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# Hydrothermal Carbonization of Digestate Produced in the Biogas Production Process

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**Abstract:** In agricultural biogas plants, besides biogas, the by-product digestate is also produced. Due to its high moisture content and organic origin, it can successfully be applied in the hydrothermal carbonization process to avoid the fate of landfilling. This paper reviews the properties of agricultural digestate and its hydrothermal conversion (HTC) into hydrochar and process water. The type of feedstock and the parameters of the HTC process, such as temperature, pressure and residence time, affects the physical and chemical characteristics of hydrochar. Therefore, its possible application might be as a biofuel, fertilizer, soil improver, adsorber, or catalyst. In this paper, the properties of hydrochar derived from agricultural digestate are widely discussed.

**Keywords:** biogas; digestate; hydrochar; hydrothermal carbonization; biofuel

## 1. Biogas Production and Fermentation Process

Agricultural biogas plants are installations where biogas is produced. Biogas is a fuel which can be converted into heat or electricity. Biogas is primarily made from organic waste and biomass, so it is classified as a renewable energy source, e.g., wind and solar [1]. Biomass is a renewable energy source, an organic residue from agriculture, forestry and urban development that can be reused with environmental benefits [2]. Agricultural biomass consists mainly of cellulose, hemicellulose, lignin, and lipid extracts. It has a high hydroxyl, carboxyl, and phenolic group content and a low initial carbon content [3]. The most popular method used to obtain biogas is anaerobic digestion. This is a biochemical process where microorganisms convert waste into biofuel. Biogas contains predominantly methane and carbon dioxide but also hydrogen sulphide and nitrogen [4]. To increase the concentration of methane, various purification methods are used.

Water and amine scrubbing, adsorption, and membrane technologies are the most popular. As a result, purified biogas is produced, which is called biomethane [4,5]. Biomethane contains more than 95% of methane. Thus, it can be directly used in industry [6]. In Europe, the combined production of biogas and biomethane in 2020 was around 200 TWh. It is estimated that the production will increase fivefold by 2050, reaching more than 1000 TWh. This amount of biomethane could cover up to 30–40% of gas consumption in the EU [7,8]. In 2020, Denmark and Sweden were the leaders in producing biomethane as a transport fuel in Europe, followed by the Netherlands, the United Kingdom and Norway [9].

Figure 1 depicts a scheme of biogas and digestate production. Firstly, the feedstock is directed into the fermentation chamber. As a result of the anaerobic digestion, biogas and digestate are obtained. The biogas can produce heat, electricity and be purified to become biomethane. Digestate is a solid by-product of biogas production. The proper management of this by-product might be beneficial for the environment. Digestate is a nutrient-rich substance that stimulates the growth of plants. A lack of odour in comparison to initial feedstock, for instance, manure, is another advantage [10]. It consists of organic compounds, macronutrients, and micronutrients. Digestate is mainly built of carbon,

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nitrogen, phosphorus, potassium, and sodium. The amount of carbon in the digestate indicates the efficiency of the anaerobic digestion process. Nitrogen is a crucial compound if the intention for digestate is used as a fertilizer. Phosphorus is also an essential element in the digestate. According to Wang et al. [11], the phosphorus content of silage and manure digestate was 1.35%, sewage sludge 2.7%, and swine manure 11.5% in their research [11]. Digestate can also contain cellulose, hemicellulose, and lignin. To produce more biogas, digestate with a high amount of cellulose and a trace of lignin is returned to the reactor, where the anaerobic digestion process is performed [11].

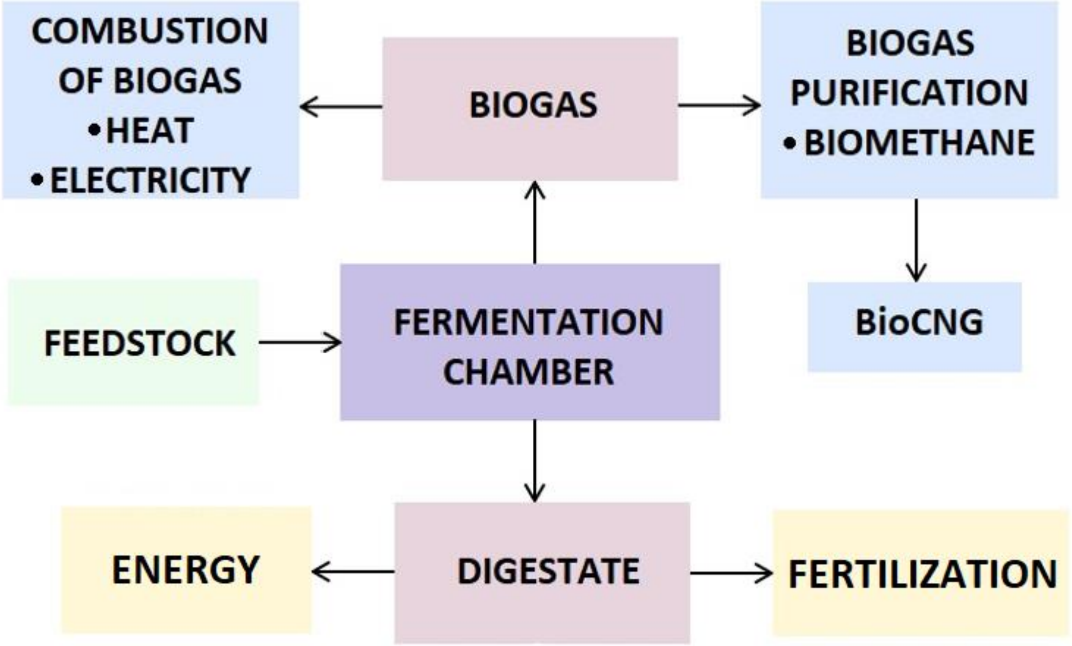

**Figure 1.** Scheme of biogas and digestate production.

Each year around 180 million tonnes of digestate are produced in Europe, of which 120 million tonnes come from agricultural biogas plants. Germany has 87 million tonnes and Italy 30 million tonnes [12]. Due to the relatively high nitrogen content, digestate is generally used in agriculture as a fertilizer. It is also considered a material which has the potential to store 50–80% carbon in the soil. This contributes to the reduction of emissions of carbon dioxide into the atmosphere [13].

