	300	64.0 (1:0.25); 58.2 (1:0.5); 58.3 (1:1); 55.1 (1:3); 77.2 (0.4 AA); 83.6 (0.8 AA); 58.5 (1.2 AA)	---	---	[58]
Sewage sludge co-treated with pine sawdust	Batch (1000 mL)	---	180–250	1:30–1:10	---	60–180	54.0–94.2	---	---	[59]
Digested and dewatered sewage sludge co-treated with microalgae	Batch (1000 mL)	---	180/215/250	---	---	120	42.9–70.4	---	---	[60]
Primary sewage sludge	Batch (250 mL)	---	140/160/180/200	---	---	15–240	60.5–81.1	---	Methane yields: 44.6% (140 °C); 43.2–46.8% (160 °C); 43.8–45.5% (180 °C), and 43.7–44.6% (200 °C)	[52]
Anaerobic digestion effluent from sewage sludge	Batch (1000 mL)	---	163/180/220/260/277	---	0.83/1.10/2.24/4.96/6.07	30–70	62–78	9–27	1–22	[61]

As per Table 4, and considering works being conducted on process optimization and product distribution, Danso-Boateng et al. [52] investigated the effects of reaction conditions on the characteristics of products obtained from HTC of primary sewage sludge, by developing models to tailor reaction conditions for specific end uses, identifying optimal conditions for hydrochar characteristics, carbon recovery, and methane yields. Their results suggest that HTC at 180 °C for 60 min and 200 °C for 30 min resulted in hydrochars with optimal characteristics, namely carbon content between 37.8–37.9 wt.%, db, HHV between 17.6–18.3 MJ/kg and energy yield between 67.1–76.4%. Huezo et al. [61] explored the impact of temperature and pH on the yield and properties of hydrochar derived from anaerobic digestion effluent of sewage sludge. Their study revealed that temperature and pH significantly influenced hydrochar yield and properties, with higher temperatures leading to increased carbonization and decreased yields. Despite the hydrochar presenting low HHV, their high ash content suggested potential applications as a soil amendment.

Other works also focus on the use of catalysts in HTC, or pre-treatments for sewage sludge prior to HTC, to affect hydrochar properties and characteristics. Wilk et al. [55] explored the influence of sulfuric acid addition on the properties of hydrochars derived from sewage sludge. This work indicated that hydrochars showed enhanced carbon content, higher heating value, and improved combustion characteristics compared to untreated sewage sludge. Additionally, the addition of the acidic catalyst led to significant changes in the elemental composition of hydrochars, affecting the migration of heavy metals and enhancing phosphorus recovery from post-processing water. The authors

concluded that their results suggest that acid-catalyzed HTC has significant potential for producing hydrochars with improved properties and environmental benefits. Furthermore, Wang et al. [56] examined the advantages of combining Fenton oxidation (FO) with HTC for sewage sludge treatment. They found that FO pre-treatment effectively regulated hydrochar yield and properties, resulting in hydrochars with improved carbon content, combustion reactivity, and porosity compared to direct HTC. This study highlighted the potential of FO-HTC for enhancing hydrochar properties and providing insights into the underlying mechanisms governing the process.

There is also very important work being conducted regarding the applications and potential of hydrochar, particularly the application of co-hydrothermal carbonization (co-HTC) to find synergies of sewage sludge with other less problematic feedstocks. Piboonudomkarn et al. [57] proposed the co-HTC of sewage sludge with spent coffee grounds or bagasse as a sustainable method for producing biocoal-like solid fuel. Their study demonstrated that co-HTC significantly improved the fuel properties of solid products, increasing fixed carbon content, combustion reactivity, and HHV while reducing ash content, suggesting that co-HTC sewage sludge with organic residues holds promise for enhancing the value addition of sewage sludge feedstock. Cavali et al. [59] investigated the co-HTC of pine residual sawdust and non-dewatered sewage sludge to produce hydrochars without adding extra water. The author's findings showed the influence of temperature and reaction time on hydrochar yield and characteristics, particularly that higher temperatures resulted in an increased degree of coalification and the improved fuel properties of hydrochars. Benavente et al. [60] explored the co-HTC of microalgae and sewage sludge and concluded that the addition of sewage sludge reduced the degradation rate of solid feedstock components and influenced the composition of hydrochars. Despite limitations such as the presence of heavy metals and potentially toxic compounds, hydrochars derived from sewage sludge showed promise for environmental applications, while those from microalgae were more suitable for combustion.

3.3.2. Hydrothermal Liquefaction

The HTL process can also be applied to raw materials with a high moisture content without the need for additional pre-treatment steps such as drying and is carried out under sub-critical and supercritical water conditions and at temperatures between 250 °C and 370 °C [62]. Table 5 presents different works regarding the HTL of sewage sludge, including the main operating conditions and product yields.

Table 5. HTL of sewage sludge with different operating conditions, presence of catalyst, and product distribution.

Feedstock	Type of Reactor	Catalyst	Temperature (°C)	Moisture Content/Solid-Liquid Ratio	Pressure (MPa)	Residence Time (min)	Production Distribution (wt.%)			Ref.
							Hydrochar	Liquid	Gas	
Sewage sludge	Batch (1000 mL) Batch (19 L)	---	350	1:1 (Solid-Liquid)	180	30	43.9	18.9	10.3	[63]
		Na ₂ CO ₃					41.5	17.7	8.7	
		Li ₂ CO ₃					41.1	19.8	9.7	
		K ₂ CO ₃					41.8	16.8	8.5	
		Ba(OH) ₂					46.6	17.2	9.1	
		Fe ₂ O ₃					51.7	17.0	9.3	
		CeO ₂					47.9	16.2	8.3	
		NiMo/MoO ₃					49.5	18.4	9.0	
		MoS ₂					50.8	17.3	9.0	
		Ni/NiO					48.6	19.7	9.4	
SnO ₂	48.8	20.3	9.8							
FeS	48.4	15.8	6.6							

Table 5. Cont.

Feedstock	Type of Reactor	Catalyst	Temperature (°C)	Moisture Content/Solid Content/Solid–Liquid Ratio	Pressure (MPa)	Residence Time (min)	Production Distribution (wt.%)			Ref.
							Hydrochar	Liquid	Gas	
Sewage sludge*	Batch (25 mL)	-	350	75 wt.% (moisture content)	2.5	30	4	53	7	[64]
		KOH					8	47	10	
		HCOOH					4	38	10	
	Continuous (2 kg/h)	-				10	-	-	-	
		KOH				38	5	-		
	HCOOH	40	<1	-						
Sewage sludge							50.7	68.8	23.0	
Sewage sludge/wheat straw	Batch (10 mL internal volume)	---	300	1:10	---	90	35.6	31.9	32.5	[65]
Sewage sludge/cow manure							42.4	28.2	29.4	
Sewage sludge/chlorella pyrenoidosa							27.3	39.4	33.3	
Sewage sludge	Batch (50 mL)	K ₂ CO ₃	320	1:6	2.5	15	≈13.0	≈67.0	≈20.0	[66]
		Al ₂ O ₃					≈17.5	≈70.0	≈12.5	
		Co–Mo/ATP					≈12.0	≈74	≈14.0	
		Co–Mo/Al ₂ O ₃					≈18.0	≈66.0	≈16.0	
Sewage sludge	Continuous (2 kg/h)	-	350	10 wt.% (solid content)	25	8	1.9	80.2	17.9	[67]

* wt% daf basis.

