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Hydrothermal carbonization of sewage sludge and biofuels as a sustainable energy source

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ABSTRACT

Sewage sludge is nowadays a permanent, renewable element of our lives. One promising and up-to-date idea is to turn these wastes into energy fuels. Research into the utilisation of a wide range of organic wastes to produce renewable and valuable products such as biofuels, fertilisers or absorbents has led to the strengthening of the potential of a low temperature thermochemical method commonly referred to as hydrothermal carbonisation (HTC). Recently, special attention has been given to the possibility of applying the HTC process in the context of sewage sludge (SS) utilisation - a problematic waste generated on a massive scale in many countries around the world. While many scientific articles suggest the use of HTC products in agriculture, this review focuses on the energy application of HTC products in the context of replacing solid fuels, with lignite and liquid fuels as potential co-substrates in an anaerobic co-digestion process in a biogas plant (AD), due to the positive life cycle assessment (LCA) of the environmental efficiency of the integrated HTC+AD sludge management system. There is also a real threat from heat-resistant contaminants remaining in HTC products, the use of which in agriculture may involve the risk of legislative changes regarding their future use in this sector. HTC is a very promising technology, however, a potential barrier to the implementation of this type of technology, despite the technical solutions available, may be both the lack of authoritative data on long-term economic and environmental benefits and the legal restrictions associated with the further use of the products. In addition, incomplete knowledge in the field of subcritical water effects on the complex and irregular structure of SS may not provide a guarantee for the appropriate application of this method. This article attempts to systematise the information, insights and research deficiencies related to the HTC process of various forms of sludge towards the energetic possibilities of using the products obtained.

INTRODUCTION

The sequence of wastewater treatment processes, both mechanical and biological, results in different types of waste and treated wastewater. The solid fractions after mechanical pre-treatment can be gravels, sands, or screenings - containing a mixture of food waste, plastics, textiles, paper, etc. [1,2]. Subsequently, depending on the pre-settlement tanks used in the mechanical part of the treatment plant, raw sludge (RS) is produced, while the following biological processes result in the formation of highly hydrated, suspended microorganisms in the form of flocs called activated sludge (AS). While treated wastewater discharged into

flowing waters, strictly regulated, does not pose a major challenge to wastewater treatment plant (WWTP) facilities, wastes such as sands, screenings and in particular the huge SS quantities generated require a further independent disposal route, due to limited landfill capacity or implemented legal regulations prohibiting on-site storage of SS, especially in EU countries [3,4].

Long-term implementation of the strategy under the directive 91/271/EEC to increase the total volume of treated wastewater contributes to a continuous increase in the volume of sewage sludge (SS), successively creating disproportions between its production and the real demand for agricultural, reclamation or thermal use. In addition, the problematic properties of sludge [tab 1] and thus restrictive regulations related to its further management, the constantly increasing prices of external disposal services [5] as well as controversial socio-ecological aspects regarding uncontrolled amounts of emerging contaminants (EC) - pharmaceuticals, steroids, WWA etc. [6,7,8] pose serious challenges to many WWTP recipients around the world. Thus, the idea of expanding the sludge management system directly at the WWTP could significantly reduce the cost of sewage sludge disposal, which often accounts for up to 50% of total financial expenditure, as well as reducing the problems associated with its further management [9,10]. A prime example of this is the implementation of a biogas plant coupled with a cogeneration system (CHP), which, in addition to significantly reducing the organic matter of the SS through anaerobic digestion (AD), allows for the recovery of valuable energy from the biogas produced, thereby reducing the ongoing operating costs of the wastewater treatment plant [11,12,13]. Furthermore, anaerobic digestion reduces a certain group of pathogens and, depending on temperature, stabilises residual sludge called anaerobically digested sludge (ADS), which is the current recommended practice especially for the management of this waste in agriculture. Therefore, the implementation of this method is cost-effective in terms of the further costs of external disposal of ADS [14,15,16], despite the benefits of using ADS as fertilizers to improve soil porosity and water-holding capacity, as well as to supply organic matter (humic acids), macronutrients such as phosphorus, nitrogen, calcium, potassium, and other microelements [17,18,19,20]. Several articles have reported contribution of the above-mentioned EC and heavy metals cause undesired toxic effects, endangering the health and life of living organisms [10,21,22]. Therefore, in many countries around the world, one can observe a gradual abandonment of the use of sewage sludge in agriculture or increasing restrictions and supervision by the relevant environmental institutions [23].

Implementation of thermal methods of sludge reduction can be considered in combination with biological methods to maximise sludge reduction and minimise the operating costs of sludge management, where an unacceptable sludge composition is systematically obtained that limits its agricultural perspective. Construction of dryers at larger WWTPs can significantly reduce a high moisture content from ADS or SS from 80 % to about 10 % moisture content [24,25]. However, depending on the technology used, the operation of the dryer may be subject to climatic conditions and seasons, requiring relatively long drying times and higher temperatures, and thus additional energy requirements, even when using waste heat from cogeneration systems of biogas plants [26,27]. In addition, factors such as the susceptibility to spontaneous combustion of dried sludge, which should be stored under special conditions and subject to additional safeguards, should also be considered [28]. In contrast, the use of high-temperature methods after the drying process, such as incinerators, can only be economically justified if certain levels of profitability are exceeded, depending on the size of the WWTP [29].

Thus, a much more frequently used method of sewage sludge management from smaller treatment plants is its external disposal in the process of co-combustion with coal or to produce cement in cement plants. However, attention must be paid to the broad fuel properties of biomass. A low calorific and bulk value can determine low process efficiency, while higher ash and alkali content exacerbates slagging processes and thus causes boiler clogging, poor heat transfer and increased plant corrosion. In addition, these are just a few of the factors that require upgrades to power boilers or the additional costs of transporting, storing, and preparing diverse biomass. Furthermore, the need to maintain a low ratio of sludge in the fuel mix in order to compensate for the loss of boiler efficiency [30] and to meet emission standards during co-incineration is the best example of the disproportion between the continuous growth of sludge generated and its real possibility to be used in thermal processes [31].

Thermochemical processes have been widely considered methods of SS utilisation for a long time. Systems based on dry pyrolysis i.e., thermolysis at temperatures of about 200 - 1000°C [32,33,34,35] and moderate pressure under no-oxygen conditions, or gasification in a controlled oxidising agent at about 700 °C – 1200 [36,37] can be an alternative to combustion processes, although they also have their drawbacks [38]. The undoubted advantages of these processes are lower toxic emissions (compared to incineration) and the ability to convert SS into valuable solid, liquid, and gaseous products [39] [40] [41]. In the case of gasification, chars are produced, but primarily high-energy synthesis gases with high energy recovery potential [42]. However, the required pre-drying process, high investment costs, as well as the production of an operationally problematic by-product - tar - may be a barrier to the implementation of this type of solution at WWTP [60]. Depending on operating conditions, sludge pyrolysis can produce bio-oils, pyrolysis gases and solid waste called biochars with properties that allow reuse in the energy industry, metallurgy, pharmaceuticals, and even as effective adsorbent materials for removing problematic antibiotics and other micropollutants from wastewater [43,44]. While pyrolysis gases could be treated and burned in compact systems to recover some of the thermal energy, bio-oils, (considered attractive fuels), have limited potential for reuse in the WWTP and would require further management strategies [35,45]. For this reason, special attention has been given to low-temperature (200-300°C) endothermic slow sludge pyrolysis processes (called torrefaction or high-temperature drying), which improve the yield and quality of biochars, at the expense of other by-products, [35,37,**Error! Bookmark not defined.**]. The carbonates produced, with improved fuel properties, could be successfully used in downstream thermal processes, i.e. gasification, or as a pre-treatment in downstream pyrolysis processes to reduce NO_x, SO [46]. Nevertheless, the overall life-cycle environmental impact of pyrolysis, among the various SS disposal alternatives, has been assessed negatively primarily in terms of resource depletion, including the natural gas used to dry the wet sludge [34,19]. In order for the process to be completely autothermal, energy use of all products on site would be required, and thus additional capital expenditures, such as for gasification facilities [47]. However, there are technical solutions, e.g. at pilot scale [48], that enable direct processing of wet waste with simultaneous efficient energy recovery under slow pyrolysis conditions, nevertheless such solutions would have to be tested at industrial scale for sewage sludge.

Relatively recently, systems based on low-thermal conversion of SS (140-250°C) in an aqueous environment under increased pressure (6-100 bar) called thermal hydrolysis (HT) or hydrothermal carbonization (HTC) have been implemented [49,50,51]. Such solutions are considered promising because they do not require energy-intensive drying processes, using

sludge moisture to initiate the degradation of resistant components of the SS matrix, e.g. before further biological treatment - to intensify biogas production / or after AD treatment, to reduce and sterilize the final volume of solid mass [52,51]. The implementation of HT + AD systems can be seen in wastewater treatment plants in many European countries such as Poland, Ireland, Norway, etc. However, low heat recovery temperatures and thus additional operating costs may not compensate for the disposal costs of the resulting solid waste, which still has a high moisture content. Such systems require further development strategies or consideration of additional HT modules after HT+AD, which in turn could valorise solid products and increase its final dewatering [52]. In this case, the use of the HTC process seems to be a promising alternative, due to the possibility of obtaining value-added products and energy recovery at higher temperatures of hydrothermal processes. HTC solid products are characterized by better stabilization and sanitary properties [51], as well as a lower amount of organic impurities [53], increased concentration of carbon in the structure and hydrophobic properties that affect the final dewatering even up to 70% of dry matter [54]. In addition, these systems can guarantee energy savings, thanks to the recirculation of chemical energy obtained during the process at individual stages. Moreover, they can use coupled processes of wet air oxidation (WO) of hot HTC liquids in order to partially reduce high organic pollutants (COD) [55], while the heat generated as a result of these exothermic reactions can be successfully used to operate the HTC reactor in autothermal mode [56,57]. Interestingly, it is HTC liquids as the main by-products that show attractive possibilities of their reuse for WWTP's own needs due to the concentrations of such components as TOC mg/l or VFA mg/l. According to recent reports C.I. Aragón-Briceño, show potential in the processes of anaerobic co-digestion with SS in order to intensify the production of biogas (additional energy recovery) and can be a source of carbon in denitrification processes in biological reactors, and thus support the reduction of total nitrogen in treated wastewater [58]. Nevertheless, HTC processes require additional electric energy input, therefore the implementation of these solutions should be considered individually, depending on the size and capabilities of WWTPs.

While many research articles suggest the use of HTC products in agriculture, this review focuses attention on the energetic applications of HTC products in the context of solid fuels replacing lignite and liquid fuels as potential co-substrates in the anaerobic co-digestion process in biogas plant (AD), due to the positive life cycle assessment (LCA) of the environmental performance of the HTC+AD integrated sludge management system [59], but also because of the real threat from thermo-resistant contaminants remaining in HTC products, whose use in agriculture may imply a risk of changes in legislation regarding their future use in this sector.

[Tab1.] Physico-chemical and microbiological properties of different types of sludge

TYPES OD SLUDGE				
Physico-chemical properties	Raw sludge (RS)/ primary sludge (PS)	Activated sludge (AS)	Sewage sludge (SS)	Anaerobic digested sludge (ADS)
Total dry solids (%TS)	2,0 – 9,0 [60,61] 2,4 - 23,6 [62]	0,8 – 1,2 [60,49] 2,6 - 26,5 [50]	0,83 - 12,0 [63]	6 - 12[49] 2 - 5 [64] 2,5 - 30[50]
TS (% of TS)	60 – 80,5 [48,49,31]	35,35±0,79 [65]	21,0 [66]	30-60 [64]

Protein (% of TS)	20 – 30 [60,6260,67]	33 – 41 [60,61] 15,2 - 19,6 [50] 32,0 - 41,0 [67]	15,0 - 41,0 [63]	15 - 20 [61] 15 - 34,1 [62] 5,0 - 20,0 [67]
Cellulose (% of TS)	8 - 15 [62,67]	7,0 - 7,9 [67]	n.d	8 - 15 [64,67]
Lignin (% TS)	26 [62]	0,14 - 4,4 [62]	n.d	1,8 - 10,0 [62]
Grease and fats (% of TS)	7,0 - 65,0 [67]	5,0 - 12,0 [67]	n.d	
Lipids (% TS)	7 - 35 [62]	5,6 - 8,3 [62]	n.d	6,3 - 23,3 [62]
Humic substances (% TS)	8 - 14 [62]	3,8 - 23,9 [62]	n.d	11 - 19 [62]
TN (g/L)	2,99±0,10 [68] 4,2 [69]	1,523 [65]	n.d	n.d
NH ₄ ⁺ -N (g/L)	0,17±0,00 [68]	0,019 [65]	n.d	n.d
TP (g/L)	1,73±0,06 [68]	0,938 [65]	n.d	n.d
PO ₄ ³⁻ -P (g/L)	0,04±0,00 [68]	0,096 [65]	n.d	n.d
pH	6,41 [68] 7,8±0,01 [70] 6,3 [69] 5 - 7,4 [62]	5,8 - 8,1 [62] 6,2 [71]	7,07±0,28 [72] 5,83 [73] 5,0-8,0 [63]	6,5-7,5 [64] 6,4-8,5 [62]
HHV (MJ/kg)	23 - 29 [64] 7,6 - 20,9 [62]	19,1 - 22,3 [74] 13,09±0,10 [75] 1,1 - 18,1 [62]	10,2±0,45 [72] 21,21 [76]	14,9 [77] 6,3 - 20,0 [62]
Inorganic contaminants				
Heavy metals mg/kg DM ppm, db mg/L				
Cu	706,5±6,5 [70] 246-500 [62]	149 [78] 117-6329 [62]	2,6-131,2 [78] 388,69 [76]	204-337 [64] 130-1175 [62]
Zn	1645,5±26,2 [70] 303-1322 [62]	548 [78] 325-4306 [62]	28-2436 [78] 848,77 [76]	487-871 [64] 100-1258 [62]
Pb	BDL [70] 34-62,9 [62]	18 [78] 36-830 [62]	0,4-194,0 [78] 28,86 [76]	58-167 [64] 0-150,7 [62]
Cd	BDL [70] 0,8-1,9 [62]	0,6 [78] 0,5-7 [62]	0,08-16 [78] 0,77 [76]	1-18 [64] 0,9-48,3 [62]
Ni	582,0±19,3 [70] 0,02-32,11 [62]	26,4 [78] 28-119 [62]	0,4-25 [78] 48,07 [76]	17-29 [64] 16-2078 [62]
Cr	1353,5±24,8 [70] 1,93-82,3 [62]	27,6 [78] 22-739 [62]	2,8-2855 [78] 75,45 [76]	38-3800 [64] 19-150,7 [62]
Ash content (wt%)	28,7 [69]	13,7 [74]	51,9±0,41 [72] 17,5 [76]	41,5 [79] 40,9 [77]
C content (wt%)	19,4-47,8 [62]	7,6-44,4 [62]	18,87 [73]	31,5 [79] 32,7 [77] 17,1 - 46,1 [62]
H content (wt%)	3,2-7,0 [62]	2,3-6,2 [62]	3,45 [73]	4,3 [79] 4,9 [77] 2,3-6,6 [62]
N content (wt%)	1,9-8,3 [62]	0,37-7,9 [62]	3,18 [73]	4,8 [79] 5,1 [77] 0,3-9,6 [62]

S content (wt%)	0,37-1,68 [62]	0,69-2,85 [62]	n.d	1,7 [79] 1,0 [77] 0-6,78 [62]
P content (wt%)	0,69-3,5 [62]	1,02-4,1 [62]	1,36 [73]	0,17-7,9 [62w]
Organic contaminants				
tCOD (mgCOD/L)	19100±800 [80]	43,877 [71]		
PAH (µg/kg)	n.d	0,009-6,00 [67]	1,4-169 [81]	0,009-6,00 [67]
PCBs	n.d	n.d	65,5-157 [81]	n.d
AOX (mg/kg dm)	n.d	n.d	167 [63]	n.d
Microplastic (mg/kg)	n.d	n.d	22,0-53,0 [82]	n.d
Microbiological contaminants				
Salmonella (MPN g-dw ⁻¹)	1,35x104±2,08x103 [83]		7,9x102 [81]	
Bacteria (gene/ml)	n.d	103-108 [67]	n.d	103-108 [67]
Eggs of parasitic helminths (eggs/g)	n.d	0-2910 [67]	n.d	0-2910 [67]
Fungi (cfu/ml)	n.d	108 [67]	n.d	108 [67]
Viruses (cfu/l)	n.d	103-105 [67]	n.d	103-105 [67]