The type of agricultural biogas plant depends on the technology used and the applied substrate. Agricultural waste is used in most biogas plants. It is primarily manure, slurry and plant residue, e.g., plant stems and leaves or food waste. European farms produce 1.4 billion tonnes of manure annually [14]. The common disposal methods are usually burning or scattering crops. Scattering is dangerous for the environment as it contributes to increased carbon dioxide and methane emissions into the atmosphere. As a result, excessive greenhouse gas emissions occur [15].

Another problem is landfilling, which is responsible for c.a. 30% of the total methane emission into the atmosphere. If properly managed, this emission could be used for energy purposes and may contribute to reducing the greenhouse effect [16]. Nowadays, food waste is a growing problem. Spoiled or expired food is predominantly obtained from restaurants, bars, and the food industry [17]. Around the world, food waste production is c.a. 1.3 billion tonnes annually, with India producing the most waste [17,18]. Currently, the disposal of food waste is usually landfill or incineration. A eco-friendlier alternative is the fermentation process. Food waste also contains sugar and cellulose, which improves the parameters of biogas. The sugar, cellulose and hemicellulose content depends on the type and quality of waste. Cellulose and hemicellulose can be formed from plant polysaccharides called sugar polymers. During their fermentation, the sugar required for biogas production is obtained [18,19]. Different kinds of waste can also be used as feedstock in biogas plants, namely: from the dairy industry (waste from the production of cheese, milk, and yoghurt, e.g., whey), distilleries (waste from the production of beer, e.g., malt dust and yeast beer) and slaughterhouses (e.g., meat or animal blood) [20].

In 2020, global biogas production capacity reached 20.1 GW. There were 17,662 biogas plants in Europe, and the total electricity generated from the biogas amounted to 167 TWh [5,21]. The leader of the biogas market is Germany, where in 2019, 9692 biogas plants were established [22]. Table 1 shows the European country's total biogas energy supply per capita in 2019. According to the data, the biogas supply per capita is the highest for Germany, followed by Denmark, then Finland, which reached the same level as Italy and Austria resulting in 1 GJ/cap. Biogas supply per capita for Belgium, Croatia, Sweden, Norway, France, Switzerland, and Estonia was below 1 GJ/cap. Table 1 also presents a comparison of the supply of biogas in 2019 to the natural gas supply. In the case of Sweden, Denmark and Germany, the supply per capita was above 0.1 GJ/GJ_NG, whereas for Sweden, the highest value, 0.193 GJ/GJ_NG, was found. Other countries are listed below 0.1 GJ/GJ_NG, with Belgium reaching a 0.026 GJ/GJ_NG [23].

**Table 1.** Total biogas energy supply per capita and a comparison of the supply of biogas to the natural gas supply by country in Europe in 2019 [23].

| Country | Total Biogas Energy Supply per Capita [GJ/cap] | Supply of Biogas to Natural Gas Supply per Capita [GJ/GJ_NG] |
|---|---|---|
| Germany | 3.8 | 0.1 |
| Denmark | 2.9 | 0.155 |
| Finland | 1.4 | 0.089 |
| Italy | 1.4 | 0.033 |
| Austria | 1 | 0.028 |
| Belgium | 0.8 | 0.015 |
| Croatia | 0.8 | 0.034 |
| Sweden | 0.8 | 0.193 |
| Norway | 0.7 | 0.016 |
| France | 0.6 | 0.026 |
| Switzerland | 0.6 | 0.045 |
| Estonia | 0.4 | 0.036 |

To obtain homogeneity of the digestate mixture, feedstock should be properly prepared. For agricultural and food waste, shredding and mixing are pretreatment processes. In the case of food waste, it is essential to remove the packaging before placing it in the biogas digester [17]. The organic waste is placed in the fermentation chamber, where anaerobic digestion is performed (Figure 2). The process can only start in an oxygen-free environment. The process consists of four phases (I–IV). The phase I is hydrolysis, where the organic compounds are released and transformed into simpler compounds. The phase II is acidification, where organic acids are created, and the pH gradually decreases. In the phase III, hydrogen, carbon dioxide, and acetate are produced. The final phase (phase IV) is methanogenesis. Finally, the biogas is obtained. It contains methane up to 70% and carbon dioxide up to 45%. It can also include traces of hydrogen sulphide, ammonia, and nitrogen [24]. Table 2 shows the composition of biogas produced from agricultural waste. According to the data, biogas consists mainly of methane and carbon dioxide, the content of which can be up to 75% and 33%, respectively. In addition to the previously mentioned ingredients, traces of thiols, sulphides, and thiophenes may also appear in biogas [21,22].

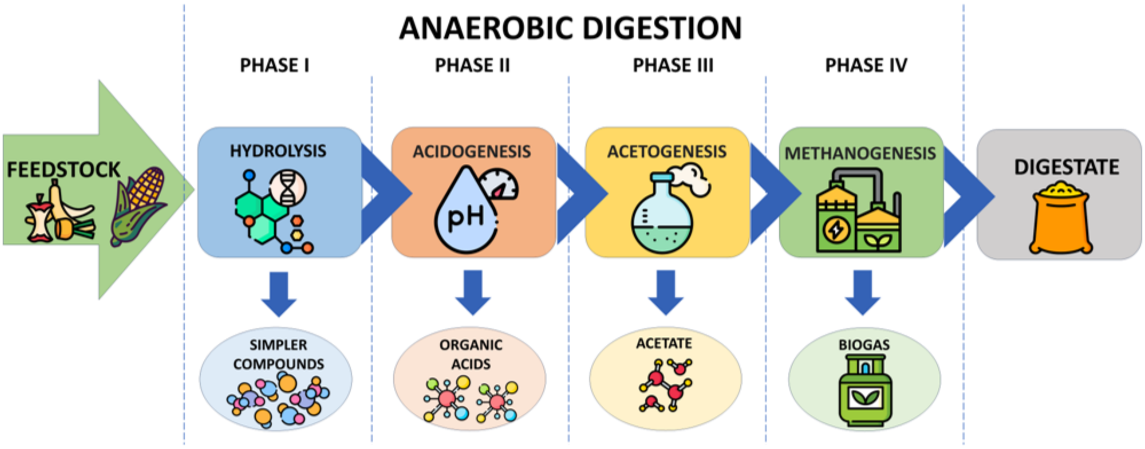

**Figure 2.** Anaerobic digestion process.

**Table 2.** Composition of biogas produced from agricultural waste [25,26].

| Component | Unit | Agricultural Waste |
|---|---|---|
| $CH_4$ | mol.% | 60–75 |
| $CO_2$ | mol.% | 19–33 |
| $H_2S$ | ppm | 2160–7200 |
| $NH_3$ | ppm | 72–144 |
| $N_2$ | mol.% | 0–1 |
| $O_2$ | mol.% | <0.5 |
| $H_2O$ | mol.% | <6 |
| Thiols | $ppm_v$ S | 0.1–10 |
| Sulphides | $ppm_v$ S | 0–5.5 |
| Thiophenes | $ppm_v$ S | 0–0.5 |