In the HTL process, catalysts are sometimes added to increase the biocrude fraction or even increase the quality of the products themselves. Strugała-Wilczek et al. [63] studied the effect of the presence and behavior of the metals and metalloids present in sewage sludge on various products generated during the HTL process. Their study highlighted the importance of understanding metal migration in HTC byproducts, as it influences process efficiency and product quality. The results also showed that some metals can increase the efficiency of the process, acting as catalytic mediators, while other metals were only considered as contaminants, reducing the efficiency of the process and the quality of the biocrude produced, underscoring the need for the comprehensive characterization of HTL products and downstream processing to maximize resource utilization and minimize environmental impact. Zhu et al. [66] studied the catalytic activity of heterogeneous catalysts (Co/ γ -Al₂O₃, Co-Mo/ γ -Al₂O₃, Co/ATP, and Co-Mo/ATP) in the HTL of sewage sludge. The authors reported that the bimetallic catalyst (Co-Mo/Palygorskite (ATP)) was more effective and increased the biocrude production and quality. Also, the authors observed that all catalysts added to the system promoted the formation of phenols and hydrocarbons and detected that the presence of Mo in catalysts inhibited the formation of amide. Still on the topic of using catalysts in HTL, Zhang et al. [65] proposed a catalytic co-HTL route to enhance high-quality biocrude production from sewage sludge and wheat straw. This study investigated the synergistic effects between different biowastes and catalysts, demonstrating the potential of Ni@CSB catalyst in improving biocrude quality. Also, results indicated increased carbon content and HHV in biocrude, offering a promising route for valorizing biowastes into high-quality biocrude.

A very pressing issue related to HTL is the transition from batch to continuous production, which is generally more adequate for this technology scale-up. Prestigiacomo et al. [64] compared the operation of the HTL process in batch and continuous regimes. The need to reduce the initial concentration of solids in the feed from 10% to 3% to increase the stability of the feed flow to the continuous reactor was verified. Also, the authors highlighted issues such as flow rate instability and valve wear hindering system operability. They conclude that adjustments in feed concentration affect productivity, with basic or acidic compounds showing promise as additives to maintain stability at higher concentrations. Thomsen et al. [68] also reported that during studies of sewage sludge HTL in a continuous regime, some technical difficulties during the tests meant that the flow rates in the reactor were not constant. This shows that HTL in continuous operation still suffers from a lack of information and that it has some technical challenges, as it is difficult to maintain stable flow rates in the reactors.

Comparing the abovementioned works, it is evident that each study contributes unique insights into various aspects of HTL, ranging from metal behavior to operational challenges and catalyst effects. Together, these studies advance the understanding of HTL and co-HTL processes and offer valuable perspectives for optimizing biocrude production from sewage sludge and other biomass feedstocks.

3.3.3. Hydrothermal Gasification

In supercritical water gasification, temperature is a crucial factor for the composition of the producer gas formed. If HTG is carried out at low temperatures (374–550 °C), the production of methane is thermodynamically favorable over the production of a hydrogen-rich gas. To increase the selectivity of hydrogen over methane, the temperature needs to be between 550 and 700 °C or the catalysts need to be used at low temperatures to enhance the water–gas shift reaction [69,70]. Some works on the HTG of sewage sludge, and the main operating conditions and product yields, are shown in Table 6.

Table 6. HTG of sewage sludge with different operating conditions, presence of catalyst, gas LHV, and methane and hydrogen yields.

Raw Material	Type of Reactor	Catalyst	Sludge Concentration (wt.%)	Temperature (°C)	Pressure (MPa)	Residence Time (min)	LHV (MJ/Nm ³)	CH ₄ Yield (%)	H ₂ Yield (%)	Ref.
Sewage sludge	Batch	---	8.9	750	22.5–27.5	30	10.3	≈12.0	≈52.0	[71]
		---		≈12.0			≈19.0	≈39.0		
		K ₂ CO ₃		≈11.5			≈18.0	≈45.0		
		RNi-Mo2		650		20	≈10.5	≈14.0	≈47.0	
		K ₂ CO ₃ /RNi-Mo2		≈11.0			≈17.0	≈43.0		
Sewage sludge	Fluidized bed	---	2	540	25	---	---	≈10.5	≈43.0	[72]
		NaOH						≈9.0	≈50.0	
		KOH						≈7.0	≈56.0	
		K ₂ CO ₃						≈7.0	≈53.0	
		Na ₂ CO ₃						≈6.0	≈52.0	
Sewage sludge	Continuous	---	---	550	25	0.08	---	≈18.0	38.5	[73]
				600				≈27.0	39.4	
Sewage sludge	Batch	-	10	400	30	60	---	≈17.0	≈34.0	[70]
		Na ₂ CO ₃						≈16.0	≈33.0	
		K ₂ CO ₃						≈14.0	≈33.0	
		KOH						≈17.0	≈37.0	
		NaOH						≈18.0	≈36.0	

Table 6. Cont.

Raw Material	Type of Reactor	Catalyst	Sludge Concentration (wt.%)	Temperature (°C)	Pressure (MPa)	Residence Time (min)	LHV (MJ/Nm ³)	CH ₄ Yield (%)	H ₂ Yield (%)	Ref.		
Sewage sludge	Batch	-	10	450	25–27	60	---	18.9	40.9	[74]		
		NaOH						=23	=45.0			
		KOH						=18	=48.0			
		Ca(OH) ₂						=17	=47.0			
		K ₂ CO ₃						=14	48.7			
Na ₂ CO ₃	=16	=48.0										
Sewage sludge	Batch	---	3	380	27	6	---	16.6	22.6	[75]		
				460				22.9	55.7			
Sewage sludge	Batch	---	10	380	25	---	8.7	≈15.0	29.3	[76]		
				460				28	10.5		≈13.0	50.1
				Activated carbon				400	25		---	---

Chen et al. [71] explores sewage sludge gasification in supercritical water using a high-heating-rate batch reactor. This study investigates the effects of temperature, pressure, residence time, and catalyst on hydrogen yield, gasification efficiency, carbon gasification efficiency, and hydrogen yield potential. At 750 °C and 30 min, the maximum hydrogen yield, gasification efficiency, carbon gasification efficiency, and hydrogen yield potential reached 20.7 mol/kg, 73.5%, 61.2%, and 41.3%, respectively. Steam reforming, water–gas shift, and pyrolysis were identified as the main pathways for H₂ and CO₂ formation. The addition of mixed catalysts enhanced gasification and H₂ formation, with the RNi-Mo₂ catalyst promoting steam reforming and the alkali catalyst promoting the water–gas shift reaction. Furthermore, Chen et al. [72] investigated sewage sludge HTG using a fluidized-bed reactor. This study analyzed the effects of temperature, feedstock concentration, alkali catalysts, and catalyst loading on gaseous products and carbon distribution. The results showed that higher temperature and lower feedstock concentration favored gasification reactions and that the addition of catalyst enhanced H₂ formation, with KOH exhibiting the highest catalytic activity. The K₂CO₃ catalyst particularly enhanced gasification efficiency, primarily promoting the water–gas shift reaction. Cui et al. [74] examined the effect of alkaline additives on syngas yield and phosphorus/nitrogen migration during the HTG of sewage sludge. The authors highlight the role of alkaline additives in improving syngas yield by affecting steam reforming, water–gas shift, and methanation reactions. Among the used additives, K₂CO₃ exhibited the most significant catalytic effect, enhancing syngas yield and promoting phosphorus/nitrogen dissolution into the aqueous phase.

Differences between sub- and supercritical sewage sludge HTG in a batch reactor were studied by Yan et al. [70]. Their work focused on the effects of temperature and water-soluble additives on the process and resultant product characteristics. Increasing temperature enhanced H₂ yield and gasification efficiency, with KOH demonstrating the highest catalytic activity. This study also emphasized the conversion and dissolution of organic matters into syngas, characterized by porous hydrochar and disintegrated surface.

For the dynamics of batch versus continuous HTG, literature contributions are still scarce. Amrullah et al. [73] investigated the continuous recovery of phosphorus and gas generation from sewage sludge using supercritical water gasification. This study examined the behavior of phosphorus, gas composition, and reaction kinetics under varying temperatures and residence times. The authors observed a rapid conversion of organic phosphorus to inorganic phosphorus, and that gaseous products were mainly composed of H₂, CO₂, and CH₄, with the reaction following first-order kinetics. Moreover, the works from Weijing et al. [75] and Hantoko et al. [76] focused on the batch and continuous HTG of sewage sludge, respectively, highlighting the effects of temperature, retention time, and

catalysts on gas composition, yield, and efficiency. Both studies emphasize the significance of process parameters and catalyst selection in optimizing gasification performance. The results underscored the potential of HTG as an efficient and environmentally friendly approach for sewage sludge treatment and energy recovery.