CHARACTERISTICS OF HYDROTHERMAL PROCESS - VARIABLE PHYSICO-CHEMICAL PROPERTIES OF THE REACTION MEDIUM

The use of hydrothermal methods in the context of SS disposal is based on the conversion of these wet organic wastes into value-added materials in an aqueous environment with moderate temperatures and autogenic pressure generated in a closed system. This system aims to change the reaction environment by altering the physico-chemical properties of water (moisture) in sludge under sub-critical conditions. The products of a thermochemical reaction lasting several minutes/hours are hydrochars, i.e., solid waste, hydrothermal fluid also called process liquid, and various types of gases [84, **Error! Bookmark not defined.**]. The range of temperatures and pressures characterises the specific hydrothermal conversion method (HT) (tab 2) in which we distinguish thermal hydrolysis process (THP), hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) [85,86]. The fundamental difference between these processes is the composition and amount of the products obtained, since the physico-chemical properties of the reaction medium (tab 2) and thus the degree of degradation of materials immersed in the medium, strongly depend on two state parameters - hydrothermal temperature and pressure [Fig. 1]. The reaction products of THP and HTC are mainly hydrochars, HTL generates mostly a water-oil phase with high organic carbon content and insoluble organic matter called biocrude while the products of supercritical water gasification HTG are mainly gases rich in H₂, CH₄ and residual CO₂ and CO [87]. In this section the influence of temperature as a fundamental modifier of the hydrothermal processes of selected physicochemical properties of water are discussed: dielectric constant, ionic

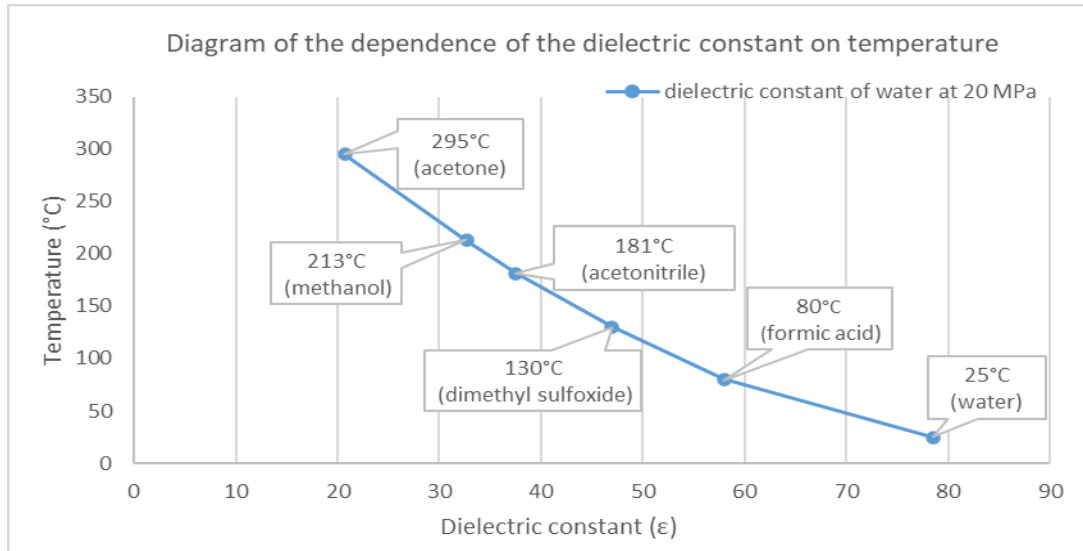
product, density, surface tension and diffusion coefficient. These parameters are the starting point for further analysis and interpretation of mechanisms of transformation of SS components into HT products.

[Tab 2.] Characteristic of various hydrothermal methods

Methods	Temperature [°C]	Pressure [bar]	Process conditions	Main products	By - products	Literature
Thermal hydrolysis process (THP)	140 - 170	6 - 9	Subcritical	Hydrochar	Aqueous phase, bio-crude, gas (mainly CO ₂)	(Ngo <i>et al.</i> , 2021)
Hydrothermal carbonization (HTC)	180 - 250	10 - 100	Subcritical	Hydrochar	Aqueous phase, bio-crude, gas (mainly CO ₂)	(Kim, Lee and Park, 2014a; Liu <i>et al.</i> , 2021)
Hydrothermal liquefaction – (HTL)	250 – 380	100 - 200	Subcritical/ Supercritical	Bio-crude	Aqueous phase hydrochars, gas (mainly CO ₂)	(Liu <i>et al.</i> , 2021)
Hydrothermal gasification (HTG)	> 380	>200	Supercritical	Syngas (rich in H ₂ or CH ₄)	Aqueous phase, bio-crude, hydrochar	(Liu <i>et al.</i> , 2021; Lachos-Perez <i>et al.</i> , 2022)

- **Dielectric constant – measure of the polarity and dissolution of compounds**

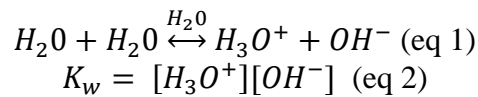
Water under subcritical (SW) conditions can be both a polar and semipolar solvent (alcohols, ketones), while under supercritical conditions it can be a non-polar solvent (benzene), simultaneously acting as a reactant and catalyst for chemical reactions. Carr *et al.* [88] described subcritical water as a solvent for hydrophobic organic compounds (for example, glycerol, fatty acids, and amino acids), from which the fundamental importance of the behaviour of hydrogen bonds under thermodynamic conditions emerged. With increasing water temperature, a decrease in the strength of these bonds and a decrease in the value of the dielectric constant, which is a measure of the polarity of a substance and solvent that determines the degree of dissociation of compounds with ionic bonds, were observed [89]. As explained by the researchers [90] the weakening of the nature of hydrogen bonds, due to temperature changes, favours London dispersion forces, showing only temporary dipole moments in molecules, due to the deformation of electron clouds. It is worth noting that such bonds occur between all atoms and molecules that approach each other and are the least stable. A similar result of weakening of bonds was also observed in the case of other intermolecular interactions: van der Waals or dipole-dipole interactions [91]. Thus, water under normal conditions has a relatively high dielectric constant value, which is a fundamental property of a solvent, and its polarity is responsible for the dissolution of ionic and other polar compounds, in contrast to non-polar (apolar) solvents with a low dielectric constant value. Thus, the key point seems to be that, once certain temperature thresholds are exceeded (*fig.1*) under hydrothermal conditions, water becomes similar to polar organic solvents, among others, enabling the dissolution of hitherto insoluble organic compounds forming the sludge matrix, and then the hydrothermal temperature can imply the first step of HTC hereafter referred to as hydrolysis [92].



[Figure 1]- Diagram of dependence of dielectric constant on temperature (based on Özel, M.Z.et al.[91])

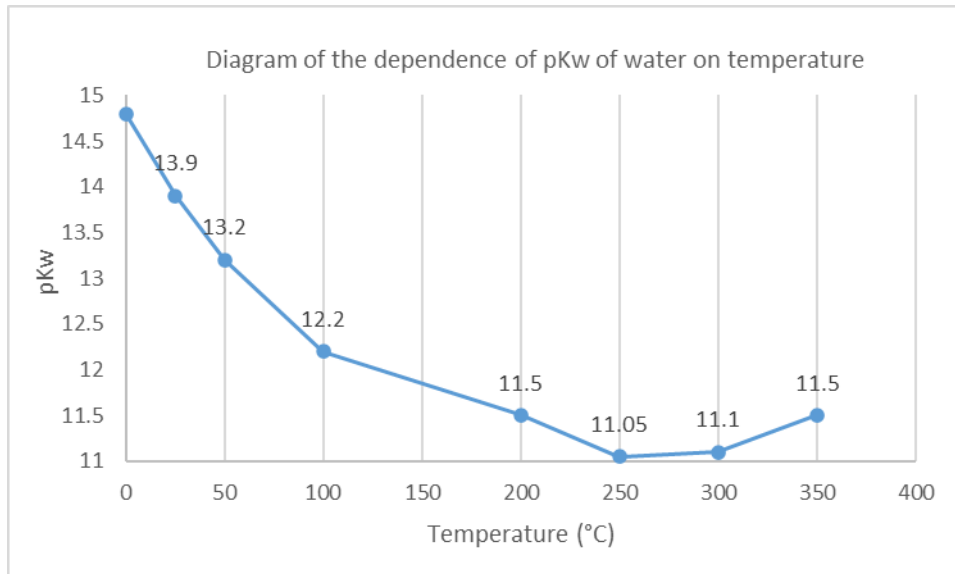
- **Ion product water K_w and Ionic product pK_w**

Another important parameter, dependent on external factors, is the ionic product of water K_w , which can be one of the initiators of hydrothermal reactions. The reaction of two water molecules produces an oxonium ion with a positive charge and a hydroxide anion. The process of auto dissociation, also known as (self-ionisation) of water, is shown in equation 1 [89]. Due to the small degree of dissociation, the concentration of water molecules at equilibrium is practically the same as the concentration before the dissociation reaction, so that when writing down the equilibrium constant, the form of undissociated molecules can be ignored and the equation can be presented as equation 2.



The value of the ionic product of water is closely related to temperature. At 293 K, the K_w of water is 1×10^{-14} and forms the basis of the logarithmic scale of pH (eq 3). Möller et al. [93] and Okaji Zhenget al. [89] indicate a 1000-fold increase in the ionic product in the temperature range $25^\circ\text{C} - 250/300^\circ\text{C}$ (fig. 2), promoting ionic chemistry under subcritical conditions and inhibiting free radical reactions which are promoted for $K_w < 10^{-14}$ [94]. As a result, there is a successive increase in the concentration values of hydrogen (oxonium) and hydroxide ions responsible for catalysing chemical reactions. On (fig 2), a decrease in the ionic product pK_w of the water is simultaneously observed, with the pH value starting to change from a value of 7 to around 5.5 over the temperature range shown [90]. In this way, hydrothermal water behaves as if acid catalysts were added to initiate the first degradation step - hydrolysis. Additionally, Wang et al. [Error! Bookmark not defined.] present the possibility that a limited amount of water, usually in the form of sediment moisture, may be retained as a reactant or product affecting hydrogen exchange or further chemical reaction steps such as condensation. So, the further fate of the behaviour of the sludge matrix in the aqueous environment will depend on the temperature in the superheated water and the composition of the SS matrix. The process may proceed towards the degradation of the macromolecular substance due to initiated hydrolysis and formation of new chemical compounds, or towards the complete dissolution of the matrix component in question, retaining the properties of the neutral extract, minimising the degradation of the desired analyte [90,91].

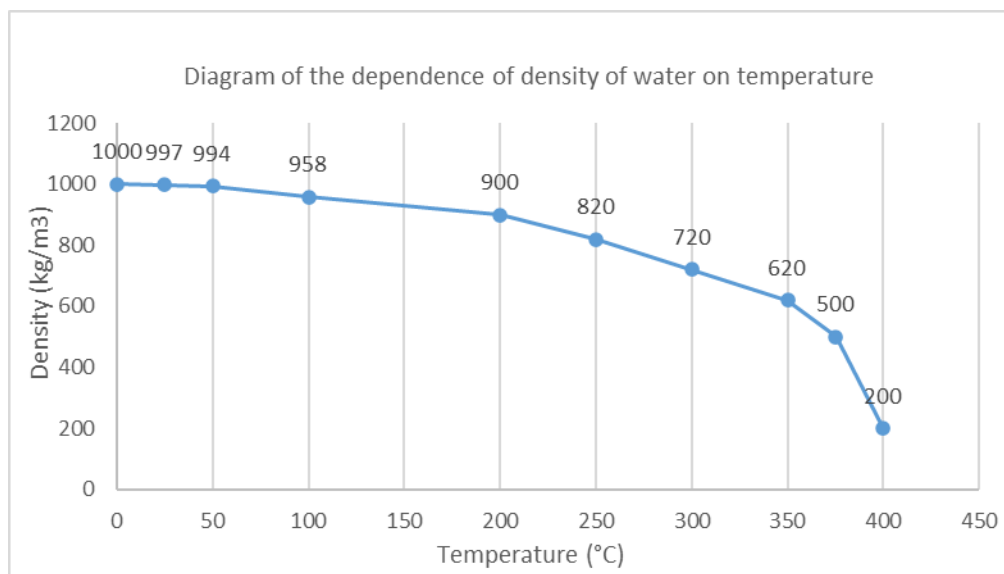
$$\text{pH} + \text{pOH} = \text{pK}_w = -\log_{10}K_w \quad (\text{eq3})$$



[Figure 2] – Dependence of pK_w on temperature (based on Wang et al [Error! Bookmark not defined].)

- **Density**

The increase in liquid temperature under hydrothermal conditions contributes to the breaking and alteration of hydrogen bonding networks, resulting in a rapid decrease in viscosity, but a relatively slow decrease in liquid density [95]. The decrease in density appears to favour free-radical reactions, which in turn significantly affect the reaction pathways and thus the degradation and decomposition of SS components. Nevertheless, the environment for these reactions is possible at temperatures of 300 - 450 °C, as there is a rapid decrease in water density in this range. Thus, high water density (relatively low hydrothermal temperatures) favours an ionic reaction chemistry that is mainly temperature dependent and characterises the conditions under which the main hydrochar products are obtained, while low water density is a feature of supercritical conditions where both temperature and pressure affect the conversion efficiency of the more resistant fraction of components, consequently enriching the bioconcentrate or gas fraction at the expense of solid product yields [96,97].



[Figure 3] – Dependence of density on temperature (based on Wang et al [Error! Bookmark not defined.])

- Mass transfer properties - diffusion, surface tension

From the point of view of water as extract, catalyst, and reactant, it is important to consider the kinetics of mass transfer by diffusion, which affects the extraction efficiency and the rate of chemical reactions. In order to elucidate the mass transfer phenomenon, a model of the behaviour of a single component trapped in an organic matrix and its interaction with the environment under subcritical conditions was considered. In the first phase, the wetting of the matrix immersed in the subcritical fluid was considered. The surface tension is responsible for this phenomenon, the decrease of which favours the increase of the phase contact area, ensuring a more effective penetration of the particles [90]. The parallel desorption of the substance, occurring due to changes in intermolecular interactions in the organic matrix, and the diffusion of SW towards the surface and within its pores initiates the solubility of the substance. The last step involves the increase of the concentration of the component in the liquid phase and its escape from the solid phase [91]. The increase in the diffusion coefficient D , responsible for the propagation of momentum in the fluid may be interpreted and expressed by the Stokes-Einstein equation. According to it, the diffusion process of large spherical particles (eq. 4) will mainly depend on the dynamic viscosity of the solvent, closely related to the temperature of the process, and indirectly responsible for the rate of matter transfer in the reaction medium [90]. Despite favourable mass transport conditions with regard to improved liquid properties, Möller et al [93] point out the possibility of so-called "water clusters" - molecules forming uniform clusters, caused by disordered hydrogen bonds, as in the case of water under normal conditions. Such systems may contribute to local concentration imbalances between the concentrations of the reactants and the average concentrations in solution, and consequently adversely affect mass diffusion and the local increase in the rate of chemical reactions. Therefore, the use of even heating and mixing during HTC processes seems essential and has a key impact on carbonisation time and efficiency.

$$D = \frac{k_b T}{6\pi\mu r}, \text{ where } \mu(T) = 2,414 \cdot 10^{-5} \cdot 10^{\frac{247,8}{T-140}} \text{ (eq 4)}$$

The modified physico-chemical properties of water have an indisputable influence on the initiation of the decomposition of the SS matrix components as they primarily affect their solubility in superheated water, the enhanced hydrolysis, the nature of compound decomposition, the interaction and ultimately the timing and quality of the hydrothermal carbonisation process.

MECHANISMS AND CHEMICAL REACTIONS OF INDIVIDUAL SLUDGE MAIN COMPONENTS DURING HTC

Converting complex structures of the sludge into hydrochars, liquids and gas is the result of consecutive and parallel path reactions such as hydrolysis, decarboxylation, dehydration, condensation, polymerization, aromatization, and special reactions characteristic of defined components – deamination or even Maillard reaction. Its combinations and duration depend on feedstock and major determinants of process: temperature, SS/water ratio, resident time, pH, concentration of specific ingredients as well as its interactions, finally affecting product performance and quality [98]. In addition, each path of chemical conversion compounds has its own kinetics of reaction and may influence other kinetics [99]. Knowledge of HTC chemical reactions and mechanisms based on the structure of quantitative models have a key impact on mass-energy balance and optimization of process conditions, by determining the effect of the composition of the feedstock on its conversion to HTC products.

The previous section presented the role of subcritical water as a specific organic solvent, one which dissolves macrostructure and lowers the activation energies required for the cleavage of chemical bonds in the feedstock, initiating and catalysing the first step of the hydrothermal reaction called hydrolysis [**Error! Bookmark not defined.**,98]. As a result, reactive soluble intermediates accumulate in the aqueous phase, and further reactions towards smaller components or formation of secondary char will depend on how high the process temperature and residence time are [100]. The following reaction is dehydration (intramolecular dehydration), called dewatering, consisting of the elimination of the hydroxyl group from the matrix. With this reaction, the oxygen heteroatom can be removed in the form of H₂O feeding the process liquid during the HTC process [98]. Parallel decarboxylation is a process of the elimination of carboxyl groups, removing CO₂ from the matrix of the SS molecule to liquid as well as gas phase [99,101]. However, significant decarboxylation can only occur after significant dehydration due to higher dehydration rates [102,98].