The anaerobic digestion process depends on the parameters and technology implemented in the biogas plants. The most critical parameters of the process are temperature, pH, carbon-to-nitrogen ratio, organic loading rate, hydraulic retention time and feedstock composition. Each of these parameters must be appropriately selected for the type of feedstock and microorganisms utilized to obtain the stable conditions of the process. Temperature stability is a crucial factor that must be measured and controlled throughout the process. The anaerobic digestion process can be performed for three different temperature ranges: lower than 25 °C (psychrophilic), 35–40 °C (mesophilic), and 50–60 °C (thermophilic) [27]. The most popular range is mesophilic, which provides the best range of temperatures for commonly used microorganisms. To measure the acidity, a pH control meter is used. The pH level varies in each phase and depends on the microbial groups. Whenever the pH level drops under six or rises above 8.3, the process is stopped [28–30].

Furthermore, the carbon-to-nitrogen ratio (C:N) is crucial. It is often set between 20:1 and 30:1. Various feedstock technologies used in biogas plants require different ratios. For instance, for cow manure, it is 9:1 and for swine manure 6:1, respectively. The application of organic waste, which contains a high amount of carbon, results in an increase in methane production. In addition, waste containing a large amount of fat results in greater amounts of methane [31]. Therefore, it can be concluded that the organic loading rate is the biogas production rate. In particular, it is the quantity of waste in the reactor daily. The last-mentioned parameter is the hydraulic retention time, during which the waste must remain in the chamber to be treated by the microorganisms [32]. In brief, all parameters must be correctly selected because various species of bacteria are sensitive to sudden environmental changes. Optimal conditions provide high efficiency in the growth of microorganisms [32]. According to Ekstrand et al. [33] composition of residual digestate fractions significantly correlates with various operational and chemical parameters affecting the residual methane potential.

Biogas production is an incredibly prospective technology. Simultaneously, gaseous fuel and digestate are obtained using organic waste, which can be used in numerous ways. The most efficient biogas production process is co-fermentation, during which various components necessary for methane production are provided and, thus, a larger quantity of biogas with a higher methane content is obtained [34]. Biogas contains large amounts of carbon dioxide and small amounts of other gases. A complex gas is hydrogen sulphide, which is present in very small amounts. It has proved to be an extremely corrosive agent in a humid environment [35]. However, redundant gases (such as $CO_2$, $H_2S$, and $N_2$) can be removed from biogas, resulting in biomethane with a methane content of up to 99.9%. Biomethane can produce Bio-CNG, be pumped into the gas network or be used as a reburning fuel [36]. Another product from digestate can also be used in other applications, e.g., as fertilizer, soil amendment or biofuel.

Agricultural biogas plants produce biogas from organic waste containing heavy metals and organic pollutants. Therefore, the digestate might contain some of these substances as well. When it is turned into fertilizer, the hazardous substances may cause danger to the environment and living organisms. To obtain material without hazardous pollutants, sulphuric and phosphoric acid sanitize and neutralize the toxic compounds. In addition, free amino acids and peptides are formed, which according to Catenacci et al. [37] and Skrzypczak et al. [38], allow for the creation of fertilizer with far superior parameters [37,38]. In Europe, special regulations, and directives control digestate parameters and quality. Some countries test the amount of polycyclic aromatic hydrocarbons, polychlorodibenzodioxins, and adsorbable organic halogens in digestate, especially when fertilizer in agriculture [37]. Digestate derived from agricultural biomass contains some organic ingredients and, thus, can be transformed into fuel. For instance, a pyrolysis process can be performed in which the by-products are char and fractions of liquid and gas. Subsequently, the resulting products are further transformed into products for industrial use. Due to the high moisture content in the digestate, pyrolysis is not a suitable process because it requires less than 15% of moisture in the feedstock. For that reason, digestate before thermal utilization has to be adequately pretreated. A promising option is hydrothermal carbonization, which is dedicated to feedstocks with a high moisture content [39].

The main aim of this review is a detailed discussion of the properties of agricultural digestate from biogas production and its hydrothermal conversion (HTC) into hydrochar and process water. Therefore, the comparative analysis of feedstock type and HTC products obtained under different process parameters was presented.

## 2. Hydrothermal Carbonization of Agricultural Origin Digestates

In the HTC process, the feedstock is heated within a temperature range of 160–280 °C in an aqueous environment and at autogenous pressure. The products of hydrothermal carbonization are solid, liquid, and gaseous phases (Figure 3). The solid fraction is called hydrochar, which can be used as a solid fuel; for the production of syngas, as a fertilizer and soil improver (due to the content of nutrients, e.g., phosphorus, nitrogen, and potassium, it improves soil properties and helps in creating a humus layer) [38]. Hydrochar can also be used as an adsorbent for environmental remediation [39]. The temperature of HTC is the most important parameter responsible for the course of the entire process [35], while the residence time of the process is a key function parameter [39–41]. The HTC method does not require drying of the feedstock because the process's environment is already aquatic. The process is usually applied to organic waste and biomass with high moisture content, up to 85% [39]. The high-water content of digestate is associated with an increase in transport costs and, thus, an increase in expenditure on energy production [40]. It is a very effective method that improves dewaterability and disinfection of various viruses, bacteria, and pathogens [42].