4. SWOT Analysis

The successful implementation of sewage sludge conversion technologies relies not only on their technical feasibility but also on their economic viability and broader market considerations. This section presents a brief analysis of the techno-economic aspects associated with pyrolysis, gasification, HTC, HTL, and HTG, as potential pathways for sewage sludge valorization. To provide a structured assessment, a SWOT (Strengths, Weaknesses, Opportunities, Threats) analysis framework was employed, offering a systematic approach to evaluating the internal and external factors influencing the feasibility and sustainability of each technology. By examining the strengths, weaknesses, opportunities, and threats associated with these sewage sludge conversion technologies, this analysis aimed to elucidate their comparative advantages, potential challenges, and strategic implications for waste management and resource recovery initiatives. Figure 2 shows this work's SWOT analysis.



Figure 2. SWOT analysis of different thermochemical processes for sewage sludge conversion.

The SWOT analysis reveals that pyrolysis and gasification demonstrate robust pathways for energy recovery, offering high yields of biochar and syngas, albeit with significant capital and operational costs associated with complex reactor systems and downstream processing [10,77,78]. Despite these challenges, the potential for energy generation and resource recovery presents an attractive long-term investment opportunity, with the prospect of reducing dependency on fossil fuels and mitigating greenhouse gas emissions. In contrast, HTL, HTC, and HTG offer alternatives with lower energy requirements and potentially lower operational costs [50,79,80]. However, these processes face challenges related to product quality control, catalyst stability, switching from batch to continuous operation and scaling up, which may affect process efficiency and overall economic viability. Nevertheless, the growing demand for renewable energy and sustainable waste management solutions presents lucrative opportunities for technology adoption and commercialization [49]. With supportive policies and incentives aimed at promoting renewable energy development and mitigating environmental impacts, sewage sludge conversion technologies have the potential to contribute significantly to the transition towards a more sustainable and circular economy. By leveraging these opportunities and addressing the

associated challenges, stakeholders can unlock the full potential of sewage sludge as a valuable resource for energy production and waste management.

5. Current Challenges and Mitigation Strategies

Besides the results from the SWOT analysis regarding the more techno-economic aspects of the thermochemical technologies to convert sewage sludge, this feedstock also entails more technical challenges. Sewage sludge has the disadvantage of having high contents of moisture, ash, metals, and organic pollutants, requiring proper treatment that can make it energetically viable.

5.1. Sewage Sludge Drying

The water content of sewage sludge is an important factor to consider when recovering it through thermochemical processes. Energy costs in sludge drying should be considered, as they depend on the amount of sludge to be dried and the water content present [81]. In addition to the energy costs associated with sludge drying, the technical problems that arise during this stage must be considered. During the drying process, structural changes occur in sewage sludge, making it highly viscous, sticky, and tough. This change in sludge consistency may lead to technical consequences during drying [82,83]. For example, Schnell et al. [82] reported that during screw conveyance in sludge drying, the adhesion of the sludge to the screw itself caused extreme forces on the screw conveyor, damaging it completely. To avoid this problem, sewage sludge can be pre-mixed with dry material before drying to avoid this problem of adhesion on the equipment [84], or multi-stage dryers or remixing systems can be used for sewage sludge drying [85].

5.2. Gasification

The main challenges for the effective use of sewage sludge in gasification are mostly the feedstock's high moisture and ash contents and the low quality of the obtained products. Usually, to process sewage sludge with this technology, the feedstock must be dried between 105 °C and 120 °C before being gasified [19,30,33,34], which leads to the issues described in the previous section.

As for ash content, Kang et al. [30] studied the catalytic gasification of dried sewage sludge and observed a large quantity of solid residues, notably due to the presence of a large amount of ash (>40 wt.%). This ash concentration can result in agglomeration and blockage of the reactor, requiring successive extensive cleaning and separation after each cycle. The authors recommended washing the sewage sludge with distilled water or acid leaching to reduce the ash content and thus avoid agglomeration and blockage of the reactor.

The major product in gasification, syngas, usually presents a lower quality than what is required for further applications due to the physical–chemical characteristics of sewage sludge. Co-gasification of sewage sludge with coal, woody biomass, straw, forestry residues, and manure is known to improve the quality of syngas. However, it is necessary to optimize the operating conditions and the mixing ratios, because although there is an improvement in the gas produced, the yields of tar in the syngas and the ash content can increase [10].

As already mentioned throughout this work, the use of catalysts in gasification has shown good results in reducing impurities (COS, H₂S, NH₃, and tars) in the syngas. This result not only decreases costs in producer gas-cleaning systems but also reduces the problems of tar condensation in the gasification pipelines or valve blocking and downstream equipment [28,32]. Kang et al. [30] suggested that the mixture of activated carbon and biochar is a strategic combination since the mixture would allow the adsorption/cracking of tar and an enhancement of the gasification reactions by increasing H₂ production, which is favored due to the presence of alkaline metal species in the biochar. The authors also state that the possibility of using sewage sludge biochar obtained from gasification as a catalyst should be addressed due to the high amounts of heavy metals that can enhance gasification

reactions, even though the formation of tars and coke can cause the deactivation of the catalyst [10].

Additionally, the products obtained from gasification have associated toxicities. Contaminants present in the gaseous phase (NO_x , SO_x , HF, HCl, NH_3 , PAHs, and dioxins) can lead to an increase in GHG emissions, tars (compounds of N, O, and S), and biochar (heavy metals), which can increase soil toxicity if used in agricultural and land applications [10]. The proper selection of co-gasification of sewage sludge with other feedstocks and the use of catalysts to reduce pollutants and tar can be interesting solutions, although they present challenges due to the high ash, tar, and solid content of sewage sludge, which affects product quality and causes problems for catalyst regeneration [32].

5.3. Pyrolysis

The pyrolysis of sewage sludge presents two challenges: the high moisture content and the presence of metals. The high moisture content together with the organic species present in the sludge decreases the quality of the bio-oil produced (e.g., there is water mixed with the bio-oil and there are oxygenated and nitrogenous compounds present in the bio-oil). The presence of these compounds makes it necessary to upgrade the bio-oil through reactions such as deoxygenation and denitrification to remove oxygenated and nitrogenous compounds, thus increasing the quality of the bio-oil. These reactions require the use of suitable catalysts [23,86].

Another way to increase the quality of sewage sludge pyrolysis products would be to dry the sewage sludge, usually at 120 °C (which requires a large amount of energy to be supplied), or to mix it with a biomass with a lower moisture content and in this way achieve co-pyrolysis [19]. However, deoxygenation and denitrification are still a challenge. Nitrogenous compounds present in the gas, and biochar, can cause the emission of toxic compounds and toxicity in biochar if they are used in land and agricultural applications (much like the biochar from sewage sludge gasification, even though it is produced at higher temperatures).

Due to the high ash and metal content of the sewage sludge, the catalysts can become deactivated due to the formation of coke or other species that can block the pores of the catalyst [87,88].

The pyrolysis of sewage sludge faces other very pressing challenges, namely scaling up and energy efficiency. Scaling up sewage sludge pyrolysis to commercial levels demands innovative equipment design tailored for large-scale operations and eliminations of historical shortcomings by simplifying the process, coupled with continuous process optimization to maximize productivity and minimize costs [89]. This needs close collaboration between researchers, engineers, and industry stakeholders to ensure the development of robust and cost-effective pyrolysis systems. Conducting comprehensive techno-economic analyses is also of extreme relevance for assessing the economic viability of commercial-scale pyrolysis plants and identify strategies for optimizing process economics. On the other hand, enhancing energy efficiency in sewage sludge pyrolysis involves integrating the process with other energy-intensive operations, implementing efficient heat recovery systems, and exploring advanced pyrolysis technologies (e.g., microwave pyrolysis or hydrothermal processes). By researching these solutions, sewage sludge pyrolysis can overcome the described technical challenges and advance towards sustainable and energy-efficient waste-to-resource conversion processes.