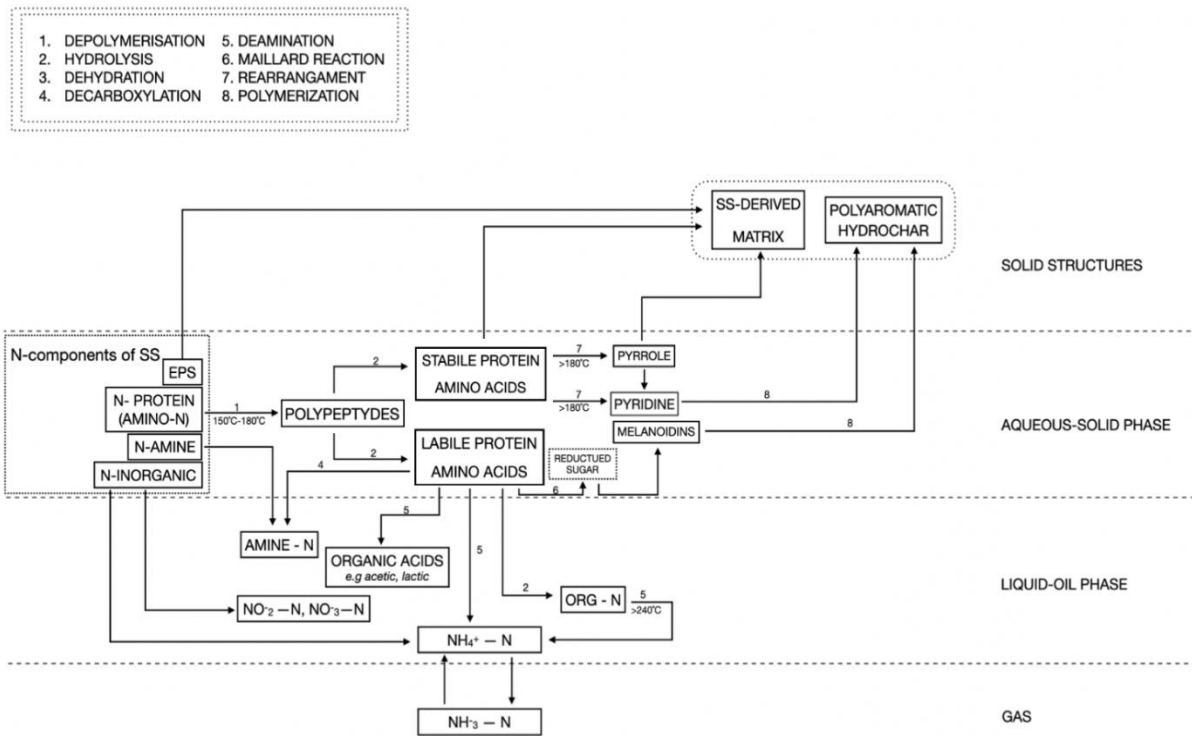
The further formation of hydrochars structure from intermediates is accompanied by polymerisation, condensation, and in certain cases - aromatisation reactions. [103,104] also distinguish the pathway by solid-solid conversion preserving the original structural components and morphology of the SS structure. The initial degradation half-product is called bio-crude, which is a further successive formation into hydrochars for three reported ways: reaction between components in biocrude-biocrude phase, biocrude – non degraded matrix solid, and between solid-solid components [99]. The processes of polymerisation, condensation and aromatisation are the result of the high reactivity of the fragments remaining after the degradation step and are more active under enhanced process conditions (higher temperature and residence time) in contrast to the hydrolysis of SS macromolecules dissolved in liquid, which dominates at lower temperatures [100].

This section will summarise the existing information on the behaviour of individual SS components: proteins, polysaccharides, lignins, lipids, as well as humic substances during the HTC process in the form of reaction mechanisms. In addition, this article also focuses on the results of the latest studies based on the transformation of natural compounds from the SS matrix during HTC, but the experience in this area is still incomplete and remains for further research.

- **PROTEINS**

Huang et al. [105] grouped the nitrogen species in raw sludge obtained: protein-N (78.4%), amine-N (2.7%), inorganic-N (18.9%). In the first stage protein depolymerisation has been observed, creating polypeptides in the aqueous product, and then cleavage of peptide bonds by hydrolysis as well as non-uniform release of amino acids already at temperatures of about 150 - 160°C. Other articles reported an even higher temperature required to initiate the hydrolysis reaction. Nevertheless, Huang et al. [105] has distinguished 16 types of amino acids in SS products. The type of products and the degree of decomposition of amino acids between solid phase and aqueous phase depended on its type of functional groups, such as aromatic/heterocyclic, hydroxyl, alkyl and carboxyl groups and a further increase in temperature enhanced its degradation towards the formation of amines and organic acids (acetic, formic, lactic), NH_4^+ - N (ammonium) in liquid and oil phases by a series of decarboxylation and deamination reactions respectively. In addition, ammonium from protein may be the result of deamination and ring opening reactions of labile amides, but a lot of dissolved NH_4^+ - N in liquid fraction can come from inorganic matter. Zhuang et al. [106] seem to confirm this and, according to them, amino-N consists of a labile and a stable protein differing in the energy required to cleave the peptide-N bonds, with the labile protein hydrolysing to Org-N dissolved in the liquid phase, which is due to deamination forms NH_4^+ - N. This mechanism has been also confirmed in several other literature reviews [**Error! Bookmark not defined.**,100]. Thus, it can be summarised that the decomposition of amino acids follows two pathways, the first of which is decarboxylation generating amines and CO_2 , while the second pathway is deamination generating NH_4^+ - N and organic acids [107].

Nevertheless, not all types of amino acids are degraded, e.g., with an alkyl group, due to their high thermal stability. At this point, it is also worth noting that activated sludge has problematically complex EPS structures – extracellular polymeric substances, consisting of mainly proteins, polysaccharides lipids or humic substances [108] which by a highly hydrated biofilm matrix link microbial cells. Their degradation demands temperatures over 240°C, as a result proteins often remain in the hydrochars, determining low-rate carbonization [109]. On the other hand, the hydrothermal resistance of SS biopolymers may be due to their high molecular weight, resulting in limited hydrolysis reactions. Considering the above information, some proteins are not susceptible to the HTC process causing a high oxygen content in the hydrochars/carbon and a high content of soluble proteins in the aqueous phase [110].



Mechanism 1. Fate of decomposition of nitrogen compounds in model sewage sludge during hydrothermal carbonization (150 – 250°C)

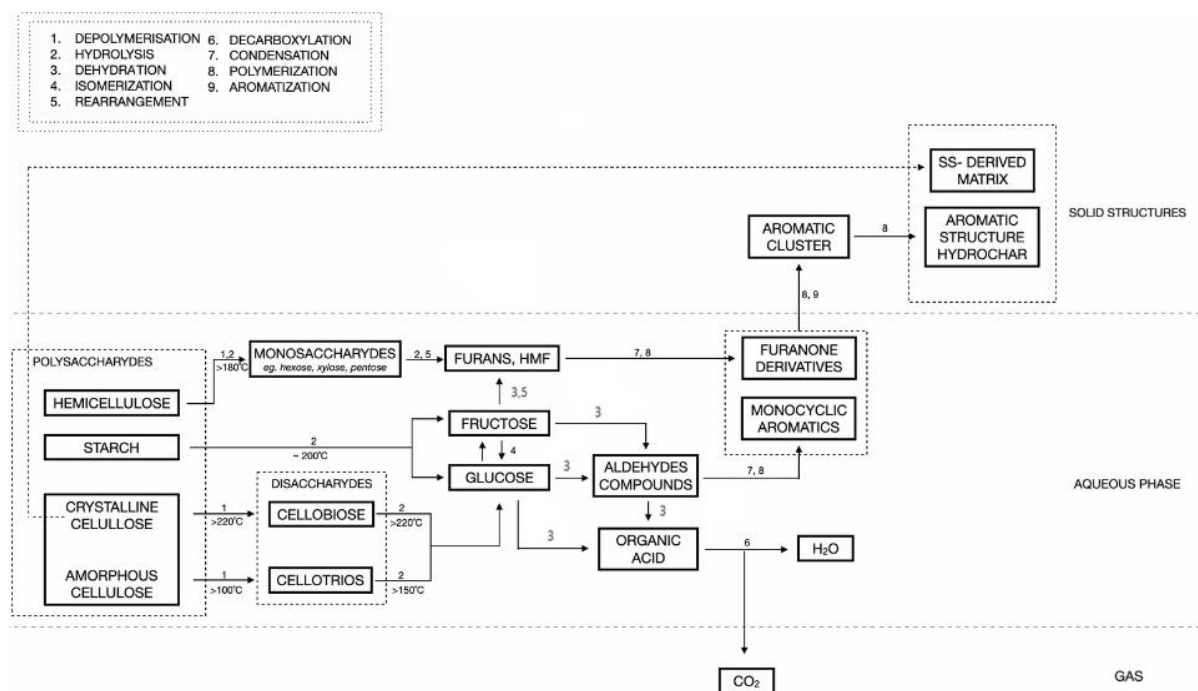
In summary, amino acids can degrade to amines, organic acids, and ammonium (NH_4^+ -N), thus enriching the liquid-oil phase, and the higher the intensity of the reaction the more NH_4^+ -N is formed from proteins, as these components are more susceptible to ammonification [Error! Bookmark not defined.]. At higher temperatures, above 180°C , amino acids during the HTC process are able to self-arrange directly to pyrrole and pyridine, creating monocyclic aromatics or dicyclic aromatics, also polymerization to a polyaromatic structure [100,107]. Moreover, this interaction with other compounds does not remain neutral. Much research has shown interaction occurring between amino acids and monosaccharides forming/generating N—containing heterocyclic compounds during the Maillard reaction, with typical odour, and brown appearance, which are subsequently polymerised to polyaromatic hydrochars structure [103,111]. In turn Wang et al. [112] emphasize that the Maillard reaction occurs between the amino group of an amino acid and the carbonyl group of a sugar to form products generally called melanoidins. The rate of the Maillard reaction is affected by factors such as the types of sugars, the types of proteins and their derivatives, the concentration of the reactants, as well as the temperature, reaction time, and initial pH. [113,114] present the possibility of Maillard reactions between both derivatives' carbohydrates and derivatives' amino acids, but its sequence and complexity turn out to be much more complicated and requires a deeper consideration of reaction pathways. For instance, carbonyl groups of aldehydes (furans, furfurals) during the condensation with groups of amines produce compounds called imines or Schiff bases. After the dehydration process ring closure may generate N-heterocyclic compounds. At this point it should be emphasised that many complex reactions take place between the solid, liquid oil and gas phases and all of this depends on temperature and residence time [106]. Complementary to the Schiff reaction the Mannich reaction, was shown, which occurs under the simultaneous interaction of phenols (under lignin degradation conditions) with

amines and aldehydes to form, for example, pyrazines, pyridines, and next polymerize towards hydrochars [114]. Another example of the role of temperature is in the Diels-Alder reaction, where amines supplying the oil phase can be transformed into heterocyclic compounds [106]. In addition, Wang et al. [115] noticed the possibility also of ammonium reacting in the liquid phase with saccharides also generating heterocyclic towards a polyaromatic structure char.

- **CARBOHYDRATES**

Another important group of SS compounds are carbohydrates, which can be divided into monosaccharide, oligosaccharides, and polysaccharide. The most common forms of SS content are polysaccharides which result from condensation of a larger number of monosaccharides like glucose, mannose, fructose, creating hemicellulose, cellulose, or starch [**Error! Bookmark not defined.**]. Long-term studies of lignocellulosic biomass have provided a better understanding of the behaviour of individual components at a given temperature. Cellulose as an unbranched, linear biopolymer has β -1,4-glycosidic bonds between D-glucopyranose units forming chains of hundreds or thousands of repeating glucose units. The amorphous parts of cellulose can be depolymerized under HTC conditions as low as 100°C, but for further hydrolysis of its amorphous oligomers (cellobiose, cellotriose, cellotetraose, cellopentaose, cellohexaose) towards glucose monomers, temperatures above 150 °C are needed [116]. A lot of articles even reported temperatures of cellulose hydrolysis of about 220 - 230°C [**Error! Bookmark not defined.**,98]. This is due to the different structure of cellulose, specifically the crystalline part of its structure, which is more resistant to water conditions due to the presence of strong intra - intermolecular hydrogen bonds, and therefore it requires higher temperatures to initiate hydrolysis [116]. As mentioned, a result of the hydrolysis reaction is glucose, which isomerises to form fructose [117]. Further degradation steps include dehydration reactions and as a result fructose can degrade to aldehyde compounds and successive dehydration to organic acids. On the other hand, because of dehydration and further rearrangement processes, furans, hydroxymethylfurfural (HMF) and furfural-like compounds can be formed, which constitute a group of intermediates forming a hydrochars structure. Furthermore, some of these oil and aqueous phase products can be parallel decarboxylated and pathways lead to the formation of organic acids and then CO₂ and H₂O compounds [98]. All of this division of reaction can be autocatalyzed under acidic conditions, for example, thanks to generated organic acids, which promote the further degradation of glucose to HMF by enhanced dehydration [112,116,117]. Unlike cellulose, hemicellulose is made up of various monosaccharide units: pentoses (xylose and arabinose) and hexoses (glucose, mannose, and galactose), it has a mainly amorphous, disordered, and low-strength structure with short branches, which significantly affects its solubility under hydrothermal conditions and gives increased reactivity compared to cellulose. As a result, depolymerisation and hydrolysis occur at approximately 180°C, towards xylose, but also other pentoses and hexoses [**Error! Bookmark not defined.**,100**Error! Bookmark not defined.**]. Analogous to cellulose, monosaccharides dehydrate and rearrangement furan-like compounds form. Identified SS components such as starch are based on a similar mechanism of decomposition to cellulose, since they are a polysaccharide with a large number of glucose monomers linked by α -1,4 and α - 1,6 glycosidic bonds, consequently accumulating glucose, or fructose monomers after the first phase of the process. Nevertheless, the hydrolysis of starch requires a lower amount of heat supplied, in the range of 200 °C, due to the scrupulous differences in α - 1,6 bonds compared to cellulose [118]. Starch, like cellulose and

hemicellulose, is converted to monosaccharides and then by dehydration and decarboxylation to similar half – products [98].



Mechanism 2. Fate of polysaccharides compounds in model sewage sludge during hydrothermal carbonization (150 – 250°C)

Carbohydrate degradation produces intermediates mainly in the form of furans and HMF (phenolic aldehydes) forming the aqueous phase. These compounds have been proposed as the main precursors of hydrochars in many reports [Error! Bookmark not defined.,98,99,100,103,112,115,112119]. In turn N. Shi et al [120] proposed other precursors in the form of chain aldehydes, which can be formed in three different ways: 1) by hydrolytic ring opening of phenolic aldehydes to a-carbonyl aldehydes, 2) retro-aldol condensation and B elimination to a-carbonyl aldehydes from carbohydrate derivatives 3) B elimination and keto-enol tautomerism to a-carbonyl aldehydes also from carbohydrate derivatives. Further polymerisation of these components was supposed to lead to the formation of hydrochars structures. By analysing single components, [112,117117,121] presented a model for the formation of char from cellulose derivatives based on parallel reaction pathways of polymerisation and condensation of phenolic aldehydes, (aldehyde compounds, organic acid) during which reverse-aldol condensation and intermolecular dehydration occurred. Meanwhile, the increased production of soluble polymers containing C=O, C=C double bonds has been noticed, which resulted from intramolecular dehydration and keto-enol tautomerism reactions respectively, favouring the aromatization phenomenon. Many publications agree on the successive growth of so-called aromatic clusters as a result of increasing aromatisation reactions in aqueous solutions, which at a certain point can reach a so-called critical supersaturation point and nucleation breakdown [112,117,120]. Hydrochars microspheres are thus produced, and their further behaviour is described by the LaMer model [122,98].