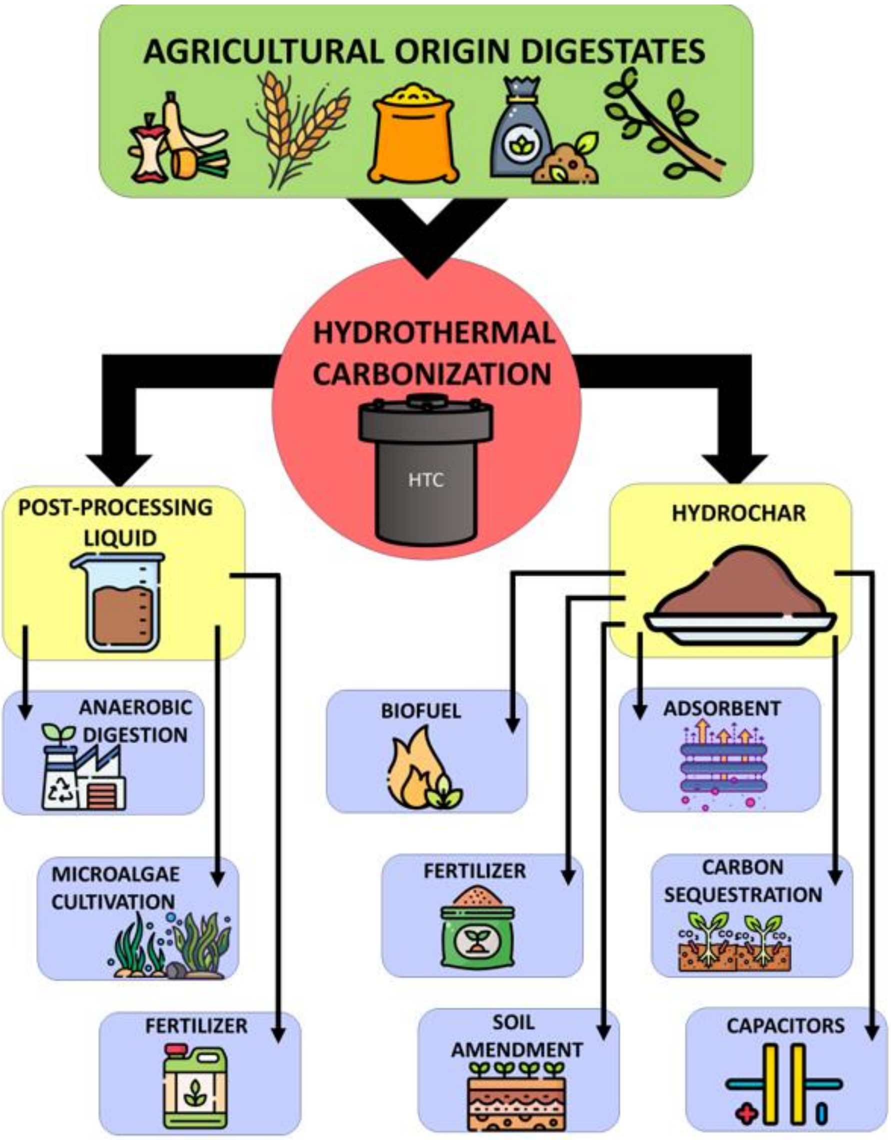

**Figure 3.** Hydrothermal carbonization products disposal.

The chemical processes of raw materials during HTC are hydrolysis, dehydration, decarboxylation, condensation, polymeric condensation, and aromatization [43,44]. For reactions to occur, the temperature must exceed 100 °C. At 180 °C, substantial hydrolysis takes place. The raw material must be immersed in water, and the pH should be lower than 7 [45]. Hydrolysis occurs in the presence of water and leads to the breakdown of ester and ether bonds of molecules. The rate of the hydrolysis of biomass is influenced by diffusion. Above 200 °C, cellulose hydrolysis takes place, and at 180 °C, hemicellulose [45]. The hydrolysis of lignin occurs above 260 °C because it has more ether bonds [46]. Alkaline conditions were estimated to give the highest reaction rates compared to acidic and neutral conditions. An acidic reaction is essential in the case of a later stage of glucose degradation. The substrates usually contain cellulose and lignin. In the first stage of hydrolysis, glucose is formed from cellulose and phenol from lignin.

Further processes are very complex. Performing the process of glucose dehydration leads to form, e.g., organic acids, ketones, and phenols. Biomass of agricultural origin consists of different lignin, cellulose, and hemicellulose contents. Moreover, there is a likelihood of hemicellulose interacting with lignin. As a result, there may be a better solubility of its aromatic structures. These two components together form an oligomer that is stable under hydrothermal conditions. From oligomers, monomers are formed, from which organic acids are created. Acetic acid affects the gradual lowering of pH and, as a result, it leads to dehydration and decarboxylation. The next stage is dehydration, i.e., removing water from the raw material. This process results in a reduction in H:C and O:C ratios in biomass. The following stages are decarboxylation and aromatization, which are associated with the carbonization of carbohydrates [45]. In the polymerization stage, as a result of intermolecular dehydration or aldol condensation, soluble polymers are formed [47]. The residence time affects the polymerization of degraded products in the liquid phase. A longer time increases the formation of microspheres and the polyaromatic hydrochar structure. When the pressure is too high, it can lead to a decrease in the intensity of decarboxylation and an increase in the intensity of polymerization [45,48].

During the HTC of biomass, furfural is formed, and polymerization takes place, leading to the production of hydrochar. During the process, HTC decreases the oxygen and hydrogen content. Most of the carbon found in biomass remains in the produced hydrochar [49]. Its content depends on the feedstock and the condition of the process. For instance, Tippayawong et al. [50] researched hydrochar obtained from maize residue and the carbon content increased by approximately 5% [50]. Poomsawat et al. [51] studied hydrochar derived from aquatic biomass. The research confirmed the increase in carbon content for obtained hydrochars compared to raw materials [51]. However, some parts are dissolved in process water or might be transformed into gas [49].

A significant aspect is energy recovery from the by-products of the HTC process. Both hydrochar and process water can be used for energy supply [52]. Process water contains various kinds of sugar, volatile fatty acids, and aromatic organic compounds. In addition, the dissolved organic carbon in this fraction accounts for up to 30% of the feedstock placed in the reactor. Water acts as a catalyst for the whole reaction and supports the conversion of organic waste into biofuel and organic liquid fraction. The severity of the process plays a key role in the carbon content of the final product. As it increased, the efficiency of the carbon content in hydrochar decreased. Hydrochar contains the largest amount of carbon of all three HTC products. The smallest amount of carbon is in the gas phase, the main component of which is carbon dioxide. This can cause a significant increase in reactor pressure above the water saturation pressure [49].