5.4. Hydrothermal Methods

Major HTC challenges correspond to its high capital investment, the need to transition from batch to continuous processes, and process water valorization. As with any hydrothermal process, the use of extreme pressure conditions requires a high capital investment. In addition to the high investment, there is also the challenge of changing the HTC process from batch to continuous. The development of a hydrothermal carbonization reactor that can operate in a continuous process for sewage sludge conversion is important for large-

scale applications [90,91]. HTC process water is composed of phenols, acids, nutrients, and recalcitrant compounds, offering potential for use in chemical manufacturing. The recirculation of process water represents a valorization pathway that can reduce the cost of wastewater treatment and the need for external heat in the process [91,92]. However, the recovery of these compounds from the aqueous phase to manufacture chemicals can add unit operations to the whole process, which will represent an increase in costs. Other solutions to harness this process water are its use in anaerobic digestion to produce methane and as liquid fertilizer [90]. The lack of development of a kinetic model associated with the HTC process parameters, the initial composition of the sewage sludge, the catalytic effects of heavy metals, and the organic acids formed in the process means that it is not possible, for example, to predict the yields, distributions, and characteristics of the final product [90]. The lack of a kinetic model also means that it is not possible to properly design an HTC reactor. As such, for HTC, more research on reactor design, catalysts and their regeneration, and water reuse are needed to overcome technological gaps and economic and environmental constraints.

Despite the many promising approaches that have proven the efficiency of HTL in converting sewage sludge into value-added products, there are some challenges that need to be solved before its application at the commercial scale. These challenges concern the quality of the obtained products, as well as procedural problems limiting the application of this process at larger and continuous scales. Many studies report the low quality and calorific value of the biocrude, and the lack of management of the aqueous phase and solid waste produced in the HTL process [62]. High temperatures and pressures in HTL can lead to water acidity or basicity, imposing the use of stainless steel or nickel-based alloys. Hastelloy alloys may offer corrosion resistance but pose cost challenges [80]. Pumping and separation challenges, including solid suspension clogging and phase separation, limit HTL scalability and continuous operation [62]. In the HTL process, one of the uses is to use the produced biocrude as a fuel with characteristics equivalent to petroleum fuels. However, biocrude produced in the HTL process has higher contents of compounds with O, N, and S atoms than most refinery streams. The excessive amount of oxygenated compounds in biocrude decreases the calorific value, and increases instability and corrosivity [62]. Nitrogenous compounds in biocrude are also undesirable due to the pollution of the atmosphere by NO_x emissions during combustion. Thus, the produced biocrude must be subjected to hydrotreatment processes such as hydrodeoxygenation and denitrification to remove oxygenated and nitrogenous compounds, respectively. This upgrading of the biocrude will increase its quality and applicability as a fuel. However, the use of catalysts and the use of high H_2 pressures make the process more expensive [62]. Also, heavy metals (e.g., Cr, Cu, Ni, and Zn) have been reported to be concentrated in the hydrochar produced via HTL. This high concentration of metals is one of the main challenges of the applicability of hydrochar to soils, making them inadequate for this application whenever heavy metal concentration exceeds limits [93]. Still, the HTL of sewage sludge allows the efficient recovery of phosphorus in the forms of struvite and calcium phosphate and nitrogen in the form of ammonium sulfate. These compounds can be used as agricultural fertilizers [94]. As for HTL process water, the valorization solutions are the same as for HTC process water, with the same constraints. Nevertheless, the presence of phenols or the high concentration of ammonia in this aqueous phase are considered inhibitors of anaerobic digestion. One solution for this issue would be to first recover these compounds for the manufacturing of value-added products and only then treat the aqueous phase by anaerobic digestion [95,96].

The HTG of sewage sludge is a promising technology to produce hydrogen-rich fuel gas. However, there are still technical challenges related to the deactivation of the catalysts, corrosion, plugging, and, finally, the high operational cost due to extreme temperature/pressure conditions. These challenges could be prevented through appropriate pre-treatments, chemical conditioning, and the use of catalysts to make the process economically viable using milder temperature/pressure conditions. However, the use of homogeneous catalysts in HTG, such as inorganic alkaline salts, can cause process prob-

lems such as equipment blockage due to their precipitation and corrosion [80,97,98]. In addition, high temperatures and pressures can result in sintering of these salts or phase change of the support materials such as the presence of sulfur and deposition of coke can deactivate the catalysts [80,98,99]. The corrosion of reactor walls used in HTG due, for example, to the formation of corrosive acids or the use of K_2CO_3 as a catalyst, has been reported in the literature [80,98,100]. One way to reduce corrosion is to dope high-temperature water with salts (esp. sodium phosphates), though this solution will cause clogging problems due to salt precipitation [97].

6. Conclusions

An environmentally favorable solution for the end of life of sewage sludge is to convert it into value-added products (biochar, biofuel, and renewable gases) using thermochemical processes. The brief overview presented in this paper highlights the various thermochemical conversion technologies for sewage sludge valorization, including pyrolysis, gasification, hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG). Each technology offers unique strengths and faces specific challenges that must be addressed for successful implementation at a commercial scale. Pyrolysis and gasification exhibit robust pathways for energy recovery, albeit with significant capital and operational costs, while HTC, HTL, and HTG present alternatives with lower energy requirements but possess challenges related to product quality control and process optimization. Despite these challenges, the growing demand for renewable energy and sustainable waste management solutions presents lucrative opportunities for technology adoption and commercialization.

Sewage sludge thermochemical treatment faces significant technical drawbacks, notably stemming from the feedstock's high moisture content, ash concentration, metal presence, and organic pollutant levels. Diverse strategies, including drying, gasification, pyrolysis, and hydrothermal methods, are used to address these challenges. The utilization of catalysts, optimization of process parameters, and integration of waste streams for resource recovery emerge as pivotal approaches discussed for enhancing the efficiency and efficacy of sewage sludge conversion processes. And critical factors such as safety concerns, environmental impacts, and scalability considerations are identified as imperative aspects requiring careful consideration during technology development and deployment.

Future research on sewage sludge thermochemical conversion should entail a more detailed exploration of the challenges overviewed in this work; specifically, elucidating the details of addressing the sewage sludge's physical–chemical properties, which involves the development of innovative strategies for efficient moisture removal, ash management, and overall pollutant removal. Furthermore, the technical difficulties that are unique to each thermochemical conversion technology highlighted in this work should also be addressed through process optimization, catalyst development, reactor design, and the integration of waste streams for resource recovery.

Despite these challenges, sewage sludge conversion technologies offer promising pathways for technological advancement. Leveraging technological innovations, implementing practices that can support sustainable development, and fostering collaboration across sectors can establish sewage sludge valorization in compliance with the principles of circular economy. Sustained focus on continued research, development, and investment in sewage sludge conversion technologies remains essential for realizing their full potential and effectively addressing the multifaceted challenges surrounding waste management and resource recovery in our contemporary society.