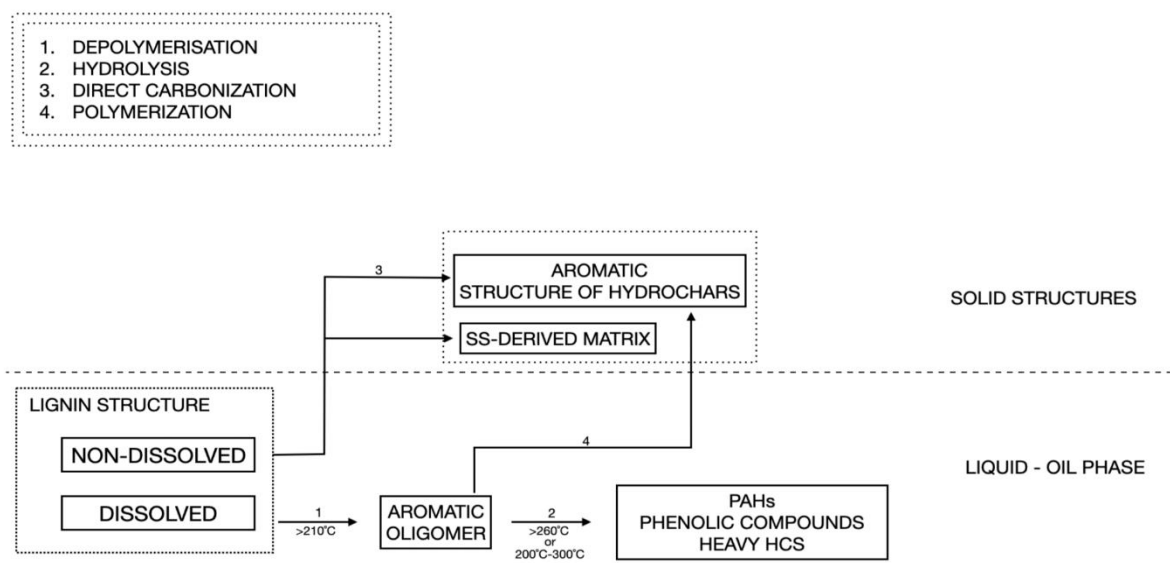
Analysis of the starch reaction pathways reveals analogous reaction mechanisms in the fructose pathway [119,98]. On the other hand, the hemicellulose intermediate is xylose, which, as a result of further dehydration and retro-aldol condensation, formed liquid intermediates in

the form of aldehydes and furfurals [Error! Bookmark not defined.]. With increasing temperature, furfurals or xylose residues polymerised to dark, insoluble substances, constituent hydrochars, mutually similar in structure [112]. Nevertheless, it is important to separate the interpretation of lignocellulosic (N-free) biomass composition studies in hydrothermal environments from non-lignocellulosic biomass (e.g., sewage sludge), as the additional presence of (N-rich) proteins may complicate polysaccharide evolutionary pathways [120]. For instance, Zhuang et al [107] compared the behaviour of polysaccharides in both the one and the other material, which showed that polysaccharides in the non-lignocellulosic structure adopted evolutionary pathways like hemicellulose, while components of the lignocellulosic structure followed more specific and peculiar conversion pathways.

- **LIGNINS**

Lignin has also been shown to occur in SS, often as an integral component of cellulose and hemicellulose [123]. Of all potential components occurring in SS, lignin is one of the more resistant ingredients to degradation and its fractions may be divided into dissolvable parts and non-dissolvable. The complex chemical structure results from three building blocks (p-hydroxyphenyl, guaiacyl, syringyl) which can be linked by seven different combinations of C-C, and C-O interunit linkages (β -O-4, α -O-4, 5-5, β - β , 4-O-5, β -5, β -1) [124]. Therefore, the soluble lignin fraction can probably depolymerize to dissolved lignin (aromatic oligomers form) above 210 °C, with further hydrolysis at about 260 °C and its intermediates are phenolic compounds, methoxylated benzenes, PAHs, and heavy HCs [98,99]. Other reports indicate a lignin hydrolysis range of 200 - 350 °C, depending on its structure, while due to the generally observed low degradation rate, the remaining lignin is not degraded in this temperature range [125].

Fang et al. [126] indicated two pathways of reaction for lignin – by dissolution intermediates in the homogeneous phase and degradation by pyrolysis-like process in the heterogeneous. In general, during the first pathway lignin soluble fragments undergo depolymerization to oligomers, hydrolysis, and cleavage of C – O - C and C - C bonds to aromatic compounds (syringols), phenolic compounds (catechol, guaiacol). Further hydrolysis and dealkylation enriches a water phase in aldehydes, acids, alcohols, catechol and phenols and the oil phase in



PAHs, heavy HCs. Finally intermediates undergo polymerization and generate phenolic char structure. Some of these half products are also responsible for gas production [98]. For insoluble

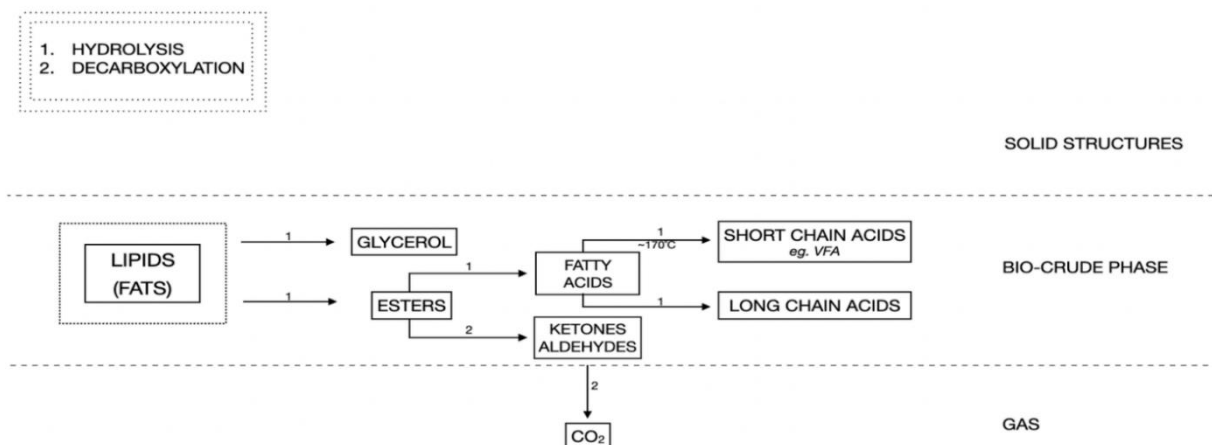
Mechanism 3. Fate of lignin structure in model sewage sludge during hydrothermal carbonization (160–260°C)

fragments in the second proposed pathway, their unreacted fractions generate aromatic structure chars by direct carbonization, but it depends on the improved process conditions [107,127].

- **LIPIDS**

Various scientific reports have indicated the potential of lipid content in SS, focusing their attention on the exact analysis of these compounds and methods for their recovery [128,129]. The reported lipid composition in SS is mostly FFAs, i.e., free fatty acids in the range (C10-C18), cellular lipids from microorganisms but also from animals and plants (triglycerides (TG), diglycerides (DG), monoglycerides, phospholipids, sterol, etc.) and wax/rubber (fat, grease, steroid) [130]. Nevertheless, the temperature of decomposition of this element is inconclusive. Wilson et.al performed [131] and described lipid hydrolysis on representative macromolecular compounds (glyceryl tristearate, glyceryl trioleate, glyceryl trilinoleate) and obtained the products, mainly VFA- volatile fatty acids and aldehydes [**Error! Bookmark not defined.**]. Their results suggest a dependence of lipid degradation not only on temperature but also on the degree of saturation of the fatty acid chain. As a result, VFA production has been observed to occur as early as 170 °C mainly for unsaturated fatty acids. Other work indicates lipid conversion even at higher temperatures than for proteins and carbohydrates [132] and still others suggest less lipid conversion even compared to lignin [124]. For example, at 200 °C the conversion efficiency for lignin is about 42%, while for lipids/oils it is about 38% [125]. In contrast, [133] in their study did not observe structural changes in lipids due to HTC even at 260 °C. The limited amount of research in this direction implies the need for precise reaction mechanisms of a wide range of lipids.

To sum up, the decomposition of fats/lipids, mainly by hydrolysis, can result in short- and long-chain fatty acids, glycerol, alkanes, while the decarboxylation of esters results in ketones and aldehydes. Overall, these compounds enrich the biocrude (liquid-oil phase). Importantly, the intensity of reaction parameters such as temperature, residence time or solid/water ratio determines the composition of this phase [134]. It has also been shown that, in



contrast to proteins and sugars, lipids, as a certain isolated fraction, do not or only slightly participate in the formation of hydrochars, while components in the form of fatty acids, due to

Mechanism 4. Fate of lipids compounds in model sewage sludge during hydrothermal carbonization (160– 240°C)

their amphiphilic character, are absorbed on the surface of hydrochars, which may influence not only the hydrophobic character of hydrochars, but also the carbonisation of other components [135,136,137].

- **HUMIC SUBSTANCES**

The last group of SS dissolved matter are humic substances (humic and fulvic acids and humins), resulting from microbial degradation of organic matter during wastewater treatment [Error! Bookmark not defined.,138]. Despite the significant value and quantity of these constituents in sewage sludge (tab 1) there is very limited research conducted into the carbonisation of these substances. Until some time ago, it was known that these substances can be refractory under HTC conditions, although at temperatures above 220°C they have been noted to degrade slightly to alkylbenzenes, polycyclic aromatic hydrocarbons and heteroaromatic compounds [139]. Recently, Wang et al. [140] carried out hydrothermal degradation of model SS constituents, including humic acids, which typically make up about 80 per cent of all humic substances in SS. The results of these studies indicated that humic acids, rather than carbohydrates as previously thought, were the main precursors to the formation of carbonates from SS, particularly due to the higher initial content of these components in the raw material. Nevertheless, these studies were carried out at temperatures above 300°C. However, other studies by Wang, et al. [141] confirmed the degradability at 250°C/30 min, during which the same model humic substances were dehydrated and further aromatised to form char. Thus, further studies of the HTC of humic substances at the limiting temperatures of this process, considering the other chemical reaction pathways and, in particular, the intermediates and by-products, are required to visualise the reaction mechanisms.

IMPACT OF INDIVIDUAL PROCESS FACTORS ON ENERGY POTENTIAL OF PRODUCTS

For many years, the characteristics of the resulting biomass HTC products have been analysed on the basis of elemental composition (C, H, O, N, S) to determine the efficiency of the carbonisation process. So far, it is known that the carbon content of the solid after the HTC process tends to increase, mainly through the conversion/transformation of aliphatic C into aromatic C-C/C-H hydrochars structures, at the expense of the migration of the other elements into the liquid-oil or gas phase. Nevertheless, according to the mechanisms presented in section 3, this phenomenon is closely related to the amount and type of the individual SS components and thus their resistance to the set operational conditions of the HTC process [142]. A useful and widely used method for visualising the quality of raw materials and determining the influence of set parameters on the directions of potential chemical reactions and thus the final quality of the obtained products is the van - Krevelen diagram [143,144]. This method involves determining the elemental content of C, H, O by elemental analysis and determining the molar atomic ratios of H:C/O:C, which graphically indicate the degree of carbonisation and the possible potential of the obtained product as a fuel [87,145]. In general, the lower the H:C/O:C ratios, the higher the degree of dehydration and decarboxylation and thus the greater the

similarity of the resulting solid product to combustible sedimentary rocks resulting from the carbonisation of plants (lignite, hard coal), due to the greater carbonisation in the structure. Thus, each material has its own individual reaction pathways or conversion routes dependent on external factors [100].

Solid fuels are subdivided into types, grades, and classes. In order to characterise the solid products obtained, this section summarises studies determining the effect of individual process conditions and additives on their basic properties necessary for quality assessment in combustion or gasification processes, such as fixed carbon (FC%) volatiles (VM%), ash content (%), HHV/LHV (MJ/kg) and other impurities in the form of nitrogen (N%) or sulphur (S%) content. In addition, the effect of heavy metal migration between the solid and liquid phases was determined, as elements such as mercury, chromium or arsenic are extremely problematic during combustion and, depending on their content, can therefore significantly limit further energy application [146]. On the other hand, the characterisation of liquid wastes was considered in terms of their use as co-substrate (COD, VFA, pH, N – NH₄⁺, TKN) in co-digestion with SS, as numerous reports have shown promising methane potential due to the high level of biodegradable carbon dissolved in the liquid [147,148,149]. The disposal of HTC liquid waste by the AD process could be considered the simplest and most favourable system, since the problematic composition of the liquid obtained, furan compounds, aromatics, aldehydes, phenols, etc., would require further, usually costly, treatment.

- **Influence of the severity factor – temperature and residence time**

Long-term studies of carbonisation in its broadest sense have focused attention on two basic parameters of the process - temperature and residence time. Thus, there is no doubt that, apart from the characteristics of the raw materials, these have a fundamental influence on the physico-chemical properties of the reaction medium, the chemical reaction pathways of the individual components, the properties of the products obtained, and, consequently, on the mass-energy balance. As already mentioned, the essence of temperature is to change the nature of the medium, to provide sufficient heat to initiate thermal dissociation, and to increase the reaction rate of reactive intermediates towards establishing equilibrium [100]. In a defined temperature range of selected components, an increase in this factor promotes the rate of polymerisation and aromatisation [100] and an increase in the degree of condensation [87]. However, a further increase in temperature may lead to an increase in the degradation of SS components and enrichment of biocrude, at the expense of a decrease in hydrochars yields [**Error! Bookmark not defined.**]. It has also been shown that with increasing hydrothermal temperature the dewatering of hydrochars/SS increases, which under normal conditions retains most of its water in the form of bound water, surface water, due to the problematic composition of the SS floc structures called EPS [150]. During hydrothermal reactions, water bound to the SS matrix is successively transformed into so-called free water, which has a significant impact on the application of mechanical methods of SS water removal [151]. On the other hand, the temperature of the process did not show a significant effect on changes in the mineral fraction content of SS, which negatively affected the increase in the content of this fraction in the solid end products [152]. It also turns out that the temperature of HTC conditions of SS has an indirect effect on biogas production in the anaerobic digestion of the resulting HTC process liquids. The reason is the enhanced hydrolysis of sewage sludge, which affects the solubility of organic carbon during HTC, hence the resulting liquid can be considered a value-added product [153].

The residence time influences both the intensity of the carbonisation process, energy consumption and product specificity [154] but, compared to temperature, it has slightly less influence on the processing [155]. It has been reported [153,154] that longer residence times can develop porosity, specific surface area and pore volume. In general, prolonged residence promotes polymerisation reactions, which favour the formation of an insoluble solid fraction at a certain temperature [112]. Ahmed et al. [149] investigated the effect of residence time on the final dewatering of the obtained hydrochars as well as on the methane potential of the HTC process liquid during further co-digestion of this waste with sludge. According to the observations, increasing the residence time could increase the final dewatering of the hydrochars by up to 7 times and decrease COD (mg/l) in the liquid.

Over time, the synergistic effect of temperature and time has been widely identified in the literature as the reaction severity factor. Based on recent literature reviews [87] a model is proposed to determine their mutual relationship (eq. 5)

$$R_o = t \exp\left(\frac{T-100}{14.75}\right) \quad \text{eq 5)}$$

The above formula was modified years later due to its applicability only at constant temperature. Rogalinski et al. [118] proposed a model (eq. 6) considering a temperature depending on the total residence time, including the heating time of the feedstock

$$R_o = \int_0^t \exp\left(\frac{T(t)-100}{14.75}\right) dt \quad \text{eq 6)}$$

where: t - residence time (min) as a ratio of reactor volume (l) to feed flow rate (l/min), T - temperature at a given residence time, 14.75 - empirical parameter related to activation energy.

The solution of the intensity factor equation $SF = \log R_o$ is presented in detail in the article [118] and is reflected both in the energy balance and in the further optimisation and simulation of HTC processes. An analysis of the severity factor during sludge treatment [156] found that the higher the temperature and residence time, the higher the bound/elemental carbon content and the higher the energy density of the products, with the increase in hydrochars energy content (HHV) mainly dependent on the severity of the temperature [152]. In general, harsher process conditions reduce the yield of hydrochars, although they have an effect on the increased formation of secondary carbonisation, which explains the increase in HHV [104,**Error! Bookmark not defined.**].

Gaur et al. [55] conducted tests over a wide range of reaction severity ratios $\log R_o = 4.4$ - 8.0 and found the lowest hydrochars yields at the highest and lowest severity ratios. The synchronisation of the two parameters and their severity affected the lowering of the methane potential of the process water (BMP), and increased water removal from solid products [157]. For example, the highest biogas yield from the leachate was achieved under conditions of 200°C and 30 min. In addition, it can be observed (tab 4.) that as the process intensity increases, the immobilisation of heavy metals such as As, Cd, Cu, Zn increases, while metals such as Cr, Pb, Hg, Ni decrease in the solid products, while in the case of process liquids their content increases but only slightly [158]. In contrast to Zhang et al. [159] the opposite trend was observed for some heavy metals, which may mean that their fate may depend on other boundary conditions, e.g., such as initial moisture content or pH. For both co-fermentation processes and hydrochars combustion processes, low concentrations of heavy metals (especially As, Cr, Hg) are desirable

or required, so observation of the subsequent fate of these components under different process conditions is essential.