Maintaining the correct temperature and not too long a retention time [53]. For instance, Cao et al. [41] conducted the process at a temperature of 210 °C with different residence times: 30 min to 5 h. The digestate of cow manure and energy crops was the feedstock used in the HTC process, and half an hour of residence time resulted in a decrease in higher heating values. However, there was a boost in the slagging and fouling indexes observed. The 30 min process demonstrated the highest efficiency and better quality of the digestate [41]. Gao et al. [54] conducted the HTC process for water hyacinth. The effect of residence time within 0.5 h to 24 h at 240 °C was examined. Studies have shown that the calorific value of the obtained hydrochars rises with an increase in time. The highest percentage of carbon in hydrochar was obtained for a residence time of 8 h [54]. Śliz et al. [52] researched the HTC wet fraction from mixed municipal solid waste. The effect of temperature and residence time on hydrochar was investigated. Temperatures of 200 °C and 220 °C were implemented, as well as residence times of 1, 4 and 8 h. The best hydrochar parameters were obtained at 220 °C for 1 h [52]. The HTC process can be used to increase biomethane production. A higher biomethane content is obtained during the anaerobic digestion of municipal waste. When comparing hydrochar and municipal waste, the sulphur concentration measured in hydrochar is lower than that of the municipal waste fraction. The increase in temperature also reduces its content. Moreover, hydrochar produced from municipal waste is biodegradable at lower temperatures, with the best value at 180 °C [55].

Digestate is primarily used as fertilizer but can also be transformed into fuel pellets. The composition of digestate pellets depends on the organic waste used as feedstock in biogas plants. It is possible to use digestate as a combustion material, but it has a lower calorific value than pellets made of wood. The energy efficiency of digestate pellets is around 44 kW, and the competence of the process is 85%. For comparison, the combustion of wood pellets is higher than 90% [56,57].

As mentioned above, waste from agriculture and the food industry is mainly used in biogas production. Recently, research has been conducted on using algae as a substrate in the co-digestion process. The process occurs simultaneously, and the fermentation of a homogeneous mixture of different wastes occurs. As a result, more relevant parameters for the anaerobic digestion process are obtained [58]. Koçer et al. [59] researched the possibility of process water management in the production of microalgae. Using this water to benefit the environment would be an advantage of the HTC process. The water resulting from the HTC process of orange and olive pomace was used to cultivate *Chlorella sorokiniana*. This research has confirmed that process water from HTC can produce microalgae [59].

Another study indicates that the HTC process can be used for biogas sludge, maize silage, and barley silage. Consequently, hydrochar is obtained, similar to lignite coal and peat. According to Seyedsadr et al. [60], the HTC process causes an increase in carbon by 1.4–14.4%. Additionally, higher heating values increase by about 33% on average. Furthermore, the reduced ratios of hydrogen to carbon and oxygen to carbon in hydrothermal co-carbonization resulted in a rise in aromatization [60].

As previously mentioned, the range of temperatures employed during hydrothermal carbonization is lower than in other thermochemical processes, although high-pressure values are achieved. The pressure increases with temperature [49], which is due to an increase in water vapour pressure and the formation of gas [61].

Regardless of the selected parameters of the HTC process, the most important factor is the safety of the reactor operation. Due to changes in pressure and temperature, the reactor's parameters should always be selected very carefully. In hydrothermal carbonization, different reactors can be used: batch, semi-batch and continuous, equipped with a stirrer, direct heating by steam injection or through the reactor's walls. The cost of a high-pressure reactor can be relatively high. For that reason, most research is limited to studies concerning reasonable temperature and residence time ranges while considering the potential interest of investors. As a result of the formation of reaction gases and water vapour, the pressure is usually in the range of 0.6–6.4 MPa. In the HTC process, the raw material is immersed in liquid water, whereas when it has direct contact only with water vapour, it is called steam carbonization (VTC) [61].

There is also the possibility of a simultaneous application of the HTC process, mechanical dewatering, and pyrolysis. Wang et al. [62] researched the kinetics and thermodynamics of these processes and the hydrochar obtained. One result is that HTC reduces the pyrolytic activation energies of digestate from agricultural waste [62].

Another type of HTC process is a "Two-stage HTC", which consists of dividing the process into two phases. The first is hydrolysis, where products with a low molecular weight are obtained. It occurs at relatively low temperatures, up to 175 °C. The second phase occurs at higher temperatures, up to 280 °C, called carbonization. The hydrolysis products are dehydrated and polymerized. Consequently, "Two-stage HTC" reduces power consumption by up to 25% compared to the conventional HTC process. Besides, studies indicate that extending the hydrolysis time to 200 min increases the energy content of the produced hydrochar [63].

There is also a process called co-hydrothermal carbonization (co-HTC). This kind of process affects the properties of hydrochar. Studies were conducted for different materials, for example, sewage sludge with the addition of various types of organic waste, e.g., lignocellulosic, wood, food, agriculture, municipal solid waste, and sewage sludge. The latter kind of waste is characterized by its heterogeneity of structure and its fairly low carbon content. In addition, the high nitrogen and ash content reduces the efficiency of hydrochar as a solid fuel [64]. According to the data, wastewater treatment plants in Europe produce approximately 22.5 kg of dry matter of sludge per capita per year. It is estimated that annually this number reaches 17 million tonnes of dry sludge [65]. Studies show that sewage sludge is predominantly high in phosphorus. Therefore, hydrochar produced from sewage sludge in the HTC process is characterized by a large amount of phosphorus. Hydrochar is more environmentally neutral and, thus, safer than sewage sludge. The main problem encountered is maintaining the correct pH level. The high carbohydrate content of sewage sludge can stop the transfer of phosphorus to hydrochar due to the acidic reaction of the process water [66]. HTC has proved to be a suitable sewage sludge pre-treatment method. Tests were performed by Wilk et al. [67] for hydrochars with added lignocellulosic biomass and charcoal.