Author Contributions: Conceptualization, B.R.; methodology, B.R. and C.N.; validation, P.B. and P.F.; investigation, B.R. and C.N.; resources, P.B. and P.F.; writing—original draft preparation, B.R. and C.N.; writing—review, and editing, B.R., C.N., P.B. and P.F.; project administration, P.B. and P.F.; funding acquisition, P.B. and P.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Portuguese Foundation for Science and Technology under project UIDB/05064/2020 (VALORIZA—Research Centre for Endogenous Resource Valorization) and the HYFUELUP project (European Union’s Horizon Europe research and innovation programme) under grant agreement no. 101084148.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Eurostat Sewage Sludge Production and Disposal. Available online: https://ec.europa.eu/eurostat/databrowser/view/H_LTH_PS_PREV__custom_7978672/bookmark/table?lang=en&bookmarkId=827e0163-fd0f-4ed7-9cd3-f2c20574cb07%0Ahttps://ec.europa.eu/eurostat/databrowser/view/tec00118/default/table?lang=en%0Ahttps://ec.europa.eu/euros (accessed on 26 February 2024).
2. Rahman, T.; Jahromi, H.; Roy, P.; Adhikari, S.; Hassani, E. Hydrothermal Liquefaction of Municipal Sewage Sludge: Effect of Red Mud Catalyst in Ethylene and Inert Ambiences. *Energy Convers. Manag.* **2021**, *245*, 114615. [CrossRef]
3. Hoang, S.A.; Bolan, N.; Madhubashani, A.M.P.; Vithanage, M.; Perera, V.; Wijesekara, H.; Wang, H.; Srivastava, P.; Kirkham, M.B. Treatment Processes to Eliminate Potential Environmental Hazards and Restore Agronomic Value of Sewage Sludge: A Review. *Environ. Pollut.* **2022**, *293*, 118564. [CrossRef]
4. Panepinto, D.; Fiore, S.; Genon, G.; Aciri, M. Thermal Valorization of Sewer Sludge: Perspectives for Large Wastewater Treatment Plants. *J. Clean. Prod.* **2016**, *137*, 1323–1329. [CrossRef]
5. Cano, R.; Pérez-Elvira, S.I.; Fdz-Polanco, F. Energy Feasibility Study of Sludge Pretreatments: A Review. *Appl. Energy* **2015**, *149*, 176–185. [CrossRef]
6. Manara, P.; Zabanitotou, A. Towards Sewage Sludge Based Biofuels via Thermochemical Conversion—A Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2566–2582. [CrossRef]
7. Syed-Hassan, S.S.A.; Wang, Y.; Hu, S.; Su, S.; Xiang, J. Thermochemical Processing of Sewage Sludge to Energy and Fuel: Fundamentals, Challenges and Considerations. *Renew. Sustain. Energy Rev.* **2017**, *80*, 888–913. [CrossRef]
8. Chan, W.P.; Wang, J.Y. Comprehensive Characterisation of Sewage Sludge for Thermochemical Conversion Processes—Based on Singapore Survey. *Waste Manag.* **2016**, *54*, 131–142. [CrossRef]
9. Kathi, S.; Singh, S.; Yadav, R.; Singh, A.N.; Mahmoud, A.E.D. Wastewater and Sludge Valorisation: A Novel Approach for Treatment and Resource Recovery to Achieve Circular Economy Concept. *Front. Chem. Eng.* **2023**, *5*, 1–20. [CrossRef]
10. Gao, N.; Kamran, K.; Quan, C.; Williams, P.T. Thermochemical Conversion of Sewage Sludge: A Critical Review. *Prog. Energy Combust. Sci.* **2020**, *79*, 100843. [CrossRef]
11. Gururani, P.; Bhatnagar, P.; Bisht, B.; Jaiswal, K.K.; Kumar, V.; Kumar, S.; Vlaskin, M.S.; Grigorenko, A.V.; Rindin, K.G. Recent Advances and Viability in Sustainable Thermochemical Conversion of Sludge to Bio-Fuel Production. *Fuel* **2022**, *316*, 123351. [CrossRef]
12. Bianchini, A.; Bonfiglioli, L.; Pellegrini, M.; Saccani, C. Sewage Sludge Drying Process Integration with a Waste-to-Energy Power Plant. *Waste Manag.* **2015**, *42*, 159–165. [CrossRef]
13. Alves, O.; Garcia, B.; Rijo, B.; Lourinho, G.; Nobre, C. Market Opportunities in Portugal for the Water-and-Waste Sector Using Sludge Gasification. *Energies* **2022**, *15*, 6600. [CrossRef]
14. Singh, S.; Kumar, V.; Dhanjal, D.S.; Datta, S.; Bhatia, D.; Dhiman, J.; Samuel, J.; Prasad, R.; Singh, J. A Sustainable Paradigm of Sewage Sludge Biochar: Valorization, Opportunities, Challenges and Future Prospects. *J. Clean. Prod.* **2020**, *269*, 122259. [CrossRef]
15. Durak, H. Comprehensive Assessment of Thermochemical Processes for Sustainable Waste Management and Resource Recovery. *Processes* **2023**, *11*, 2092. [CrossRef]
16. Zaker, A.; Chen, Z.; Wang, X.; Zhang, Q. Microwave-Assisted Pyrolysis of Sewage Sludge: A Review. *Fuel Process. Technol.* **2019**, *187*, 84–104. [CrossRef]
17. Hu, M.; Hu, H.; Ye, Z.; Tan, S.; Yin, K.; Chen, Z.; Guo, D.; Rong, H.; Wang, J.; Pan, Z.; et al. A Review on Turning Sewage Sludge to Value-Added Energy and Materials via Thermochemical Conversion towards Carbon Neutrality. *J. Clean. Prod.* **2022**, *379*, 134657. [CrossRef]
18. Su, Y.; Liu, D.; Gong, M.; Zhu, W.; Yu, Y.; Gu, H. Investigation on the Decomposition of Chemical Compositions during Hydrothermal Conversion of Dewatered Sewage Sludge. *Int. J. Hydrogen Energy* **2019**, *44*, 26933–26942. [CrossRef]
19. Ronda, A.; Haro, P.; Gómez-Barea, A. Sustainability Assessment of Alternative Waste-to-Energy Technologies for the Management of Sewage Sludge. *Waste Manag.* **2023**, *159*, 52–62. [CrossRef] [PubMed]
20. Li, M.; Xiao, B.; Wang, X.; Liu, J. Consequences of Sludge Composition on Combustion Performance Derived from Thermogravimetry Analysis. *Waste Manag.* **2015**, *35*, 141–147. [CrossRef]
21. Nyashanu, P.N.; Shafodino, F.S.; Mwapagha, L.M. Determining the Potential Human Health Risks Posed by Heavy Metals Present in Municipal Sewage Sludge from a Wastewater Treatment Plant. *Sci. Afr.* **2023**, *20*, e01735. [CrossRef]