Tab [3] Influence of severity factors for/on energy potential and value of the HTC products

Literature	Ro	T°C (t _{min})	Type	Physico-chemical properties					
				Yields	Moisture	VM	FC	Ash	HHV
				[%]	[%]	[%] TS	[%] TS	[%]TS	[MJ/kg] TS
Zhan et.al, (2014)			SS	n.d	n.d	n.d	n.d	33,1	17,5
		190 (60) 260 (60)	H	n.d	n.d	n.d	n.d	46,6 50,9	16,7 17,2
		190 (360) 260 (360)	H	n.d	n.d	n.d	n.d	49,3 50,2	16,8 17,6
Aragón-Briceño et al, (2017)			ADS	-	4,7	55,8	7,7	31,8	16,6
		160 (30) 220 (30) 250 (30)	H	68,8 73,4 56,8	2,6 2,0 2,8	49,6 43,8 51,1	9,2 9,1 9,2	38,6 45,1 36,9	17,0 14,3 17,8
			ADS	-	n.d	n.d	n.d	n.d	18
Gaur et al, (2020)	4,4 - 5,0	200 (30 - 120)	H	72,9-56,8	n.d	n.d	n.d	n.d	18,2 - 19,0
	5,9 - 6,5	250 (30-120)	H	66,0 -54,7	n.d	n.d	n.d	n.d	20,4 - 19,4
	7,4 - 8,0	300 (30 - 120)	H	63,9-48,9	n.d	n.d	n.d	n.d	21,5 - 20,2
Literature	Ro	T°C (t _{min})	Type	COD	TOC	N-NH ₄ ⁺	TKN	VFA	*BMP _{exp}
				g/l	g/l	g/l	g/l	g/l	ml CH ₄ /gCOD
Aragón-Briceño et al, (2017)			ADS	1,84	0,46	1,34	1,49	0,005	n.d
		160 (30) 220 (30) 250 (30)	L	12,60 12,90 12,10	4,69 4,58 4,88	1,29 1,70 1,69	2,07 2,19 2,35	0,191 0,406 0,716	n.d
			ADS	51,4 - 45,2	18,6 - 18,3	n.d	n.d	n.d	51,4 - 45,2
Gaur et al, (2020)	4,4 - 5,0	200 (30 - 120)	L	48,0 - 43,8	22,7 - 12,4	n.d	n.d	n.d	48,0 - 43,8
	5,9 - 6,5	250 (30 - 120)	L	40,6 - 33,8	14,3 - 12,1	n.d	n.d	n.d	40,6 - 33,8
	7,4 - 8,0	300 (30 - 120)	L	51,4 - 45,2	18,6 - 18,3	n.d	n.d	n.d	51,4 - 45,2

* estimated values, read from the chart

Tab [4] Influence of severity factors for main contaminant HTC products during combustion

Literature	Ro T°C (t _{min})	Type	Heavy metals							
			As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
-	-	-	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
		SS	40	5	78	141	57	4	27	602
		H	50	6	75	145	43	2.2	26	598

Wang, et.al (2019)	0,18 (210, 60)	L	0,53	0,06	2,34	2,08	1,00	0,18	0,45	8,2 2
	0,71 (300, 180)	SS	40	5	78	141	57,29	4	27	602
		H	78	10	61	179	29	1,45	21	622
		L	1,62	0,23	5,95	6,67	2,81	0,59	0,05	22, 78
Zhang, et al. (2014)	(190, 60)	SS	26,26	3,47	53,87	99,97	25,21	nd	868	868
		H	30,33	3,52	98,93	152,36	39,41	nd	nd	134 7
	(260, 60)	SS	26,26	3,47	53,87	99,97	25,21	nd	868	868
		H	19,55	4,58	146,09	168	41,99	nd	nd	141 9

- **Effect of moisture of feedstock**

Moisture is one of the most important parameters characterising the physical properties of sewage sludge due to the enormous costs of disposing of this material. A typical value for mixed, unstabilised sludge can range from 95 - 97%, while for digested sludge it is approximately 97%. Hence, the moisture content of sewage sludge is highly dependent on the system and operation of the wastewater treatment plant. After dewatering, these values vary on average between 75 - 82% while even with better filter presses vary between 65 -70% moisture content. The effect of the loading ratio of the hydrothermal reactor with different types of sludge has been studied in several publications. It turns out that this parameter directly affects the composition of hydrochars and process water [158], and, more importantly, it can be controlled. From a sludge dewatering cost point of view, it would be advantageous to use sludge with the original moisture content. However, the quality of the hydrochars and its efficiency decreases as the water-to-sludge (W/S) ratio increases [160]. This is because with an increased amount of water in the waste, which is both reactant and reaction medium, among other things, hydrolysis is enhanced, leading to more efficient decomposition of products in a relatively short time, obtaining very low hydrochars yields and lower calorific values [161,98]. In contrast, when the moisture content of sewage sludge is reduced, a polymerisation reaction is promoted due to increased solids accumulation and interaction, ultimately increasing FC, thickening the capacity of the hydrochars in a shorter time [156,87]. While the range of FC values changes significantly, this is not observed for HHV (tab 5). Interestingly, despite the generally higher ash content of hydrochars compared to feedstocks, as the load increases, the ash content decreases as with VM, although this parameter is generally lower compared to the feedstocks. In the case of liquids, an increase in parameters such as COD, TOC and VFA was observed, which may have had a positive effect on the anaerobic digestion process up to a certain point. On the other hand, undesirable concentrations of components such as $\text{NH}_4^+ - \text{N}$ also increased. However, the BMP tests conducted showed that the highest methane yield was not obtained for the highest degree of COD or TOC in the leachate at the highest load, probably due to an increase in inhibitors of the fermentation process after exceeding the 10% db of feedstock (90% moisture) for which the highest methane value was obtained (325,6 ml CH_4 / g COD), which then began to decrease. On the other hand, Kiran R. Parmar et al [162] obtained other results for which the highest biogas yield was obtained for the highest COD and TOC content. Thus, sludge dewatering in HTC processes appears beneficial from the point of view of the quality of the solid products obtained and, in some cases, liquid products. Nevertheless, it would be necessary to optimise this system in terms of the applicability of the process liquids as potential co-substrates, the quality of the hydrochars and the cost of sludge dewatering. In addition, the influence of raw

material moisture content on heavy metal speciation during HTC should be investigated, as it may affect the immobilisation trends of individual heavy metals.

Tab [5] Influence of initial moisture for/on energy potential and value of the HTC products

Literature	Moisture of sludge [%]	T°C (t _{min})	Type	Physico-chemical properties				
				Yields	VM	FC	Ash	HHV
				[%]	[%] TS	[%] TS	[%] TS	[MJ/kg] TS
F. Merzari et al., (2020)	97,1	250 (30)	ADS	-	50,25	4,76	44,99	10,66
			H	78,1	25,97	0,62	73,42	8,59
	74,9		ADS	-	65,67	5,90	28,43	16,02
			H	67,6	50,37	6,27	43,36	15,98
Aragón-Briceño et al., (2020)	70	250 (30)	ADS	-	51,8	9,34	36,7	14,4
	90		H	75	41,2	8,4	48,5	16,5
	97,5			75	42,4	8,4	48,4	15,8
Kiran R. Parmar et al., (2019)	70	250 (60)	ADS	-	51,0	2,1	46,9	14,9
	90		H	69,5 – 65,6	46.6 - 44.3	6.8 - 6.2	46.6 - 49.5	15,7-15,2
Literature	Moisture of sludge [%]	T°C (t _{min})	Type	COD	TOC	VFA	N - NH ₄ ⁺	BMP _{exp}
				g/l	g/l	g/l	g/l	ml CH ₄ /gCOD
F. Merzari et al., (2020)	97,1	250 (30)	ADS	0,4	n.d	n.d	0,88	n.d
			L	8,3	n.d	n.d	1,0	n.d
	74,9		ADS*	47,2	n.d	n.d	0,60	n.d
			L	57,5	n.d	n.d	6,90	n.d
Aragón-Briceño et al., (2020)	70	250 (30)	ADS	2,1	0,66	0,35	1,32	135
	90		L	72,3	29,78	4,61	5,26	288
	97,5			24,1	10,0	2,0	2,74	325
Kiran R. Parmar et al., (2019)	70	250 (60)	ADS	n.d	n.d	n.d	n.d	n.d
	90		L	51,6 – 23,4	20,3 – 7,1	5,5 – 3,5	n.d	160 -140**

* Based on 1g of dry biomass dissolved in one litre of distilled water, **estimated values, read from the chart

• Influence of pH on HTC process

- Initial pH of feedstock

During the HTC process, the pH changes due to hydrothermal conditions [90] and the successive degradation of SS components to acidic and basic compounds in the process liquid such as VFA, ammonium nitrogen or amino acids [152]. The pH value during HTC will depend on the type and origin of the feedstock and on temperature, residence time and humidity/moisture [163,164]. When considering the general mechanism of SS decomposition, it has been found that low pH within a certain temperature range can be the result of the formation of large amounts of organic acids, albeit only for a certain period of time. Jain et al. [165] and Aragón-Briceño et al. [152] noted that above 220°C, the pH of the process begins to rise, probably due to the degradation of proteins in the SS to form ammonium in the liquid. The use of catalysts in the form of acids and bases can greatly assist the HTC process by increasing ionic strength and accelerating chemical reactions. T. Wang et al. [166] and L. Huezco et al. [145] have shown that initially lowering the pH of anaerobic digested sludge with H₂SO₄ has an equivalent effect to increasing the process temperature, which promotes depolymerisation, hydrolysis and dehydration (significantly reduced carbon oxygen content), consequently increasing the solubility of the components in the liquid and promoting the decomposition of

the more difficult oligomers and monomers to smaller fragments - at the expense of lowering the yield of hydrochars. This is also confirmed by other studies, in which the acidic conditions provided by the use of organic acids in the primary HTC liquid in SS promoted a more efficient degradation of proteins and amino acid derivatives contained in the SS matrix [166]. On the other hand, prolonged residence time at lower pH promoted the growth of intermediates, polymerization and thus the formation of secondary chars with better energetic properties – HHV [165,167]. Sometimes, however, lowering the pH does not show a significant effect on the hydrochars yield, while it may have influence on a lower ash content [168]. In contrast, it has been observed that the use of catalysts that increase pH accelerated hydrolysis reactions and promoted biocrude formation at the expense of lower hydrochars yield [160]. Additionally, Mäkelä et al. [169] reported that after the addition of NaOH, the carbon content decreased, and the O/C ratio increased compared to the HCl used. Overall, the effects of individual organic and inorganic reagents on the parameters of HTC products are summarised in tables 6 and 7. Table 6 shows that the use of organic catalysts may be the most attractive, as they reduce the ash, nitrogen and sulphur content of the hydrochars, increasing its energy values as HHV, and, compared to inorganic acids such as H₂SO₄, generate less contamination by increased sulphur content in both leachate and solid product [170]. In contrast, for heavy metals (tab. 7), no significant effect of pH was observed on changes in the concentration of individual elements in the hydrochars.

Tab [6] Influence of initial pH and type of catalyst added for/on energy potential and value of the HTC products

Literature	Catalyst	T°C (t _{min})	Initial pH	Type	Physico-chemical properties					
					Yields	Moisture	VM	FC	Ash	HHV
					[%]	[%]	[%]	[%]	[%]	[MJ/kg]
Huezo et al.,2021	H ₂ SO ₄ (98%) ¹	220 (22)	8,2	ADS	-	n.d	n.d		48,7±0,2	11,64±0,76
				H	n.d	n.d	n.d	21,2-28,8	61	10,9
			6,8	ADS	n.d	n.d	n.d		44,2±0,4	10,95±0,30
				H	n.d	n.d	n.d	21,2-28,8	62	12
X. Liu et al., 2019	CH ₃ COOH (99,5 wt. %) or KOH (82%) ²	270 (120)	-	SS	n.d	MCe 89,32	n.d	2,66	49,85	n.d
			2	H	52,27	54,5	n.d	n.d	81,79	n.d
			7	H	55,14	54,76	n.d	n.d	76,99	n.d
			12	H	53,00	52,77	n.d	n.d	69,55	n.d
V. Ekanthalu et al., 2021	Natural pH/ADS	220 (120)	-	SS	n.d	76,53	n.d	5,71	32,83	14,66
	CH ₃ COOH 0,25M ³		5,63	H	n.d	n.d	n.d	8,84	43,92	15,56
	HCOOH 0,25M		5,45	H	n.d	n.d	n.d	8,44	43,49	15,37
	H ₂ SO ₄ 0,25M		3,47	H	n.d	n.d	n.d	4,41	44,50	14,32
	NaOH 0,25M		10,98	H	n.d	n.d	n.d	6,88	6,88	14,46
Song,E, et al, (2019)	ADS	200 (60-120)	n,d	ADS	-	n,d	69,95	10,78	18,17	18,83
	Natural pH		n,d	H	65,76	n,d	59,81	12,48	27,6	20,7
	(Oxalic acids)		n,d	H	54,71	n,d	70,31	12,83	17,34	22,4

	(Citric acids)		n,d	H	51,07	n,d	72,31	14,19	13,61	23,8
	(Tartaric acids)		n,d	H	55,28	n,d	67,94	12,63	19,3	21
Literature	Catalyst	T°C (t _{min})	Initial pH	Type	Yields [%]	COD g/l	N - NH ₄ g/l	Ash [%]		
Huezo et al.,2021	H ₂ SO ₄ (98%) ¹	220 (22)	8,2	ADS	n.d	10,23	n,d	48,7		
				L	n.d	18,6	n,d	10		
			6,8	ADS	n.d	9,31	n,d	44,2		
				L	n.d	15,4	n,d	10,0		

Tab [7] Influence of initial pH on main contaminant HTC products

Literature	pH	T°C (t _{min})	Type	Heavy metals							
				As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
	-	-	-	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Huezo et al.,2021	8,2±0,4	220(22)	ADS	14,2	5,24	59,7	338	72,1	n,d	39,7	1,401
			H	7,7	5,10	63,1	385	81,0	n,d	43,5	1,624
			L	<0,9	<0,9	<0,9	<0,1	<0,5	n,d	<0,3	<0,3
	6,8±0,4		ADS	15,4	5,17	62,2	329	74,9	n,d	40,3	1,383
			H	9,2	4,88	65,7	386	79,0	n,d	46,1	1,569
			L	<0,9	<0,9	<0,9	<0,1	<0,5	n,d	<0,3	<0,3

- Influence of aqueous phase recycling

The use of the recirculation of the water phase after process HTC instead of only the natural moisture content of the waste is one of the methods to improve some properties of the solid materials and at the same time to dispose of liquid wastes, acting as a substitute catalyst for the HTC process. The origin of the raw material and consequently the composition of the final water phase determines the nature of the catalyst - acidic or basic. In contrast to (lignocellulosic) biomass, sewage sludge is a form of matter rich in protein, and therefore due to its degradation at higher HTC temperatures and further N migration pathways, the process water has an alkaline character, due to the high presence of NH₄⁺ - N ammonia in the HTC liquid [171,172]. Other results [173] related to recirculation seem to confirm this, as a gradual increase in pH over the temperature range (200°C - 260°C) was observed as a function of the number of HTC water returns. Both the number of recirculations and the temperature favoured the hydrolysis and deamination of proteins dissolved in the liquid phase, thus an increase in TOC and TN and HHV content in the hydrochars was observed. Due to the limited number of publications on the impact of aqueous phase recirculation, but the high potential for improving the energy values of the products obtained and the possibility of on-site water management, recent studies based on the synergy of co-carbonisation and aqueous phase recirculation processes were also considered [174,175]. The results confirmed an improvement in the solid yields, FC, HHV, however, their mutual synergy had a significant effect on the increase of ash in the solid product and on the COD, TN concentration in the liquid product as a function of the number of returns. Thus, the use of these two process additives would need to be tested in terms of the proportion of co-substrates added and the amount of aqueous phase recirculation for subsequent optimisation. Due to the limited number of studies, it was not possible to determine the effect of phase recirculation on heavy metal distributions.