Furthermore, the HTC process has improved the drainage of the sewage sludge. Hydrochar, adding 20% fir enhanced the best properties of the obtained fuel [67]. Wilk et al. [68] also demonstrated that when the HTC process is applied to sewage sludge, it reduces the activation energy of hydrochars by 50% [68]. Liu et al. [69] used co-HTC for cellulose from wheat straw, xylan and soy protein and proved co-HTC has an impact on the efficiency of hydrochar. The highest hydrochar yield was observed for cellulose. In addition, co-HTC reduces the ratio of O:C and raises N:C in the resulting hydrochar. In addition, the effect of the co-HTC process with aqueous phase recirculation has been investigated [69]. Sample studies were conducted for aquatic plants of water hyacinth and cattail, as they have cellulose, hemicellulose, and lignin in their composition. According to previous studies, hydrochar obtained in the HTC process from those plants was characterized by better combustion efficiency and lower ash content [70]. Wilk et al. [71] researched the effects of the HTC process on acacia. The analysis showed that the HTC process caused degradation of hemicellulose and cellulose contained in the acacia samples, while lignin was only partially degraded [71].

Further studies were performed by Wang et al. [72] on hydrochar obtained from a mixture of food waste and a mixture of wood sawdust. At high temperatures, a delayed degree of carbonization was observed. Coal retention was high for hydrochar from wood sawdust, rising by approximately 89%. The surface of hydrochar from wood sawdust was smooth at 180 °C and cracked for hydrochar produced at 220 °C. This is due to hemicellulose, which breaks down at 180 °C, and cellulose, which decomposes above 200 °C. Nitrogen retention was best at a lower process temperature. In addition, superior carbonization, and thermal stability of hydrochar are obtained for a higher blended ratio of food waste [72].

Recently, the combined processes of anaerobic digestion and hydrothermal carbonization have become increasingly popular. Parmar et al. [73] investigated the co-processing of sewage sludge with lignocellulosic biomass. The results indicated that there was an increase in the calorific value. Adding lignocellulosic material to the digestate can also increase the solid-loading of the HTC process, which can improve the performance of the process. The efficiency of co-processing is mostly influenced by the composition of the raw material [73]. Reza et al. [74] conducted experiments regarding wheat straw's anaerobic digestion and HTC process. These studies confirmed the increase in bioenergy when co-processing is used [74]. To ensure stability, additional anaerobic digestion should be performed to treat process water. This liquid is a by-product of the HTC process and contains, e.g., alcohols and carboxylic acids. Therefore, it can be used for anaerobic digestion [40]. Ferrentino et al. [75] investigated the enhancement in biogas production by hydrothermal carbonization of organic solid waste and digestate in an inter-stage treatment configuration proving that biogas production increased by an increase in the percentage of municipal organic waste in the mixture of organic solid waste fed to HTC process. Czerwińska et al. [76] researched the liquid recovered from the HTC of sewage sludge. The water was filtered to remove impurities. Methods such as membrane, ultrafiltration, nanofiltration and double nanofiltration were proven.

Furthermore, the research confirmed the effectiveness of reducing the tested contaminants using these technologies [76]. Studies conducted for maize silage digestate as a substrate indicate that during the HTC process, increasing the temperature from 180 °C to 220 °C causes weight loss. The best parameters for the obtained hydrochar and process water were recorded at a temperature of 180 °C with a residence time of 30 min. Lower temperatures and shorter residence times cause a lack in the production of non-biodegradable or toxic substances in the process water [40].

In addition to the HTC process, two other processes stand out: hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG). The first occurs within a temperature range of 200–400 °C and at a pressure of 10–25 MPa in an aqueous environment. As a result, the production of bio-petroleum occurs. In the HTG process, the conversion of biomass into gaseous components such as hydrogen, methane, and carbon dioxide. These gases can be used in heat production [44]. According to previous research, hydrochars contain greater values of higher calorific value and fixed carbon content than the initial feedstock. However, volatile matter and ash content are higher for agricultural waste [62].

## 3. Comparative Analysis of Hydrochar's Chemical and Physical Properties

Regarding hydrochar as a material rich in carbon content, it might be concluded that its properties are similar to lignite. Hydrochar has a higher percentage of labile carbons, is less aromatic and has a lower ash content than raw materials. Accordingly, it could be applied on an industrial scale to be more profitable. The price of hydrochar is likely to be estimated on local conditions, raw material costs and energy input [77].

The HTC process converts the feedstock by altering its chemical and physical properties, e.g., it reduces the moisture and volatile content in hydrochar compared to raw biomass, transfers hydrophilic structures to hydrophobic ones, changes the aromatization of the material, etc. Hydrochars are rather hydrophobic materials. This is influenced by their surface functional groups and porosity [78,79]. The HTC process allows for the recovery of water from the municipal solid waste digestate. Aragon-Briceño et al. [78] established that hydrothermal carbonization increased its recovery by 40–48%. Hydrochar has not been dewatered and has a moisture content of approximately 72–78%. After dewatering, the moisture drops to about 51–56%. This process allows for more efficient dewatering and the consequent drying process of hydrochar, which results in a better combustion efficiency of the product [80,81]. In addition, the theoretical biomethane potential decreases as the temperature of the HTC process increases [78]. Studies by Malghani et al. [82] have demonstrated that the degradation of hydrochar in the soil is c.a. 50% after 100 days. Thus, they are characterized by high degradability [82]. Hydrochar is brittle and might easily be crushed, which significantly facilitates its transportation and storage and reduces economic and operating costs [83]. The effect of temperature is essential when it concerns nitrogen transfer during HTC. Its impact on products obtained from the HTC process of food waste was investigated by Wang et al. [84]. The change in temperature from 180 °C to 220 °C has a major impact on the nitrogen content of hydrochar and its surface. In this temperature range, the nitrogen yield in hydrocarbon decreases. Additionally, the HTC process affected the surface of the hydrochar, with small spherical particles appearing on its structure. Hydrochar produced in the 220–260 °C temperature range was characterized by greater cross-linking and more microspheres [84].