22. Urbaniak, M.; Baran, A.; Giebu, J.; Bednarek, A.; Giebułtowicz, J.; Bednarek, A.; Serwecińska, L. The Occurrence of Heavy Metals and Antimicrobials in Sewage Sludge and Their Predicted Risk to Soil—Is There Anything to Fear? *Sci. Total Environ.* **2024**, *912*, 168856. [[CrossRef](#)] [[PubMed](#)]
23. Hu, M.; Ye, Z.; Zhang, H.; Chen, B.; Pan, Z.; Wang, J. Thermochemical Conversion of Sewage Sludge for Energy and Resource Recovery: Technical Challenges and Prospects. *Environ. Pollut. Bioavail.* **2021**, *33*, 145–163. [[CrossRef](#)]
24. Quan, L.M.; Kamyab, H.; Yuzir, A.; Ashokkumar, V.; Hosseini, S.E.; Balasubramanian, B.; Kirpichnikova, I. Review of the Application of Gasification and Combustion Technology and Waste-to-Energy Technologies in Sewage Sludge Treatment. *Fuel* **2022**, *316*, 123199. [[CrossRef](#)]
25. Tezer, Ö.; Karabağ, N.; Öngen, A.; Ayol, A. Syngas Production from Municipal Sewage Sludge by Gasification Process: Effects of Fixed Bed Reactor Types and Gasification Agents on Syngas Quality. *Sustain. Energy Technol. Assess.* **2023**, *56*, 103042. [[CrossRef](#)]
26. Hu, M.; Gao, L.; Chen, Z.; Ma, C.; Zhou, Y.; Chen, J.; Ma, S.; Laghari, M.; Xiao, B.; Zhang, B.; et al. Syngas Production by Catalytic In-Situ Steam Co-Gasification of Wet Sewage Sludge and Pine Sawdust. *Energy Convers. Manag.* **2016**, *111*, 409–416. [[CrossRef](#)]
27. Farooq, A.; Ko, C.H.; Park, Y.K. Sewage Sludge Steam Gasification over Bimetallic Mesoporous Al-MCM48 Catalysts for Efficient Hydrogen Generation. *Environ. Res.* **2023**, *224*, 115553. [[CrossRef](#)] [[PubMed](#)]
28. Jeong, Y.S.; Mun, T.Y.; Kim, J.S. Two-Stage Gasification of Dried Sewage Sludge: Effects of Gasifying Agent, Bed Material, Gas Cleaning System, and Ni-Coated Distributor on Product Gas Quality. *Renew. Energy* **2022**, *185*, 208–216. [[CrossRef](#)]
29. Yang, X.; Kan, T.; Kheradmand, A.; Xu, H.; Strezov, V.; Yu, A.; Jiang, Y. Tunable Syngas Production from Two-Stage Sorption-Enhanced Steam Gasification of Sewage Sludge. *Chem. Eng. J.* **2021**, *404*, 126069. [[CrossRef](#)]
30. Kang, B.S.; Farooq, A.; Valizadeh, B.; Lee, D.; Seo, M.W.; Jung, S.C.; Hussain, M.; Kim, Y.M.; Khan, M.A.; Jeon, B.H.; et al. Valorization of Sewage Sludge via Air/Steam Gasification Using Activated Carbon and Biochar as Catalysts. *Int. J. Hydrogen Energy* **2023**, *54*, 284–293. [[CrossRef](#)]
31. De Andrés, J.M.; Narros, A.; Rodríguez, M.E. Air-Steam Gasification of Sewage Sludge in a Bubbling Bed Reactor: Effect of Alumina as a Primary Catalyst. *Fuel Process. Technol.* **2011**, *92*, 433–440. [[CrossRef](#)]
32. Schmid, M.; Hafner, S.; Biollaz, S.; Schneebeli, J.; Waizmann, G.; Scheffknecht, G. Steam-Oxygen Gasification of Sewage Sludge: Reduction of Tar, H₂S and COS with Limestone as Bed Additive. *Biomass Bioenergy* **2021**, *150*, 106100. [[CrossRef](#)]
33. Pedroza, M.M.; Sousa, J.F.; Vieira, G.E.G.; Bezerra, M.B.D. Characterization of the Products from the Pyrolysis of Sewage Sludge in 1 Kg/h Rotating Cylinder Reactor. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 108–115. [[CrossRef](#)]
34. Chanaka Udayanga, W.D.; Veksha, A.; Giannis, A.; Lisak, G.; Lim, T.T. Effects of Sewage Sludge Organic and Inorganic Constituents on the Properties of Pyrolysis Products. *Energy Convers. Manag.* **2019**, *196*, 1410–1419. [[CrossRef](#)]
35. Feng, C.; Xie, W.; Zhang, D.; Gao, X.; Qiao, Y.; Xu, M. Pyrolysis of Sewage Sludge under Conditions Relevant to Applied Smouldering Combustion. *Proc. Combust. Inst.* **2023**, *39*, 3447–3456. [[CrossRef](#)]
36. Gao, N.; Li, J.; Qi, B.; Li, A.; Duan, Y.; Wang, Z. Thermal Analysis and Products Distribution of Dried Sewage Sludge Pyrolysis. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 43–48. [[CrossRef](#)]
37. Qiu, Z.; Zhai, Y.; Li, S.; Liu, X.; Liu, X.; Wang, B.; Liu, Y.; Li, C.; Hu, Y. Catalytic Co-Pyrolysis of Sewage Sludge and Rice Husk over Biochar Catalyst: Bio-Oil Upgrading and Catalytic Mechanism. *Waste Manag.* **2020**, *114*, 225–233. [[CrossRef](#)] [[PubMed](#)]
38. Agar, D.A.; Kwapinska, M.; Leahy, J.J. Pyrolysis of Wastewater Sludge and Composted Organic Fines from Municipal Solid Waste: Laboratory Reactor Characterisation and Product Distribution. *Environ. Sci. Pollut. Res.* **2018**, *25*, 35874–35882. [[CrossRef](#)] [[PubMed](#)]
39. Alvarez, J.; Lopez, G.; Amutio, M.; Artetxe, M.; Barbarias, I.; Arregi, A.; Bilbao, J.; Olazar, M. Characterization of the Bio-Oil Obtained by Fast Pyrolysis of Sewage Sludge in a Conical Spouted Bed Reactor. *Fuel Process. Technol.* **2016**, *149*, 169–175. [[CrossRef](#)]
40. Fonts, I.; Juan, A.; Gea, G.; Murillo, M.B.; Sánchez, J.L. Sewage Sludge Pyrolysis in Fluidized Bed, 1: Influence of Operational Conditions on the Product Distribution. *Ind. Eng. Chem. Res.* **2008**, *47*, 5376–5385. [[CrossRef](#)]
41. Sun, Y.; Jin, B.; Wu, W.; Zuo, W.; Zhang, Y.; Zhang, Y.; Huang, Y. Effects of Temperature and Composite Alumina on Pyrolysis of Sewage Sludge. *J. Environ. Sci.* **2015**, *30*, 1–8. [[CrossRef](#)]
42. Hu, Y.; Yu, W.; Wibowo, H.; Xia, Y.; Lu, Y.; Yan, M. Effect of Catalysts on Distribution of Polycyclic-Aromatic Hydrocarbon (PAHs) in Bio-Oils from the Pyrolysis of Dewatered Sewage Sludge at High and Low Temperatures. *Sci. Total Environ.* **2019**, *667*, 263–270. [[CrossRef](#)] [[PubMed](#)]
43. Huang, Z.; Qin, L.; Xu, Z.; Chen, W.; Xing, F.; Han, J. The Effects of Fe₂O₃ Catalyst on the Conversion of Organic Matter and Bio-Fuel Production during Pyrolysis of Sewage Sludge. *J. Energy Inst.* **2019**, *92*, 835–842. [[CrossRef](#)]
44. de Souza Souza, C.; Bomfim, M.R.; de Almeida, M.d.C.; Alves, L.d.S.; de Santana, W.N.; da Silva Amorim, I.C.; Santos, J.A.G. Induced Changes of Pyrolysis Temperature on the Physicochemical Traits of Sewage Sludge and on the Potential Ecological Risks. *Sci. Rep.* **2021**, *11*, 974. [[CrossRef](#)] [[PubMed](#)]
45. Wang, K.; Zheng, Y.; Zhu, X.; Brewer, C.E.; Brown, R.C. Ex-Situ Catalytic Pyrolysis of Wastewater Sewage Sludge—A Micro-Pyrolysis Study. *Bioresour. Technol.* **2017**, *232*, 229–234. [[CrossRef](#)] [[PubMed](#)]
46. Azuara, M.; Fonts, I.; Bimbela, F.; Murillo, M.B.; Gea, G. Catalytic Post-Treatment of the Vapors from Sewage Sludge Pyrolysis by Means of γ -Al₂O₃: Effect on the Liquid Product Properties. *Fuel Process. Technol.* **2015**, *130*, 252–262. [[CrossRef](#)]