Tab [8] Influence of aqueous phase recycling and co-substrates for/on energy potential and value of the HTC products

Literature	Liquid returns	Type of co-substrate	T°C (t _{min})	Type	Physico-chemical properties				
					Yields	VM	FC	Ash	HHV
					[%]	[%] TS	[%] TS	[%] TS	[MJ/kg] TS
Zhi-Xiang et al.,2020	0	-	200	SS	n,d	n,d	n,d	n,d	n,d
	2			H	71	n,d	n,d	n,d	6,88
	4			H	74	n,d	n,d	n,d	8,65
	4			H	73	n,d	n,d	n,d	8,45
C, Zhang et al., 2020	1	Water Hyacinth	220(60)	WS	n,d	n,d	8,47	36,30±	11,99
	2			H	67,95	n,d	10,90	48,27	12,89
	2			H	71,21	n,d	11,67	47,72	13,05

	3	(WH) WH/SS 1:1 -WS		H	73,23	n,d	12,17	47,13	13,17
	4			H	77,52	n,d	11,34	47,76	13,87
Literature	Liquid returns	Type of co-substrate	T°C (t _{min})	Type	TOC	COD	TN	Ash	pH
					g/l	g/l	g/l	%	-
Zhi-Xiang et al., 2020		-	200	SS	n,d	n,d	n,d	n,d	n,d
	0			L	6,9	n,d	3,0	n,d	6,7
	2			L	8,5	n,d	5,2	n,d	7,2
	4			L	7,3	n,d	5,9	n,d	7,5
C, Zhang et al., 2020		Water Hyacinth (WH) WH/SS 1:1 -WS	220(60)	WS	n,d	n,d	n,d	n,d	n,d
	1			L	11	31	3	n,d	n,d
	2			L	14	39	5	n,d	n,d
	3			L	18	49	7	n,d	n,d
	4			L	17	46	6	n,d	n,d

Tab [9] Influence of aqueous phase recycling for/on main contaminant HTC products

Literature	Liquid returns	T°C (t _{min})	Type	Heavy metals	
				Cd	Pb
	-	-	-	mg/kg	mg/kg
C, Zhang et al., 2020		220 (60)	WS	2	23
	1		H	3	32
	4		H	3	28

- **Effect of process additives**

- Effect of other catalysts

Recent literature reports have focused attention on the use of various types of catalysts for the efficient deoxygenation, denitrification, and carbonisation of SS at the expense of decreasing high severity factors. Due to the problematic protein structure (including EPS content) and consequently high N content in the obtained hydrochars, generating pollutants, it is necessary to enhance several reactions - hydrolysis, dehydration, decarboxylation, and deamination, to reduce NO_x and improve the quality of hydrochars [161]. More recently, AOPs - advanced oxidation processes - have begun to be used to purify materials using oxidation. Ning et al. [176] investigated Fe (II)-activated persulphate in the context of increasing nitrogen removal efficiency from the SS matrix under relatively mild conditions (150 °C and 20 min), The results showed the ability to remove nitrogen up to 66% and even increase the solid yield at appropriate Fe (II)/PS doses. Ma et al., [110] proposed the use of Fe(NO₃)₃, which both promoted the degradation of biopolymers in SS and reduced TOC, NH₃ - N and TN concentrations in leachates. In turn Zhi-Xiang Xu et al. [177] chose the typical inorganic salts NaCl and (NH₄)₂SO₄. Unfortunately, despite the promotion of hydrolysis and the steps of dehydration, decarboxylation and carbonisation, their adsorption on the surface was observed, which seems unfavourable from the point of view of further energy applications. In addition, according to (tab 10.), the use of these catalysts can have the opposite effect to energy valorisation, as the calorific values tend to decrease. Xu et al. [178] used yet another method based on the use of Mg-Ga (LDH) and their calcined LDO samples - layered double oxides. These catalysts

favoured the removal of N from the solid products to form NH_4^+ - N in the liquid fraction, as was the case with salt.

Tab [10] Influence of process additives for/on energy potential and value of the HTC products

Literature	Type of catalyst	T°C (t _{min})	Type	Physico-chemical properties				
				Yields	VM	FC	Ash	HHV
				[%]	[%] TS	[%] TS	[%] TS	[MJ/kg] TS
Zhi-Xiang Xu et al.,(2020)		220 (60)	SS	n.d	n.d	n.d	n.d	9,75
	NaCl ¹		H	97	n.d	n.d	n.d	6,65
	(NH ₄) ₂ SO ₄		H	99	n.d	n.d	n.d	6,62
Ma, Liao, et al., (2021)		210 (60)	SS	n.d	n.d	n.d	n.d	n.d
	5% NaCl ²		H	40	n.d	n.d	n.d	7,61
	10% NaCl		H	37	n.d	n.d	n.d	6,92
Xu et al., (2020)		220 (60)	SS	73	n.d	n.d	n.d	10,18
	MGa ³		H	69	n.d	n.d	n.d	8,44
	MAa		H	72	n.d	n.d	n.d	8,07
	MGb		H	73	n.d	n.d	n.d	8,00
	MAb		H	72	n.d	n.d	n.d	7,41
Literature	Type of catalyst	T°C (t _{min})	Type	COD	N - NH ₄	TN	TOC	pH
				g/l	mg/l	g/l	g/l	-
Zhi-Xiang Xu et al.,(2020)		220 (60)	SS	n.d	0,59	2,6	g/l	n.d
	NaCl ¹		L	n.d	0,60	2,2	7,4	n.d
	(NH ₄) ₂ SO ₄		L	n.d	23,0	25,2	6,6	n.d
Ma, Liao, et al., (2021)		210 (60)	SS	n.d	n,d	n,d	7,6	n.d
	5% NaCl ²		L	n.d	1,1	2,8	n,d	n.d
	10% NaCl		L	n.d	1,2	2,9	8,2	6,8
Xu et al., (2020)		220 (60)	SS	n.d	n,d	2,8	6,3	6,7
	MGa ³		L	n.d	n,d	2,7	11	7,1
	MAa		L	n.d	n,d	3,0	10,5	7,4
	MGb		L	n.d	n,d	3,4	9,5	8,8
	MAb		L	n.d	n,d	5,8	8,1	n.d

- Influence of co-substrates

The use of more than one raw material, in specific mixtures or proportions in the HTC process, is commonly known as hydrothermal co-carbonisation (Co-HTC). The general advantage of such a solution, besides the possibility of treating different wastes in the same process, is the mutual synergy. Studies carried out on sewage sludge in various combinations combined with screenings (a wide range of organic wastes from wastewater treatment plants) have shown that they can have a relatively high energy content and thus can become carbon precursors in the context of alternative fuels [179]. It is generally known that the Co - HTC of sewage sludge and a variety of biomass is conducive to both lowering the ash content and increasing the energy density of the resulting hydrochars [180,181]. As noted by Wilk et al. [182] one of the general reasons is the higher carbon content and relatively lower ash content of the biomass, hence when mixed in appropriate proportions more favourable hydrochar properties are obtained. These observations seem to be confirmed by other results of co-carbonation of SS with biomass, showing lower H/C and O/C atomic ratios - due to synergistically enhanced decarboxylation, higher fuel index (FC/VM) and higher HHV, as well as higher final dewatering of hydrochars due to filtration [Error! Bookmark not defined.,180,183,184,185,186,187]. In contrast, in the case of digested sludge and fecal co-substrate additions, dehydration was observed as the main chemical reaction and the cause of lowering H/C and O/C atomic ratios, but the other benefits remained unchanged [187]. Moreover, the addition of, for example, lignocellulosic biomass to the Co-HTC SS process nullified/ mitigated some contaminants in the form of heavy metals [188] while the addition of sawdust favourably reduced the sulphur and nitrogen content of the hydrochars [189]. On the other hand, Wang et al. [190] investigated the precise N migration pathway mainly from SS proteins in the Co-HTC process with biomass. They observed Maillard interactions of amino - N-derived degraded moieties with carbohydrates and their intermediates from plant biomass,

forming heterocyclic compounds in the form of pyridine, pyrrole, and pyrazine. Further polymerisation favoured the formation of increased polyaromatic carbons with increased N retention in the hydrochars composition. Such a solution was not beneficial from the point of view of flue gas cleaning after using hydrochars as solid fuel. Low-nitrogen solid fuels were, though, possible to obtain from the Co-HTC process of sewage sludge and PVC after optimisation of the process [191]. Hence, Co-HTC broadens the horizons for the utilisation of many different wastes, not only organic, and their effects on hydrochars parameters are summarised in table 11 and 12. On the other hand, the effect of various substrates in co-carbonisation on selected physico-chemical properties of liquids requires further recognition and research.

Tab [11] Influence of co-substrates for/on energy potential and value of the HTC products

Literature	Type of co-substrate	T°C (tmin)	Ratio	Type	Physico-chemical properties				
					Yields	VM	FC	Ash	HHV
					[%]	[%]	[%]	[%]	[MJ/kg]
Zvimba et al., (2021)	Screenings (SC) Primary sludge (PS) Digested sludge (DS) Activated sludge (WAS)	180-240 (120)	-	PS	n.d	n.d	n.d	n.d	16,1
			PS:SC	H	n.d	n.d	n.d	n.d	20,0
			-	DS	n.d	n.d	n.d	n.d	14,9
			DS:SC	H	n.d	n.d	n.d	n.d	19,0
			-	WAS	n.d	n.d	n.d	n.d	14,3
	WAS:SC	H	n.d	n.d	n.d	n.d	23,0		
Zhang, Zhang and Li, (2017)	Pinewood sawdust (PS)	220	-	SS	n.d	n.d	7,56	20,91	n.d
			-	PS	n.d	n.d	13,33	0,39	n.d
			SS:PS 3:1	H	49,67	n.d	19,77	22,73	n.d
			SS:PS 1:3	H	65,61	n.d	24,64	4,36	n.d
He et al., (2019)	Rice straws (RS) Orange peel (OP) Peanut shell (PS) Fallen leaves (FL)	220 (720)	-	SS	n,d	42,9	5,1	52,0	9,26
			-	RS	n,d	70,2	15,6	14,2	16,93
			SS:RS 3:1	H	62,5	29,4	8,4	62,2	8,83
			SS:RS 1:3	H	49,6	39,7	21,8	38,5	16,82
			-	OP	n,d	80,0	18,3	1,7	12,06
			SS:OP 3:1	H	60,1	29,0	10,0	61,0	10,06
			SS:OP 1:3	H	47,0	44,7	28,1	27,2	21,03
			-	PS	n,d	70,8	25,4	3,8	12,60
			SS:PS 3:1	H	63,0	29,5	11,6	58,9	10,35
			SS:PS 1:3	H	49,1	41,9	33,2	24,9	21,72
			-	FL	n,d	75,7	18,9	5,4	18,40
	SS:FL 3:1	H	63,2	31,2	8,3	60,5	10,19		
	SS:FL 1:3	H	49,6	50,2	20,7	29,1	20,97		
Zhao et al., (2022)	Wet distillers grains (WDG)	180 (30)		SS	n,d	79,00	7,26	7,72	21,19
				WDG	n,d	76,67	11,27	2,79	22,75
			SS:WDG 4:1	H	90	80,70	10,17	5,36	24,47
			SS:WDG	H	89	81,17	10,06	4,27	25,28

			2:1							
Xu et al., (2019)	Cow dung biogas residue (CDBR)	240 (60)		DSS	n,d	n,d	n,d	n,d	9,50	
				CDBR	n,d	n,d	n,d	n,d	15,07	
				75% DSS + 25% CDBR	H	n,d	n,d	n,d	n,d	9,37
				50% DSS + 50% CDBR	H	n,d	n,d	n,d	n,d	13,02
				25% DSS + 75% CDBR	H	n,d	n,d	n,d	n,d	15,59
Lu, Ma and Chen, (2021)	Cellulose (CE) Xylan (XY) Lignin (LIG)	220 (60)		SS	n,d	n,d	3,36	n,d	9,04	
				CE	n,d	n,d	5,89	n,d	16,08	
				1:1 SS:CE	H	71	n,d	4,86	n,d	12,90
				XY	n,d	n,d	3,96	n,d	16,07	
				1:1 SS:XY	H	49	n,d	14,56	n,d	13,23
				LIG	n,d	n,d	0,93	n,d	13,34	
C, Zhang et al., (2021)	Banana stalk (BS) ⁶	230 (60)		SS	-	53,17	5,46	41,37	13,69	
				BS	-	82,49	13,95	3,56	17,58	
				30% BS	H	54,14	36,42	12,62	50,96	13,73
				50% BS	H	52,07	41,63	19,91	38,46	16,77
				70% BS	H	46,71	46,84	28,27	24,89	19,57

Tab [12] Influence of co-substrates for main contaminants HTC products

Literature	Type of co-substrate	(T °C and t min)	Ratio C-S/F	Sludge type and product	Heavy metals contamination factor (Cr)				
					Cr	Cu	Ni	Zn	
	-	-	%	-	-	-	-	-	
Lu, Ma and Chen, (2021)	Cellulose (CE) ⁵	220(60)		SS	1,41	3,04	3,94	13,19	
	Xylan (XY) ⁵			1:1 SS:CE	H	0,54	1,95	0,28	9, 21
	Lignin (LIG) ⁵			1:1 SS:XY	H	0,25	2,14	0,21	6,60
				1:1 SS:LIG	H	0,46	0,31	0,33	1,55

- **Influence of HTC apparatus**

A review of the influence of a wide range of process parameters allowed a demonstration of the positive aspect of hydrolysis enhancement towards the improvement of HTC technology, improving several chemical reactions: dehydration, decarboxylation, deamination and even oxidation [192]. The use of variable operating conditions or specific substrates or reactants is not the only perspective to improve product quality. According to section 2, the transport of components from the SS matrix, the solid-liquid mass exchange rate or solid-solid interactions in a thermodynamic system can be limited by diffusion and convection. Hence, the type and nature of agitator operation that maintains the homogeneity of the mixture and uniformity of the distribution of components plays a significant role in the design of HTC apparatus [193]. Nevertheless, as mentioned by M. Ubene et al. [194], there is still a limited amount of research on the effect of mixing speed or comparison of mixing effects or lack thereof on the HTC process and products. Several scientific publications on HTC but mainly on lignocellulosic biomass have pointed out the key role of heating rate. In general, a higher heating rate promotes the yield of bio-oil at the expense of the yield of solid products. Thus, a low value of reactor heating rate increases the efficiency of carbonization and hydrochars formation. As explained by the researchers [85] the reason could be the enhanced diffusion and convection phenomenon, which promotes chemical reactions, thus reducing the time required to form secondary carbon from intermediate products. Furthermore, low heating rates are also used by HTC apparatus manufacturers, which further can confirm the effectiveness.

HYDROCHARS AS FUELS IN ENERGY APPLICATIONS

- Physicochemical (technical) analysis of sludge and its hydrochars, presented in section 4, is used to initially determine the potential of a given fuel. In practice, thermogravimetric analysis (TGA), which is successfully used under laboratory conditions and widely recommended by the International Confederation of Thermal Analysis and Calorimetry (ICTAC), is used to determine the behaviour, kinetics and thus thermal degradation performance of a given material. This method is one of the few that allows experimental determination of kinetic parameters during thermochemical conversion [172]. Depending on the chosen method of thermal utilization (combustion, pyrolysis and/or gasification), the analysis is carried out under atmospheric (constant-access air), inert (N₂) and/or oxidizing (limited-access, e.g., CO₂, steam, air) conditions, respectively. With this method, changes in the mass of the sample over a given temperature range (TGA curve) are measured under controlled conditions to determine reactivity, phase transitions and thermal stability during heating. In addition to the curve analysis (TG), a complementary differential curve (DTG) is used to determine the rate of mass loss and allow a more effective interpretation of the thermal effects occurring during mass decomposition, thus determining the individual kinetic parameters for well-defined steps [136,103]. This section compares and summarizes the performance of sludge (SS, ADS) combustion, pyrolysis, and gasification and the corresponding hydrochars. Moreover, the overall effect of HTC treatment of sludge on the various stages of thermal conversion, characteristic temperatures, its parameters, performance indexes and reaction

kinetics parameters were determined.

- COMBUSTION

According to the literature review, due to the characteristic mass loss, the combustion stages were divided into: dehydration, devolatilization and combustion, oxidation (combustion) of chars, and the final burnout process. The temperature ranges of the various stages strictly depended on the type and composition of the material under study, so this article provides only sample values of these ranges. As reported by Arauzo et al. [195] for materials with moisture content, the dehydration process was characteristic of low process temperatures - up to about 160 °C. Zhuang et al. [196] on the other hand, noted a smaller temperature range during dehydration of hydrochars compared to sludge, which could be due to the hydrophobic nature of the HTC product. As the temperature increased, there was a release of gaseous parts and decomposition of low-molecular-weight organic matter, characteristic of the degassing stage in the range of about 120/140 - 350 °C [197]. During this stage, at some point there was a reduction (combustion) of volatile matters (VM%), and the following polycondensation processes of reactive organic residues implied an increase (FC%) in the remaining fraction. The stage of further oxidation, in which there was a characteristic mass loss (FC% reduction) at temperatures of 350 - 730 °C, was associated with the combustion of chars, followed by a burnout phase associated with the loss of inorganic carbonate salts with little mass loss [198]. The key parameters of the combustion process and their variation with HTC conditions are summarized in Table 13. The hydrochars had slightly higher ignition temperatures (T_i) compared to the raw materials, resulting from the lower content (VM%) and higher content (FC%) in their composition (Table 3,5,11), and were therefore more difficult to ignite and thus safer to store and transport, as they reduced the occurrence of fire or explosion [103,196]. On the other hand, higher T_i implied higher required energy to initiate the combustion stage [196], nevertheless, as suggested by He et al. [103], increased ash fractions in hydrochars may have had a catalytic effect on reactivity during the combustion stage. Most of the works suggested an increase in T_i after HTC treatment due to the increased aromatization of hydrochars. The other characteristic process temperatures, i.e., burnout (T_b) for which the weight loss was less than 1% w/w/min and maximum (T_m) associated with maximum weight loss, had different trends, probably due to different sludge compositions and different HTC process conditions. [199] According to the results of Arauzo et al [195] and Zhuang et al. [196] the T_b values during the combustion of hydrochars showed a decreasing trend, which may have generally influenced the shorter time required to complete the combustion process compared to the combustion of raw materials. In contrast, studies by He et al [103] showed an increase in T_b and T_m parameters compared to raw materials. The increase in T_b , and thus firing and combustion time, was associated with a significant residual R% (ash) in the hydrochars [136, 185]. However, as suggested by the study of Zhuang et al. [196], burn times may have been shorter for some hydrochars due to the HTC conditions and thus the values of the final ash fraction that catalysed the combustion reactions. In contrast, the results of Peng et al [199] and Ma et al. [200] indicated an increase in T_i , a slight increase in T_b , while a decrease in T_m . Moreover, most studies observed a reduction in the E_a required for oxidation/combustion of chars after the HTC treatment stage [103,199,198,136], although Zhuang et al. [196] observed an increase, which was probably related to the larger temperature range of the kinetic parameters determined. Thus, sludge as a fuel may have been more difficult to burn, and as He et al. [103] explain may have had a shorter combustion range.