Table 3 depicts the selected parameters of hydrochars obtained from different kinds of feedstock. The percentage of organic elements, ash content, fixed carbon, volatile matter, and higher heating value were compared. The temperature range was between 200–280 °C. The residence time for brewer's spent coffee was 16 h, the aqueous phase of bio-oil 8 h, Miscanthus giganteus 2 h, and sewage sludge up to 10 h. It was usually c.a. 1 h for other materials, except for rape straw and microalgae, where the time was 30 min. The choice of temperature and residence time depends on the raw material used in the HTC process. These parameters should be selected to ensure the best properties of hydrochars.

Table 3 shows that the highest higher heating value was obtained for a mixture of sewage sludge and food waste of 31.50 MJ/kg. This value is 47% higher than the lowest obtained. For brewers' spent grain and the aqueous phase of bio-oil, a similar level of about 30 MJ/kg was recorded. It can also be noted that very similar values of higher heating were obtained for maize straw, rape straw, microalgae, and beet pulp, amounting to approximately 22 MJ/kg. The lowest calorific values, below 20 MJ/kg, were obtained for swine manure and sewage sludge. This can be seen in the relationship between the values of the higher heating value and the carbon content in the resulting hydrochars. The percentage of carbon decreases with decreasing values of the calorific value.

**Table 3.** Selected parameters of hydrochars obtained from different kinds of feedstock, db.

| Feedstock of Hydrochar | Temperature [°C] | Time [h] | C [%] | N [%] | H [%] | S [%] | O [%] | Ash [%] | FC [%] | VM [%] | HHV [MJ/kg] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sewage sludge and food waste | 280 | 1 | 71.00 | 3.94 | 6.90 | 0 | 11.78 | 6.38 | 31.65 | 61.97 | 31.50 | Zheng et al. [85] |
| Brewers' spent grain | 220 | 16 | 70.92 | 3.83 | 6.70 | 0.15 | 15.50 | 2.90 | 42.80 | 52.24 | 30.95 | de Araújo et al. [86] |
| Aqueous phase of bio-oil | 260 | 8 | 75.10 | - | 5.50 | - | 19.40 | - | - | - | 30.20 | Lin et al. [87] |
| Coconut waste shell | 220 | 1 | 68.83 | 0.46 | 6.66 | 0 | 24.05 | 0 | 35.54 | 64.46 | 29.39 | Cheng et al. [88] |
| Spent coffee grounds | 200 | 1 | 65.45 | 2.61 | 7.12 | - | 24.81 | 0.98 | 29.67 | 69.35 | 27.59 | Afolabi et al. [89] |
| Maize straw | 220 | 1 | 56.50 | 0.93 | 5.59 | 0.15 | 33.24 | 3.59 | 21.53 | 74.88 | 22.80 | Wang et al. [90] |
| Rape straw and microalgae | 240 | 0.5 | 58.85 | 3.73 | 6.30 | 0.52 | 30.39 | 0.21 | - | - | 22.30 | Liu et al. [91] |
| Beet pulp | 220 | 1 | 55.10 | 1.59 | 5.67 | 0.1 | 36.67 | 0.88 | 28.56 | 70.47 | 22.10 | Wilk et al. [92] |
| Miscanthus giganteus | 200 | 2 | 54.90 | 0.16 | 5.90 | 0 | 37.3 | 1.75 | 20.18 | 75.82 | 21.10 | Wilk et al. [93] |
| Virginia mallow | 200 | 1 | 52.50 | 0.46 | 5.78 | - | 40.21 | 1.05 | 14.42 | 80.19 | 20.91 | Śliz et al. [94] |
| Swine manure | 230 | 1 | 39.36 | 1.99 | 4.60 | 0.41 | 16.75 | 36.90 | 14.47 | 48.64 | 16.37 | Lu et al. [95] |
| Sewage sludge | 200 | 10 | 33.80 | 2.80 | 3.80 | 1.33 | 5.43 | 52.84 | 6.29 | 40.17 | 14.73 | Wilk [96] |

C—Carbon; N—Nitrogen; H—Hydrogen; S—Sulphur; O—Oxygen; FC—Fixed carbon; VM—Volatile matter; HHV—Higher heating value.

The exception is the aqueous phase of bio-oil, for which 75.1% was obtained even though it does not have the highest rate for the higher heating value. This may have been affected by the longer HTC process time. The highest value of HHV is 53% higher than the lowest value for sewage sludge. The highest nitrogen contents do not exceed 4%, and trace amounts below 1% are found in coconut waste shells, maize straw, Miscanthus giganteus and Virginia mallow. The highest hydrogen value was obtained for spent coffee grounds, at 7.12%, and the lowest for sewage sludge, at 3.8%. In all tested materials, the sulphur content is merely a trace or completely absent. The exception is sewage sludge, where the content is the highest and amounts to 1.33%. For fixed carbon, the highest value was obtained for brewers' spent grain, at 42.8%, and the lowest was approx. 85% lower than for sewage sludge.

Regarding beet pulp results, a downward trend can be observed in the fixed carbon value. According to previous research, a higher degree of carbonization of biomass results in a higher value of fixed carbon content [97]. The highest volatile matter value was obtained for Virginia mallow at 80.19%. For maize straw and Miscathus giganteus, relatively high values of about 75% were also obtained. The lowest value was recorded for sewage sludge, at only 40.17%. This is almost two times lower than for Virginia Mallow. A significant issue is that the parameters of hydrochars are influenced by the process temperature, residence time, type of reactor for HTC and elemental composition of the raw material. Figure 4 depicts a van Krevelen diagram for hydrochars obtained from different kinds of feedstock, shown in Table 3.

Hydrochar can be used as a fertilizer. It contains in its composition such ingredients as nitrogen, phosphorus, potassium, and carbon. Therefore, it can become a competitive product in fertilizing plants with regard to currently used fertilizers [98]. The hydrochar obtained from the HTC process can be used as a substitute for peat in agricultural fields. In addition, a mixture of hydrochar and peat can also be used. Hydrochar makes the airspace expand in such a mixture. According to previous research, this kind of mixture does not affect the microbiological activity of the substrate [99].

The use of hydrochar in the iron and steel industries was also investigated. Hydrochar produced from lemon peels was compared with charcoal and Anthracite. Lemon peel hydrochar has a lower concentration of ash and sulphur than Anthracite. However, only 54% of the carbon in lemon hydrochar remained solid at 1200 °C. A small amount of coal has a tide to reduce the performance of metallurgical reactions occurring at high temperatures, such as carburizing and foaming of slag. This has the effect of reducing the efficiency of these processes [77].