47. Beckers, W.; Schuller, D.; Vaizert, O. Thermolytical Treatment of Dried Sewage Sludge and Other Biogenic Materials-Including Upgrading of Pyrolysis Vapours by a Cracking Catalyst and Examination of Heavy Metals by X-Ray Fluorescence. *J. Anal. Appl. Pyrolysis* **1999**, *50*, 17–30. [[CrossRef](#)]
48. Meng, J.; Wang, J.; Yang, F.; Cheng, F. Study on the Multiple Roles of CaO on Nitrogen Evolution Mechanism of Protein inside Sewage Sludge Pyrolysis. *Chem. Eng. J.* **2023**, *458*, 141039. [[CrossRef](#)]
49. Chen, W.; Haque, A.; Lu, T.; Aierzhati, A.; Reimonn, G. A Perspective on Hydrothermal Processing of Sewage Sludge. *Curr. Opin. Environ. Sci. Health* **2020**, *14*, 63–76. [[CrossRef](#)] [[PubMed](#)]
50. Lachos-Perez, D.; César Torres-Mayanga, P.; Abaide, E.R.; Zabet, G.L.; De Castilhos, F. Hydrothermal Carbonization and Liquefaction: Differences, Progress, Challenges, and Opportunities. *Bioresour. Technol.* **2022**, *343*, 126084. [[CrossRef](#)]
51. Romano, P.; Stampone, N.; Di Giacomo, G. Evolution and Prospects of Hydrothermal Carbonization. *Energies* **2023**, *16*, 3125. [[CrossRef](#)]
52. Danso-Boateng, E.; Shama, G.; Wheatley, A.D.; Martin, S.J.; Holdich, R.G. Hydrothermal Carbonisation of Sewage Sludge: Effect of Process Conditions on Product Characteristics and Methane Production. *Bioresour. Technol.* **2015**, *177*, 318–327. [[CrossRef](#)]
53. Volpe, M.; Fiori, L.; Merzari, F.; Messineo, A.; Andreatola, G. Hydrothermal Carbonization as an Efficient Tool for Sewage Sludge Valorization and Phosphorous Recovery. *Chem. Eng. Trans.* **2020**, *80*, 199–204. [[CrossRef](#)]
54. Petrovič, A.; Cenčič Predikaka, T.; Škodič, L.; Vohl, S.; Čuček, L. Hydrothermal Co-Carbonization of Sewage Sludge and Whey: Enhancement of Product Properties and Potential Application in Agriculture. *Fuel* **2023**, *350*, 128807. [[CrossRef](#)]
55. Wilk, M.; Sliz, M.; Czerwinska, K.; Sled, M. The Effect of an Acid Catalyst on the Hydrothermal Carbonization of Sewage Sludge. *J. Environ. Manag.* **2023**, *345*, 118820. [[CrossRef](#)]
56. Wang, C.; Gui, B.; Wu, C.; He, C.; Li, L.; Ling, X.; Zuo, X. Hydrothermal Carbonization of Sewage Sludge Coupled with Fenton Oxidation Pretreatment: Moderate Oxidation to Enhance Hydrochar Yield and Properties. *J. Environ. Chem. Eng.* **2023**, *11*, 110788. [[CrossRef](#)]
57. Piboonudomkarn, S.; Khemthong, P.; Youngjan, S.; Wantala, K. Co-Hydrothermally Carbonized Sewage Sludge and Lignocellulosic Biomass: An Efficiently Renewable Solid Fuel. *Arab. J. Chem.* **2023**, *16*, 105315. [[CrossRef](#)]
58. Paiboonudomkarn, S.; Wantala, K.; Lubphoo, Y.; Khunphonoi, R. Conversion of Sewage Sludge from Industrial Wastewater Treatment to Solid Fuel through Hydrothermal Carbonization Process. *Mater. Today Proc.* **2022**, *75*, 85–90. [[CrossRef](#)]
59. Cavali, M.; Benbelkacem, H.; Kim, B.; Bayard, R.; Libardi Junior, N.; Gonzaga Domingos, D.; Woiciechowski, A.L.; Castilhos Junior, A.B. de Co-Hydrothermal Carbonization of Pine Residual Sawdust and Non-Dewatered Sewage Sludge—Effect of Reaction Conditions on Hydrochar Characteristics. *J. Environ. Manag.* **2023**, *340*, 117994. [[CrossRef](#)]
60. Benavente, V.; Pérez, C.; Jansson, S. Co-Hydrothermal Carbonization of Microalgae and Digested Sewage Sludge: Assessing the Impact of Mixing Ratios on the Composition of Primary and Secondary Char. *Waste Manag.* **2024**, *174*, 429–438. [[CrossRef](#)]
61. Huerdo, L.; Vasco-Correa, J.; Shah, A. Hydrothermal Carbonization of Anaerobically Digested Sewage Sludge for Hydrochar Production. *Bioresour. Technol. Rep.* **2021**, *15*, 100795. [[CrossRef](#)]
62. Fan, Y.; Hornung, U.; Dahmen, N. Hydrothermal Liquefaction of Sewage Sludge for Biofuel Application: A Review on Fundamentals, Current Challenges and Strategies. *Biomass Bioenergy* **2022**, *165*, 106570. [[CrossRef](#)]
63. Strugała-Wilczek, A.; Basa, W.; Pankiewicz-Sperka, M.; Xu, D.; Duan, P.; Hao, B.; Wang, Y.; Leng, L.; Yang, L.; Fan, L.; et al. Distribution Characteristics and Migration Pathways of Metals during Hydrothermal Liquefaction of Municipal Sewage Sludge in the Presence of Various Catalysts. *Sci. Total Environ.* **2024**, *920*, 171023. [[CrossRef](#)] [[PubMed](#)]
64. Prestigiacomo, C.; Fan, Y.; Hornung, U.; Dahmen, N.; Scialdone, O.; Galia, A. Hydrothermal Liquefaction of Sewage Sludge: Use of HCOOH and KOH to Improve the Slurry Pumpability in a Continuously Operated Plant. *Heliyon* **2024**, *10*, e26287. [[CrossRef](#)] [[PubMed](#)]
65. Zhang, G.; Liu, Q.; Li, X.; Kong, G.; Cao, T.; Cheng, Q.; Zhang, Z.; Zhang, X.; Han, L. Catalytic Hydrothermal Co-Liquefaction of Sewage Sludge and Agricultural Biomass for Promoting Advanced Biocrude Production. *J. Clean. Prod.* **2023**, *428*, 139470. [[CrossRef](#)]
66. Zhu, Y.; Zhao, Y.; Tian, S.; Zhang, X.; Wei, X. Catalytic Hydrothermal Liquefaction of Sewage Sludge: Effect of Metal Support Heterogeneous Catalysts on Products Distribution. *J. Energy Inst.* **2022**, *103*, 154–159. [[CrossRef](#)]
67. Fan, Y.; Prestigiacomo, C.; Gong, M.; Tietz, T.; Hornung, U.; Dahmen, N. Comparative Investigation on the Value-Added Products Obtained from Continuous and Batch Hydrothermal Liquefaction of Sewage Sludge. *Front. Environ. Sci.* **2022**, *10*, 1–13. [[CrossRef](#)]
68. Silva Thomsen, L.B.; Carvalho, P.N.; dos Passos, J.S.; Anastasakis, K.; Bester, K.; Biller, P.; Bjørn, L.; Thomsen, S.; Carvalho, P.N.; Souza, J.; et al. Hydrothermal Liquefaction of Sewage Sludge; Energy Considerations and Fate of Micropollutants during Pilot Scale Processing. *Water Res.* **2020**, *183*, 116101. [[CrossRef](#)] [[PubMed](#)]
69. Baudouin, D.; Salionov, D.; Vogel, F.; Bjelić, S. Advanced Analytical Study of Process Streams for a Rational Optimization of Hydrothermal Gasification. *ACS Eng. Au* **2021**, *1*, 134–147. [[CrossRef](#)]
70. Yan, M.; Hantoko, D.; Kanchanatip, E.; Zheng, R.; Zhong, Y.; Mubeen, I. Valorization of Sewage Sludge through Catalytic Sub- and Supercritical Water Gasification. *J. Energy Inst.* **2020**, *93*, 1419–1427. [[CrossRef](#)]
71. Chen, Y.; Yi, L.; Wei, W.; Jin, H.; Guo, L. Hydrogen Production by Sewage Sludge Gasification in Supercritical Water with High Heating Rate Batch Reactor. *Energy* **2022**, *238*, 121740. [[CrossRef](#)]
72. Chen, Y.; Guo, L.; Cao, W.; Jin, H.; Guo, S.; Zhang, X. Hydrogen Production by Sewage Sludge Gasification in Supercritical Water with a Fluidized Bed Reactor. *Int. J. Hydrogen Energy* **2013**, *38*, 12991–12999. [[CrossRef](#)]