On the other hand, despite having a lower E_a value and a higher fuel ratio (FC/VM) in hydrochars, the overall fuel index S , defined as an index for evaluating the efficiency of combustion processes (related to ignition and burnout), had an overall decreasing trend in hydrochars compared to raw materials, which consequently indicated a deterioration of combustion processes. An alternate indicator used in the literature was also the ignition index (D_i). Nevertheless, the higher VM% content of the sludge may have resulted in unstable combustion and high heat loss compared to the hydrochars, so despite the lower S value (or D_i), the hydrochars may have been preferred as more thermally stable fuels. The main reason for this was the conversion of low-energy aliphatic structures into high-energy aromatic structures [198,103, 201].

According to an analysis of TGA results, the HTC process proved to be an effective, but ultimately not good enough way to improve efficiency during combustion, which depended on many factors/parameters. Arauzo et al. [195] showed that factors such as air flow rate during combustion had little effect on parameters with the exception of activation energy during different stages. Hence, other research papers have focused on studies of co-combustion of hydrochars with other fuels [202] or combustion of hydrochars after the hydrothermal co-carbonization process. When using co-substrate (food waste, sawdust) with better energy properties [136,182,183] among other things, a significant increase in the maximum combustion rate (DTG_{max}), a slightly lower average combustion rate (DTG_{mean}), as well as a decrease in T_b values were observed. The combination of sludge with different wastes, in different proportions, ultimately influenced an increase in the S -index improving the overall reactivity of the process [182,183]. Therefore, it is the processes of concurrent HTC, as opposed to tightened HTC reaction conditions, that may have improved combustion efficiency and improved flame stability [203].

Tab [13] Effect of HTC conditions on combustion process parameters

Literature	Sample	T_i	T_b	T_m	S^1	D_i^2	E_a^3	R
-	$T^\circ C (t_{min})$	$^\circ C$	$^\circ C$	$^\circ C$	$min^2 \times ^\circ C^{-3}$	-	KJ/mol	%
Peng, C. et al. (2016)	SS	220	570	500	n.d	$0,75 \times 10^{-2}$	31,34	n.d
	H 180 (30)	276	580	360	n.d	$0,60 \times 10^{-2}$	26,30	n.d
	H 220 (30)	278	580	370	n.d	$0,43 \times 10^{-2}$	24,48	n.d
Zhuang, X. et al. (2018)	SS	229,5	449,7	305,9	$2,90 \times 10^{-8}$	n.d	26,92	57,7
	H 180 (30)	232,7	396,4	306,8	$3,59 \times 10^{-8}$	n.d	28,00	71,3
	H 240 (30)	249,3	443,1	309,7	$1,82 \times 10^{-8}$	n.d	30,16	76,6
He, C. et al. (2013)	ADS	267,3	464	325	$8,17 \times 10^{-8}$	n.d	37,64	37,5
	H 200 (240)	267,3	478,5	372,3	$2,53 \times 10^{-8}$	n.d	21,25	56,5
	H 200 (360)	271,3	476	417,6	$3,46 \times 10^{-8}$	n.d	33,56	51,3
Arauzo, P.J. et al. (2020)	ADS	222,3	467,3	305,3	$9,22 \times 10^{-8}$	n.d	82,15 ⁴	n.d
	H 260 (120)	268,0	437,0	294,0	$3,21 \times 10^{-8}$	n.d	73,87 ⁴	n.d
	H 260 (240)	269,5	435,5	293,5	$3,14 \times 10^{-8}$	n.d	65,07 ⁴	n.d

¹ $S = ((dw/dt)_{max} \times (dw/dt)_{mean}) / T_i^2 \times T_b$, $(dw/dt)_{max}$ = maximum rate of weight loss (wt.%/min), $(dw/dt)_{mean}$ = mean rate of weight loss (wt.%/min) [...]

² $D_i = R_m / (T_m \times T_i)$, R_m : maximum loss rate [...]

³ E_a - Activation energy for combustion

⁴ For 20 ml/min (air flow rate)

Tab [14] Influence of co-HTC process on combustion process parameters

Literature	Type of co-substrate	Sample	T_i	T_b	T_m	DTG_{max}	DTG_{mean}	S	E_a
-	-	$T^\circ C (t_{min})$	$^\circ C$	$^\circ C$	$^\circ C$	(%/min)	(%/min)	$(\% / (min^2 \times ^\circ C^3) \times 10^{-8})$	KJ/mol
	(F) - Fir	SS	203	587	470	12,99	4,86	261	122,59

Wilk, M. et al. (2021)		H 200 (120)	245	568	371	19,24	3,75	211,6	119,55
		H 200 (120) 20% F	247	566	359	24,54	4,36	322,5	133,03
Zhao, J. et al. (2022)	(WDG) - Wet distillers grains	SS	299,8	318,7	304,9	1,43	0,41	2,03	n.d
		H 180 (30)	300,5	323,2	316,7	0,85	0,36	1,06	n.d
		H 180 (30) SS:WDG (4:1)	288,4	310,8	293,9	1,76	0,39	2,62	n.d
		H 180 (30) SS:WDG (3:1)	290,9	302,6	295,8	1,69	0,58	3,82	n.d
		H 180 (30) SS:WDG (2:1)	287,1	299,3	293,1	1,59	0,51	3,31	n.d

$$^1S = (DTG_{max} \times DTG_{mean}) / (T_i^2 \times T_b)$$

• PYROLYSIS

The stages of the pyrolysis process, carried out under inert (N₂) conditions, have been broadly divided into: dehydration, devolatilization and thermal degradation of inorganic minerals [201]. In the case of sewage sludge, the first stage was characterized by a small mass loss associated with the evaporation of moisture and light volatile compounds. The second stage of devolatilization occurred in a rather characteristic temperature range from about 150/200 - 550/600°C [201,200,199,204] in which a significant mass loss of SS components (cellulose, hemicellulose, proteins, lipids) was observed. The last stage was characterized by a slightly higher mass loss compared to the first stage at temperatures > 600°C, where degradation of inorganic compounds (e.g. calcium carbonate) in the ashes or non-biodegradable compounds (e.g. certain lignin fractions) occurred [201,200,199]. As can be seen from Table 15, both HTC and operating conditions affected the process, degassing efficiency, and kinetic parameters of pyrolysis. Moreover, they were more dependent on HTC temperature than on residence time. Liu et al. [201] observed a decrease in the initial temperature of devolatilization (T_i), final temperature of devolatilization (T_f) and peak temperature (T_p) - corresponding to a decrease in the peak rate of devolatilization R_p, as well as a decrease in the average rate of devolatilization R_v. Consequently, the CPI pyrolysis index (defined as pyrolysis yield, the course of the pyrolysis reaction) determined by the above parameters, also showed a decreasing trend, indicating a general deterioration in pyrolysis performance after HTC treatment, but on the other hand an improvement in the thermal stability of "charring" of hydrochars as in combustion. The results of previous work [...] by these authors, also suggested a deterioration in pyrolysis reactivity after HTC treatment, which was explained by the overall evolution of aromatic structures [...] Similar results could be observed in other studies by Zhang et al [204] and Ma et al. [200], but in this case T_i and T_f showed an increasing trend after HTC treatment, which increased thermal stability, but to a greater extent decreased the final values of CPI outgassing rates. Thus, the overall pyrolysis results for sludge were more favourable compared to its hydrochars, as higher R_p and R_v values and lower T_i indicated easier and faster degassing.

During the study, a significant effect of heating rate was observed (from 5 to 20 °C/min) which altered the trends of the above-mentioned parameters, effecting up to a 15-fold increase in CPI in hydrochars, for the highest heating rates. Nevertheless, according to the literature review, co-HTC processes prior to pyrolysis (e.g., with rice straw, wheat straw, sawdust) seemed to be much more attractive and beneficial, significantly improving the outgassing rates of hydrochars from various SS and waste mixtures, mainly due to the high CPI of hydrochars

from single wastes, and ultimately lowering the E_a values of hydrochars (agricultural wastes/SS) compared to HTC for single sludge [205,200,204].

Tab [15] Effect of HTC conditions on pyrolysis process parameters

Literature	Sample	T_i	$T_{f/b}$	T_{p1}	T_{p2}	R_{p1}	R_{p2}	CPI^1	CPI^2
-	$T^\circ C (t_{min})$	$^\circ C$	$^\circ C$	$^\circ C$	$^\circ C$	%/min	%/min	$\% \times ^\circ C^{-3} \times \text{min}^{-2}$	$\% \times ^\circ C^{-2} \times \text{min}^{-1}$
Liu, W. et al (2022)	ADS	228,32	839,09	283,21	327,43	4,87	4,25	$3,37 \times 10^{-5}$	n.d
	H 180 (120)	193,56	832,89	230,80	353,12	1,96	3,70	$1,31 \times 10^{-5}$	n.d
	H 200 (120)	196,24	827,08	242,79	359,43	1,68	3,00	$5,43 \times 10^{-6}$	n.d
	H 240 (120)	201,04	821,79	246,52	419,82	1,66	1,89	$1,75 \times 10^{-6}$	n.d
Zheng, X. et al. (2020) ²⁰⁶	SS	174	800 ³	269,2	321,6	0,24	0,2344	n.d	$4,75 \times 10^{-4}$
	H 180(120)	200,4	800	238,2	344,1	0,0959	0,1959	n.d	$2,00 \times 10^{-4}$
	H 200 (120)	206,7	800	231,2	349,8	0,0982	0,1642	n.d	$1,60 \times 10^{-4}$
	H 220 (120)	203,5	800	227,3	358,3	0,0992	0,1252	n.d	$1,30 \times 10^{-4}$

¹ $CPI = ((-R_p) \times (-R_v) \times M_A) / T_i \times T_p \times \Delta T_{1/2}$, where M_A - pyrolysis weight loss, $\Delta T_{1/2}$ half-peak width temperature range

² $CPI = D_{max} / (T_{max}(T_f - T_i))$, D_{max} - represents the maximum mass loss rate

³All samples were gasified at 800°C

Tab [16] Influence of co-HTC process on pyrolysis process parameters

Literature	Type od co-substrate	Sample	T_i	$T_{f/b}$	T_m	DTG_{max}	DTG_{mean}	R	D_i
-		$T^\circ C (t_{min})$	$^\circ C$	$^\circ C$	$^\circ C$	(%/min)	(%/min)	%	$\%^2 K^{-3} \text{min}^{-2}$
Zhang, S.et al. (2020)	(RS) - raw rice straw	SS	157,27	614,21	311,33	5,67	1,64	57,39	$11,25 \times 10^{-7}$
		H 200 (120)	165,29	638,61	359,56	2,85	1,05	73,71	$1,86 \times 10^{-7}$
		H 200 (120) 3RS/7SS	212,15	570,94	381,07	9,68	1,44	63,55	$32,10 \times 10^{-7}$
		H 200 (120) 5RS/5SS	223,66	559,17	381,21	13,60	1,73	55,43	$53,72 \times 10^{-7}$
Ma, J.et al. (2019)	(SD) - sawdust	SS	148	808,9	290,7	6,75	2,22	46,93	$3,57 \times 10^{-7}$
		H 220 (60)	185,9	847,1	235,6	2,91	1,48	64,46	$1,60 \times 10^{-7}$
		H 220 (60) SD:SS (1:3)	199,9	772,6	374,3	10,27	2,28	52,54	$1,18 \times 10^{-6}$
		H 220 (60) SD:SS (1:1)	212,7	723,8	377,5	13,36	2,88	46,22	$1,88 \times 10^{-6}$
		H 220 (60) SD:SS (3:1)	228,1	664,3	381,2	18,21	3,90	37,94	$3,79 \times 10^{-6}$

$D_i = (DTG_{max} \times DTG_{mean}) / (T_i \times T_m \times \Delta T_{1/2})$

• GASIFICATION

The efficiency of the gasification process depended on the quality of the fuel as well as the gasification agent in the form of CO_2 , H_2O , O_2 , air or mixtures, which determined both the final composition of the synthesis gas (energy carrier) and the thermal efficiency of the process [189]. Researchers paid particular attention to CO_2 for both increasing the thermal efficiency of the process and effective reuse in the context of global warming. Overall, gasification processes could be preceded by pyrolysis processes (gasification initiated at high temperature) and be carried out separately (supply of the gasification agent from the beginning of the thermochemical processes). In the first case, the gasification stages consisted of drying, devolatilization of organic matter, final decomposition of matter contained in chars, followed by gasification of chars, while in the second case, the gasification stages preceded by drying, consisted of the degassing of organic matter (approx. 200 - 600°C), followed by gasification (partial oxidation) of the remaining carbonates at temperatures (600-1200°C) [207,189]. A

relatively low level of conversion (mass loss) was observed during the gasification of crude SS, because, as noted earlier, the sludge had a low FC% content and a high amount of ash. Zhuang et al. [207] extracted the gasification parameters of SS and their hydrochars from two stages - degassing and gasification. According to conversion curves, HTC treatment and reaction intensification affected the increase in T_i and significantly increased T_b in the gasification stage, consequently increasing the duration of gasification. As the researchers explain, one of the reasons that occurred may have been an increase in the FC% content of hydrochars, the main reactant of the gasification process, at the expense of VM% reduction. The maximum conversion rate was also altered due to an increase in aromatics after the HTC process, which in turn resulted in a delay in reaching the gasification peak. However, these changes were negligible, and the average conversion rate remained the same compared to the raw materials (Table 17). While the above parameters were not conducive to improving the gasification rate, an increase in syngas quality and an increase in H_2 concentration due to an increase in the FC% content of the hydrochars were observed during the study [208,207]. What's more, the HTC process had a positive effect on the amount of the main by-product - tar, reducing its amount by half compared to the tar from the raw material.

Studies of pyrolysis combined with gasification of hydrochars [189] showed the same trend of parameter behaviour during pyrolysis, and as a result, a low degassing rate compared to sewage sludge, although the subsequent CO_2 gasification step at $900\text{ }^\circ\text{C}$ significantly improved the quality of syngas from hydrochars - especially H_2 and CO [189,207]. Moreover, there was a decrease in the average gasification reactivity of the samples, which was related to FC% , and the results of the kinetic parameters obtained indicated a favourable decrease in the activation energy E_a (lower gasification resistance), which decreased with increasing HTC temperature despite the increase in aromatization [208]. A similar effect was also observed in other work [209] using a steam gasification agent, showing an overall improvement in the gasification efficiency and quality of hydrochars compared to sewage sludge. There have been few literature reports on the effect of sewage sludge co-HTC on the characteristic temperatures (individual stages) and process indicators considered in Table 17. However, single studies on, for example, the addition of sawdust in the co-HTC process with sewage sludge confirmed a positive effect (enhanced effect) on gasification in the form of an increase in the calorific value of the syngas - as a result of an increase in FC% as well as an overall decrease in S and N% (also discussed in chapter 4)) in comparison to SS hydrochars. In addition, the addition of substrate also facilitated the preceding pyrolysis processes (Table 16), making co-HTC processes effective thermochemical processes [189].

Tab [17] Influence of HTC conditions on gasification process parameters

Literature	Gasification agent	Sample	T_i	T_b	T_m	$(da/dt)_{max}$	$(da/dt)_{mean}$	DTG_{max}	E_a
-	-	$T^\circ\text{C}$ (t_{min})	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$	s^{-1}	s^{-1}	(%/min)	KJ/mol
Zhuang, X.et al. (2020)	CO_2	SS	702	955	866	0,066	0,023	n.d	142,90
		H 180 (30)	745	991	883	0,067	0,023	n.d	153,59
		H 210 (30)	758	1113	886	0,073	0,025	n.d	129,79
		H 240 (30)	764	1158	878	0,071	0,024	n.d	120,62
Zheng, X.et al.(2021)	CO_2	SS	n.d	n.d	889	n.d	n.d	0,8663	467,37
		H 180 (120)	n.d	n.d	878	n.d	n.d	0,6000	403,51
		H 200 (120)	n.d	n.d	879	n.d	n.d	0,6487	410,78
		H 220 (120)	n.d	n.d	877	n.d	n.d	0,6416	401,79
		H 240 (120)	n.d	n.d	879	n.d	n.d	0,6349	394,02

SUMMARY OF THE COLLECTED KNOWLEDGE AND CHALLENGES

According to the above review of complementary thermal and thermochemical methods, the disposal of sewage sludge, on site (WWTP), is both technically and technologically challenging. Table 18 summarizes the advantages and disadvantages of available solutions compared to the proposed HTC system.