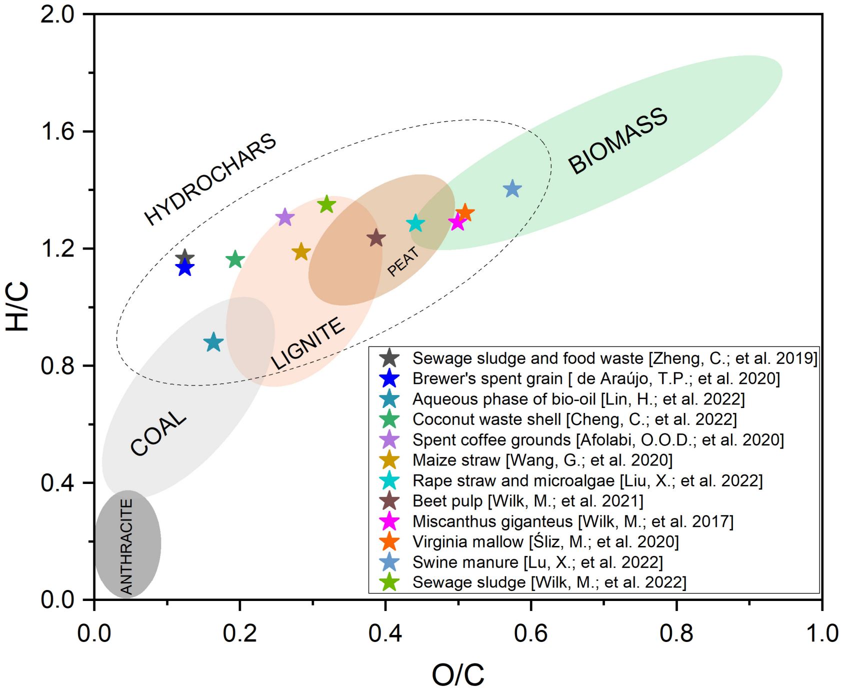

**Figure 4.** Van Krevelen diagram for hydrochars obtained of different feedstock [85–96].

Another application of hydrochar is to remove the impurities in dyes from water. Synthetic dyes are particularly dangerous and can be found, among others, in the textile industry. The presence of dyes in water leads to the blocking of sunlight and the inhibition of photochemical reactions. Additionally, it adversely affects the health of living organisms and the environment. A promising method is to use the adsorption process. Studies were carried out for crystal violet, a cationic dye, and hydrochar derived from nuts as an adsorbent. The best process conditions were at pH = 8 with a contact time of 60 min. The highest dye removal efficiency of 91% was obtained for hazelnut-based hydrochar [100]. Other studies have tested the ability of hydrochars obtained from bamboo sawdust to adsorb Congo red and 2-naphthol [101]. Both of these substances are hazardous. Congo red is a dangerous pollutant found in wastewater. It is an anionic dye that contains a biphenyl group and two units of naphthalene.

Whereas 2-napthol is a compound used in dyes and pharmaceutical compounds. It is dangerous to live organisms because excessive consumption can lead to poisoning, jaundice or even coma [102,103]. Bamboo hydrochar was produced in a hydrothermal process. For 2 h processes at 160 °C and 240 °C, the hydrochar showed the highest adsorption capacity of both tested substances [101]. It was also discovered that hydrochar from corn cobs, modified with polyethylamine, can be used to remove chromium (VI) and nickel (II) from aqueous solutions. These elements are dangerous to living organisms and the environment. Thus, finding an effective neutralization method is essential. Shi et al. [104] showed that polyethylene-modified hydrochar has better adsorption abilities than cationic nickel and anionic chromium [104]. Hydrochar also has better adsorption properties for $NH_4^+$ than biochar. This is due to its functional groups with oxygen, such as carboxyl and ketone [105].

Hydrochar has also been used as a catalyst. Its advantages include the low price of raw materials, hydrothermal stability, and catalytic efficiency. Hydrochar was exported with a corn stover, and the properties of glucose isomerization catalysts based on this hydrocarbon were investigated. In catalytic performance, the active metal centre plays a key role. Hydrochar with corn stover is characterized by carbon microspheres and has greater catalytic parameters [106]. Hydrochar catalysts can also be used to produce biodiesel. The most popular method of biodiesel production is oil transesterification. Studies were conducted for coconut endocarp hydrochar. Such catalysts have hydrophobic properties, and this contributes to the easier adsorption of triglycerides in the process of transesterification [107]. Other studies were performed concerning the esterification of oleic acid with methanol using a hydrothermal coal catalyst. The efficiency of the carbon catalyst was 91%. The most significant advantage of such a catalyst is the possibility of its recovery and reuse [108].

Another example is the catalyst obtained from sulphonated functionalized carbon. It was derived from corncob in the HTC process and then used in biodiesel production. Furthermore, this study confirmed that the resulting catalyst demonstrates good esterification activity and efficiency. In addition, it can be reused [109].

It is also possible to use sorbents and nanocomposites from hydrochar combined with functional nanomaterials to increase adsorption. As a result, nanofibrous hydrochars are formed. For example, hydrochar and $Ti_3AlC_2$ are combined. This combination increases the adsorption of hydrochar compared to activated carbon [110].

## 4. Conclusions

Biogas plants are an environmentally-friendly alternative to power plants using non-renewable fuels. Besides biogas production, which has been used in industry as a source of heat and electricity, organic waste of agricultural origin is produced in high quantities. The digestates might be disposed of as a feedstock into other “waste to energy” processes as a biorefinery concept related to the circular economy. This article presents the characteristics of the agricultural digestate and its conversion by the hydrothermal carbonization process into hydrochar and process water. Moreover, the study discusses the properties and applications of hydrochars. Therefore, it is essential to summarize the knowledge related to parameters such as the percentage of organic elements, ash content, fixed carbon, volatile matter, and higher heating value due to the organic waste feedstock, temperature and residence time of the hydrothermal carbonization process. Hydrochar applications are also studied and can be used as a fuel or agricultural fertilizer and as an adsorber, catalyst or remover of harmful substances. Research on further methods for the most appropriate use is ongoing to provide significant insight into previously collated knowledge.

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