73. Amrullah, A.; Matsumura, Y. Supercritical Water Gasification of Sewage Sludge in Continuous Reactor. *Bioresour. Technol.* **2018**, *249*, 276–283. [[CrossRef](#)]
74. Cui, J.; Wen, X.; Chen, F.; Yan, M.; Hantoko, D. Migration of Nitrogen and Phosphorus during Supercritical Water Gasification of Sewage Sludge: Effect of Alkaline Additives. *Fuel Process. Technol.* **2023**, *245*, 107727. [[CrossRef](#)]
75. Weijin, G.; Zizheng, Z.; Yue, L.; Qingyu, W.; Lina, G. Hydrogen Production and Phosphorus Recovery via Supercritical Water Gasification of Sewage Sludge in a Batch Reactor. *Waste Manag.* **2019**, *96*, 198–205. [[CrossRef](#)]
76. Hantoko, D.; Antoni, Kanchanatip, E.; Yan, M.; Weng, Z.; Gao, Z.; Zhong, Y. Assessment of Sewage Sludge Gasification in Supercritical Water for H₂-Rich Syngas Production. *Process Saf. Environ. Prot.* **2019**, *131*, 63–72. [[CrossRef](#)]
77. Xin, C.; Zhao, J.; Ruan, R.; Addy, M.M.; Liu, S.; Mu, D. Economical Feasibility of Bio-Oil Production from Sewage Sludge through Pyrolysis. *Therm. Sci.* **2018**, *22*, 459–467. [[CrossRef](#)]
78. Faragò, M.; Damgaard, A.; Logar, I.; Rygaard, M. Life Cycle Assessment and Cost-Benefit Analysis of Technologies in Water Resource Recovery Facilities: The Case of Sludge Pyrolysis. *Environ. Sci. Technol.* **2022**, *56*, 17988–17997. [[CrossRef](#)]
79. Farru, G.; Scheufele, F.B.; Paniagua, D.M.; Keller, F.; Jeong, C.; Basso, D. Business and Market Analysis of Hydrothermal Carbonization Process: Roadmap toward Implementation. *Agronomy* **2024**, *14*, 541. [[CrossRef](#)]
80. He, C.; Chen, C.L.; Giannis, A.; Yang, Y.; Wang, J.Y. Hydrothermal Gasification of Sewage Sludge and Model Compounds for Renewable Hydrogen Production: A Review. *Renew. Sustain. Energy Rev.* **2014**, *39*, 1127–1142. [[CrossRef](#)]
81. Zhao, Y.; Yang, Z.; Niu, J.; Du, Z.; Federica, C.; Zhu, Z.; Yang, K.; Li, Y.; Zhao, B.; Pedersen, T.H.; et al. Systematical Analysis of Sludge Treatment and Disposal Technologies for Carbon Footprint Reduction. *J. Environ. Sci.* **2023**, *128*, 224–249. [[CrossRef](#)]
82. Schnell, M.; Horst, T.; Quicker, P. Thermal Treatment of Sewage Sludge in Germany: A Review. *J. Environ. Manag.* **2020**, *263*, 110367. [[CrossRef](#)]
83. Li, B.; Wang, F.; Chi, Y.; Yan, J.H. Adhesion and Cohesion Characteristics of Sewage Sludge During Drying. *Dry. Technol.* **2014**, *32*, 1598–1607. [[CrossRef](#)]
84. Hamawand, I.; Da Silva, W.P.; Eberhard, F.; Antille, D.L. Issues Related to Waste Sewage Sludge Drying under Superheated Steam. *Polish J. Chem. Technol.* **2015**, *17*, 5–14. [[CrossRef](#)]
85. Deng, W.; Su, Y. Experimental Study on Agitated Drying Characteristics of Sewage Sludge under the Effects of Different Additive Agents. *J. Environ. Sci.* **2014**, *26*, 1523–1529. [[CrossRef](#)] [[PubMed](#)]
86. Sukhorukov, D.A.; Kukushkin, R.G.; Alekseeva (Bykova), M.V.; Bulavchenko, O.A.; Zaikina, O.O.; Revyakin, M.E.; Kazakov, M.O.; Yakovlev, V.A. Upgrading of Sewage Sludge-Derived Pyrolysis Oil via Hydrotreatment over NiMo-Based Catalysts. *Fuel* **2024**, *359*, 130383. [[CrossRef](#)]
87. Sadooghi, P.; Rauch, R. Mathematical Modeling of Sulfur Deactivation Effects on Steam Reforming of Producer Gas Produced by Biomass Gasification. *Fuel Process. Technol.* **2013**, *110*, 46–52. [[CrossRef](#)]
88. Cordero-Lanzac, T.; Palos, R.; Hita, I.; Arandes, J.M.; Rodríguez-Mirasol, J.; Cordero, T.; Bilbao, J.; Castaño, P. Revealing the Pathways of Catalyst Deactivation by Coke during the Hydrodeoxygenation of Raw Bio-Oil. *Appl. Catal. B Environ.* **2018**, *239*, 513–524. [[CrossRef](#)]
89. Winchell, L.J.; Ross, J.J.; Brose, D.A.; Pluth, T.B.; Fonoll, X.; Norton, J.W.; Bell, K.Y. Pyrolysis and Gasification at Water Resource Recovery Facilities: Status of the Industry. *Water Environ. Res.* **2022**, *94*, e10701. [[CrossRef](#)]
90. Wang, L.; Chang, Y.; Li, A. Hydrothermal Carbonization for Energy-Efficient Processing of Sewage Sludge: A Review. *Renew. Sustain. Energy Rev.* **2019**, *108*, 423–440. [[CrossRef](#)]
91. Tasca, A.L.; Puccini, M.; Gori, R.; Corsi, I.; Galletti, A.M.R.; Vitolo, S. Hydrothermal Carbonization of Sewage Sludge: A Critical Analysis of Process Severity, Hydrochar Properties and Environmental Implications. *Waste Manag.* **2019**, *93*, 1–13. [[CrossRef](#)]
92. Nguyen, T.A.H.; Bui, T.H.; Guo, W.S.; Ngo, H.H. Valorization of the Aqueous Phase from Hydrothermal Carbonization of Different Feedstocks: Challenges and Perspectives. *Chem. Eng. J.* **2023**, *472*, 144802. [[CrossRef](#)]
93. Liu, H.; Basar, I.A.; Nzihou, A.; Eskicioglu, C. Hydrochar Derived from Municipal Sludge through Hydrothermal Processing: A Critical Review on Its Formation, Characterization, and Valorization. *Water Res.* **2021**, *199*, 117186. [[CrossRef](#)] [[PubMed](#)]
94. Wang, Q.; Liu, X.; Jung, H.; Zhao, S.; Pavlostathis, S.G.; Tang, Y. Effect of Prestage Hydrothermal Treatment on the Formation of Struvite vs Vivianite during Semicontinuous Anaerobic Digestion of Sewage Sludge. *ACS Sustain. Chem. Eng.* **2021**, *9*, 9093–9105. [[CrossRef](#)]
95. Watson, J.; Wang, T.; Si, B.; Chen, W.T.; Aierzhati, A.; Zhang, Y. Valorization of Hydrothermal Liquefaction Aqueous Phase: Pathways towards Commercial Viability. *Prog. Energy Combust. Sci.* **2020**, *77*, 100819. [[CrossRef](#)]
96. Abeyratne, W.M.L.K.; Bayat, H.; Delanka-Pedige, H.M.K.; Zhang, Y.; Brewer, C.E.; Nirmalakhandan, N. Multi-Criteria Evaluation of Energy Recovery from Urban Wastewater Sludges by Anaerobic Digestion and Hydrothermal Liquefaction. *J. Environ. Chem. Eng.* **2023**, *11*, 109628. [[CrossRef](#)]
97. Kritzer, P. Corrosion in High-Temperature and Supercritical Water and Aqueous Solutions: A Review. *J. Supercrit. Fluids* **2004**, *29*, 1–29. [[CrossRef](#)]
98. Wang, C.; Zhu, W.; Chen, C.; Zhang, H.; Lin, N.; Su, Y. Influence of Reaction Conditions on the Catalytic Activity of a Nickel during the Supercritical Water Gasification of Dewatered Sewage Sludge. *J. Supercrit. Fluids* **2018**, *140*, 356–363. [[CrossRef](#)]

99. Lee, I.G.; Ihm, S.K. Catalytic Gasification of Glucose over Ni/Activated Charcoal in Supercritical Water. *Ind. Eng. Chem. Res.* **2009**, *48*, 1435–1442. [[CrossRef](#)]
100. Sinač, A.; Kruse, A.; Rathert, J. Influence of the Heating Rate and the Type of Catalyst on the Formation of Key Intermediates and on the Generation of Gases during Hydrolysis of Glucose in Supercritical Water in a Batch Reactor. *Ind. Eng. Chem. Res.* **2004**, *43*, 502–508. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.