Tab [18] Summary of current thermal sludge management solutions at WWTP

Literature	Methods of direct disposal of sludge	Advantages		Disadvantages	
		Technological	Technical and economic	Technological	Technical and economic
Wang et al (2018) ¹¹²	Hydrothermal carbonisation (HTC)	(+) Possibility of using wet sludge (+) low emissivity of the process (+) Increase in dewatering of solid products. (+) Sterilization and stabilization and valorisation of solid products (+) The possibility of reducing the harmfulness of HTC liquids by using WO (+) The possibility of using products (hydrochars and HTC liquids) in a closed loop on WWTPs	(+) No need for additional dryers (+) Possibility of high heat recovery (+) Reduction of costs of sludge management	(-) Retention of heavy metals in hydrochars (-) High ash content in hydrochars	(-) Installation profitability depending on the size of WWTPs (-) Difficult to collect products (-) Compared to other methods - technically complex installation
L Yan et al (2022) ⁴⁹ Ngo, P.L. et al. (2021) ⁸⁶	Thermal hydrolysis (THP)	(+) possibility of using wet sludge (+) low emissivity of the process (+) Intensification of biogas production in HT +AD system (+) Increase in dewatering of final solid products in compared to ADS (+) Sterilization of solid products	(+) No need for additional dryers (+) Partial heat recovery (+) Reduction of costs of sludge management	(-) Formation of by-products during THP (e.g melanoids) that can inhibit AD processes (-) Relatively poor dehydration of the solid products (-) The need to purchase additional reagents e.g H ₂ O ₂ for reduction of refractory materials	(-) Installation profitability depending on the size of WWTPs (-) Required to provide additional heat
L Slezak et al. (2023) ⁴⁷	Pyrolysis/ Torrification	(+) Lower amounts of flue gases and emissions of NOx, dioxins and furans (+) Sterilization and stabilization and valorisation of solid products	(+) The ability to apply the process on both large and small scales. (+) heat recovery and electricity production (+) For specific reactors - the possibility of using oil and gas as fuel for the production of	(-) Retention of heavy metals in biochars (-) High ash content in biochars (-) Volatile organic compounds, CO in the gas (-) Depending on the system - bio-oil management required	(-) Construction of additional dryers (-) Additional heat source required (-) Additional costs of gas cleaning

			reactor heat energy		
L Kiper, J. et al (2019) Kurt, M. et al (2015) Bozym. M. et al (2017)	Drying	(+) Significant weight reduction	(+) Possibility of using additional heat from AD cogeneration system (+) Energy-saving solutions for solar dryers (+) Lower export costs	(-) High explosiveness and storage problems (-) Long drying time in most cases (-) Dependent on environmental conditions (-) Increased concentration of toxic components in the final waste and the need for further disposal	(-) Cost-effective only for larger wastewater treatment plants
R.Rauch et al. (2013) 42	Gasification	(+) Production of a useful gaseous fuel (syngas) (+) Lower emission of harmful substances (+) High energy efficiency	(+) High heat recovery and electricity production	(-) The need to use dried sludges (-) The need to purify the syngas (-) Tar formation	(-) High investment and initial operating costs (-) Construction of additional dryers
Malczewska. B et al. (2017) ²¹⁰	Combustion	(+) Destruction of organic matter and complete mineralization of the sludge (+) Recovery of components from ashes, e.g. phosphorus (+) The possibility of burning both sludge: stabilized and unstabilized	(+) Possibility of autothermal combustion (+) Energy recovery used for pre-drying sludge (+) Reduction of costs of sludge management	(-) High emission of dusts, gases (SOx, NOx, HCL, HF) (-) The need for ash storage (-) The need to use dried sludges	(-) Construction of additional dryers (-) Profitable only for the largest WWTPs (-) The high investment and operating cost (-) High exhaust gas cleaning costs

As can be seen from Table 18, an appropriate product valorisation strategy appears to be an important milestone in the implementation of this type of technology at a WWTP. The results presented in section 4 on the properties of the products obtained show that adjusting most of the parameters, such as increasing the intensity of the reaction, decreasing the moisture content of the sludge prior to the HTC process, recirculating the aqueous phase, increasing the proportion of co-substrate or using acid catalysts, show a positive effect on the HHV calorific values or FC of the solid products obtained, with the best values obtained for hydrothermal co-carbonisation processes with an increased proportion of co-substrate, while the least improvement was observed when salt catalysts were used. The TGA results presented in section 5 further confirmed the attractiveness of using co-HTC as a pre-treatment to improve the efficiency of combustion, pyrolysis, and gasification processes. The overall degree of the carbonisation process, and thus its efficiency, can be also attributed to the N, O, S content [%] of the resulting hydrochars. For instance, the main component of the sludge is N-protein, which gradually decomposes into the liquid fraction depending on the process temperature [mechanism 1]. Exemplary test results [tab.4] confirm the possibility of carbonization of some proteins depending on the set process temperature due to the gradual decrease in the content of

N [%] and the increase in the content of various forms of nitrogen in the liquid fraction. These results also indicate a negligible effect of the residence time on the further reduction of these components. However, as mentioned before, a greater effect of removing N% from the matrix was achieved by the addition of AOPs or Mg-Ga (LDH), although these are reagents that would require an industrial scale cost-effectiveness analysis. Interestingly, compared to the above conditions, the greatest effect on the removal of nitrogen-N from the hydrochars matrix, and thus the elimination of gaseous pollutants during combustion, was due to the high initial moisture content of the raw material, possibly because of an enhanced hydrolysis reaction, which is a promising aspect in the case of low-cost SS dewatering before the process. The final O [%] content in the solid product can generally indicate the efficiency of the dehydration and decarboxylation processes, and consequently the degradation of a wide range of sludge matrix components to the liquid fraction, and the degree of reduction is definitely influenced by the use of AOP or Mg-Ga acid catalysts, the maintenance of a higher pH by recirculation of the aqueous phase, but also an increase in severity factors in the process. On the other hand, increasing the proportion of substrate in the sludge mixture in the co-HTC process increased the O [%] content in the HTC solid product, which was associated with a higher amount of volatile matter [VM %] in the additional substrate and had a significant impact on the thermal decomposition behaviour of hydrochars. In turn, the sulphur content in the solid products was relatively the least important, due to the low percentage [%], however, the addition of salt catalysts and phase recirculation had a positive effect on its reduction, ultimately affecting the limited pollution of hydrochars during combustion in the form of SO_x. Analysing the other properties, all the studies noted an upward trend in the mineral content - ash% - of the hydrochars, which included fractions of heavy metals, alkali metals or alkaline earth metals. The high ash content may have deteriorated the fuel quality, affecting the performance of the thermal processes, the thermal efficiency and ultimately the operating conditions during thermal conversion, causing phenomena such as slag formation. On the other hand, Gai et al. [209] and Zheng et al. [208] noted that ash rich in alkali metals, alkaline earth metals and heavy metals such as Ni, Fe could catalyse gasification processes, which, according to chapter 5, represented an interesting prospect for the use of hydrochars in the power industry instead of raw sludge. Moreover, most of the heavy metals contained in the sludge were immobilised in the solid products of the HTC, which behaved as an adsorbent for these pollutants, which could open up prospects for the safe reuse of HTC liquids, for example, in agriculture or biological processes. In the case of liquids, the HTC process significantly increases the overall COD content, but also the proportion of TN in the leachate, which may have an impact on the lower C/N ratio that determines biodegradability and optimal conditions during further methane digestion. In addition, the HTC process itself, as well as the increased operating conditions (temperature, residence time) or the increased degree of dehydration of the initial SS, has a significant impact on the high concentration of the primary inhibitor of methane fermentation processes, N - NH₄⁺. Nevertheless, the BMP tests [211], laboratory semi-continuous anaerobic digestion process [212] and industrial scale studies [147] conducted for HTC process liquids with sewage sludge have shown an increase in biogas production, and it is therefore important to further investigate the composition of leachates obtained under varying process conditions and to evaluate their co-fermentation with SS to ensure full optimisation of the solid and liquid products obtained.

Currently, on an industrial scale, organic acid catalysts are probably the most widely used, as they show both improved conversion rates and solid product quality and, compared to inorganic catalysts, are less expensive, cause fewer problems with reactor corrosion during HTC, and ultimately imply lower S [%] and thus SO_x pollution during subsequent combustion. Nevertheless, among the collected data on the HTC process, the most promising solution seems to be the use of co-HTC ADS with other available wastes, in order to energetically valorise the

final solid products (by reduction of ash content (heavy metals) [%], N [%] S [%], and increase in FC [%] and HHV), as well as the possibility of using highly concentrated (COD) HTC liquid products in the anaerobic co-digestion (AD) process with SS. The effectiveness of integrating the AD+HTC system on the WWTP is further confirmed by the positive mass and energy balance obtained by C.I Aragón-Briceño and other works included in the article [213]. Moreover, hydrochars could also be used as inoculum carriers during biogas production [214]. Thus, the approach under consideration could potentially solve the problems of disposing of other wastes, reduce the cost of the energy requirements of the HTC process as well as reduce the costs associated with the use of additional chemical reagents (catalysts). On the other hand, the use of additional waste may involve logistical difficulties, so the possibility of using external waste is strictly dependent on the location of the WWTPs, but also ultimately on legal permits. During the review, however, special attention was paid to the possibility of using screenings as co-substrate - a readily available fraction of mechanical waste from wastewater treatment plants with a high organic matter content, which, according to Zvimba et al. [179] can improve the final energy value of the resulting hydrochars. However, research in this direction is very limited, and in order to demonstrate the real potential of these wastes and the possibility of their use, research must be conducted toward the necessary required amount of these wastes toward the energy valorisation of hydrochars and their impact on the composition of process liquids used in a sewage sludge biogas plant.

CHALLENGES AND PROSPECT FOR FUTURE

This review systematizes the knowledge of the relevant physicochemical properties of water under subcritical conditions trapped in the sludge matrix and their further influence on the reaction mechanisms of the various components and, consequently, the potential final products. The influence of various operating parameters was determined, i.e. temperature, residence time, solids concentration (moisture content), pH or the ratio of various wastes (components) in the mixture on the quality of solid products in terms of renewable fuels and the quality of liquid products in terms of raw materials for biogas production. In order to definitively verify the effectiveness of the HTC method in the context of biofuel production, TGA results of combustion, pyrolysis and gasification of dried sewage sludge and its hydrochars were compared. In line with the above state of the art, the following research gaps, challenges, and future prospects are presented, crucial to the feasibility of designing and implementing HTC systems at WWTPs:

1. The study of reaction mechanisms has been extensively described in relation to the reaction severity factor - mainly temperature. It seems important from the point of view of HTC process design to present reaction mechanisms depending on parameters such as sludge moisture content or change in initial pH conditions, as these factors also have a significant impact on reaction pathways, component interactions and thus product quality, but above all affect the energy intensity (temperature and time value) of the HTC process.
2. The limited research on the degradation, interaction and/or carbonisation of important sludge components in the form of lipids and humic substances needs to be supplemented, as it may influence the further optimisation of HTC operating conditions and, consequently, the improvement of the mass-energy balance.
3. Missing findings on the effects of moisture content, aqueous phase recirculation or salt catalysts on the migration of heavy metals between the solid and liquid phases are necessary to assess further product applications in both energy and agricultural contexts. The moisture

content of the sludge is particularly important, as it is a variable that depends on the operators of the WWTPs.

4. From the point of view of biogas production from HTC liquids in WWTPs, it is important to study the influence of acid, alkaline, salt catalysts, but above all the influence of different wastes (co-substrates) and its proportions on the composition of the HTC liquid and its subsequent biomethane potential (BMP), in order to avoid inhibition of biological processes in the future, which would limit or exclude the possibility of managing additional wastes in WWTPs.
5. In view of the effective action of acid catalysts during the HTC process, improving the quality of solids in terms of energy, further research is required comparing low-cost and readily available reagents that could be economically justified for the future.
6. In line with point 5, the effect of catalyst addition on HTC liquids quality during BMP testing also needs to be investigated, as COD mg/l is not an accurate indicator due to coexisting process inhibitors.
7. Due to the interesting preliminary results of the liquid phase swirls for the HTC process, further studies are required to determine the impact on, among other things, the methane potential of the BMPs. The use of HTC leachate as catalysts is an interesting prospect for managing this fraction for WWTPs and reducing the cost of purchasing chemical reagents.
8. The intensification of mass and heat exchange through mixing processes (but also the rate of heating) can influence both hydrolysis and subsequent secondary carbonisation processes and, consequently, the quality of the HTC products (as in the case of residence time of the sludge in the reactor). Thus, research and analysis of the performance of these HTC process variables is needed to increase the effectiveness of HTC modelling.
9. The high ash content, but especially the heavy metal content of the hydrochars, may be a bottleneck for the application of HTC technology at WWTPs due to the further potential cost of hydrochars export. Waste blending, improving quality, depends on many factors, including the location of the WWTP, legal permits, etc. Thus, further research into the removal of heavy metals in a cost-effective manner is particularly important and could be a milestone for HTC at WWTPs.
10. From the point of view of WWTPs, further research into the optimisation of HTC reactor conditions (e.g. temperature, residence time, initial pH and moisture) for the energetic valorisation of solid and liquid products is important. The results of these studies will ultimately determine the need for heat and electricity, the purchase of reagents or the need for filter work (approx. 15-25% db) or thickeners (5 -11% db), which in turn affect further operating costs.
11. There is a need for further research into the use of HTC liquids at WWTPs. The potential for denitrification processes in biological reactors generally used at WWTPs may be an alternative way of managing leachate in the event of excessive quantities in relation to the hydrochars generated, which depend mainly on the initial moisture content of the feedstock. As shown in the BMP studies, the ratio of SS to HTC liquids is limited, due to process inhibitors, so increasing the potential for HTC leachate management at WWTPs may also be an important system operation issue.
12. During the analysis of the TGA studies, it was noted that there was no determination of the effect of other relevant HTC process conditions, (e.g. changes in pH or sludge moisture content), on the reactions of the resulting hydrochars during incineration, pyrolysis, or gasification. Such studies will further visualise the potential need to optimise the operating conditions described in section 10.
13. Co-HTC improved both combustion and pyrolysis characteristics and behaviour, so further research is important to determine the synergistic effect of co- HTC on gasification yield and quality, as this may be the most favourable method for further hydrochars utilisation.

CONCLUSION

Despite the availability of thermochemical solutions for sludge disposal, there is a lack of consistency in the development of a cost-effective and efficient method that rationally exploits the added value of residual waste in the context of the circular economy. Regulations in many countries around the world limit the possibility of using treated sludge as a product, due to its mandatory waste status at the point of generation, the loss of which is linked to the fulfilment of a number of different criteria, hence the reduced residual waste would require further export costs, relevant in terms of impacting total operating costs. However, the proposed HTC technology is considered in terms of a complement to biological methods (AD) and a substitute for other thermal processes available at larger wastewater treatment plants - e.g. dryers. The use of downstream disposal in the context of sludge management WWTPs, where HTC could be a pre-treatment for processes such as incineration and gasification, may be limited to the largest facilities, but this does not preclude the need to valorise these wastes for external use, which could reduce export costs in the future. Thus, taking these factors into account, the main results of the work are summarised in terms of the potential for energy valorisation of the products:

- The reaction severity factor (temperature, time) affects the increase in secondary carbonization and hydrochars dehydration, and consequently improves technical energy indicators such as HHV. The TGA results of the basic efficiency indicators of the combustion and pyrolysis processes show a general downward trend with an increase in the severity of the reaction, which is associated with an increase in aromatics, but nevertheless these fuels are characterized by an increase in stability. In the case of gasification, the reaction severity factor affects, among other things, the increase in gasification time, due to the increase in FC%, but also the improvement in syngas quality. On the other hand, it was observed that an increase in reaction severity can lead to an overall decrease in the potential for biogas production from HTC liquids. Thus, these results indicate the need to optimize the reaction severity factor, in order to achieve a compromise between the quality of solids, liquids, and operating costs of the HTC process.
- Increases in TS% in sludge in the range of 10 - 30% indicated energy improvements in hydrochars and HTC liquids quality (BMP tests) compared to feedstock, thus both filter presses and thickeners can be considered for WWTPs.
- The use of catalysts may produce an equivalent effect to the increase in temperature. Test results confirm an overall improvement in dewaterability, a reduction in N% and S% impurities, and an increase in the calorific value of HHV hydrochars. The best results are observed for organic acids, especially citric acid.
- Recirculation of the aqueous phase in the HTC process, shows a positive effect on improving the quality of hydrochars (as in the case of acid catalysts), and may prove to be another way to manage HTC liquids on WWTPs
- Co-HTC processes of sludge with various wastes significantly improved the HHV, reduced the usual undesirable fractions of ash, heavy metals, S%, N% content. TGA results further confirmed the improved efficiency of combustion and pyrolysis

processes, so this may currently be the cheapest and most effective way to valorize sewage sludge in the context of biofuels.

- Gasification processes may prove to be the most effective method for the energetic use of sludge hydrochars.
- Co-HTC processes of digested sludge and screenings from WWTPs may be a suitable way to dispose of the two wastes on site.

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