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Research article

The effect of an acid catalyst on the hydrothermal carbonization of sewage sludge

Małgorzata Wilk [*], Maciej Śliz, Klaudia Czerwińska, Małgorzata Śledź

Department of Heat Engineering and Environment Protection, Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, 30 Mickiewicza Avenue, 30-059, Krakow, Poland

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ABSTRACT

This research is focused on the addition of a catalyst, sulphuric acid (VI), to sewage sludge, and its effect on solid and liquid products resulting from the hydrothermal carbonization process. Consequently, for hydrochars, proximate and ultimate analyses, higher heating value and specific surface area were determined. Additionally, Fourier-transform infrared spectrophotometric and thermogravimetric analyses were conducted. The heavy metal contents in the ash composition of hydrochars were identified by X-ray fluorescence spectrometry. It was confirmed that the catalyst addition changed the structure as well as the physical and chemical properties of hydrochars and their ashes. Regarding post-processing water, both pH value and conductivity were determined and the element composition, including heavy metals, was conducted by the inductively coupled plasma optical emission and mass spectrometry analyses. It was found that the addition of the catalyst caused a decrease in heavy metal contents and an increase of phosphorus compound in filtrates.

1. Introduction

The common access of households to high-efficiency wastewater treatment plants induces a greater generation of wastewater and, thus, sewage sludge (Śledź, 2021). Therefore, an appropriate treatment of this waste with potential recovery of energy may close the cycle of waste processing in a circular economy. Energy recovery from waste is an alternative to primary fuels and reduces CO_2 emissions, which is the main premise of the European Union's climate policy for the coming years (Zachmann et al., 2021). It also concerns the reduction of landfill. In accordance with the National Waste Management Plan 2022 (Polish Council of Ministers, 2016), it is assumed that an obligation to limit the landfilling of waste to 10% will be imposed by 2035. According to the plan, in the years 2021–2035, the waste management policy strongly supports the successful transformation of waste into energy, and improvements in mechanical-biological waste treatment plants leading to the production of bio-waste, and including the drying process of wet fractions dedicated for thermal processes. Sewage sludge in the European Union is mainly processed by drying and thermal conversion. In Poland, according to Werle and Przydatek and Wota, sewage sludge disposal is generally in agriculture, which uses organic matter from sewage sludge to fertilize the soil (Werle, 2015; Przydatek and Wota, 2020). There are guidelines regarding the agricultural use of sewage sludge, as published by Snyman and Herselman, which provide valuable suggestions for its correct management (Snyman and Herselman, 2006). In addition, the content of elements such as phosphorus, calcium, magnesium, nitrogen and sulphur are utilized by the vegetation as nutrients (Wilas et al., 2016). The Act of December 14, 2012 on waste (Act on Waste, 2013), concerns the use of sewage sludge in agriculture, composting of sewage sludge, and the thermal treatment of sewage sludge. However, restricted requirements are imposed on sludge for its use in land recultivation. An indicator that limits its potential is the content of heavy metals, which can lead to environmental contamination (Kowalik et al., 2021). Sewage sludge contains heavy metals in the form of oxides, hydroxides, sulphates, phosphates, silicates, sulphides and compounds with complex sugars. Diverse sorts of heavy metals in the sewage sludge can leak into the ground. Heavy metals include those considered to be harmful, such as cadmium, lead, mercury and arsenic, as well as micronutrients that are necessary for proper development, such as copper and zinc (Minister of Environment, 2015). According to Urra et al. the physical and chemical form of particular heavy metal elements occurring in sewage sludge may cause their toxicity (Urra et al., 2019). Hence, it is not possible to determine the threats they pose to the environment on the basis of their total content (Khakbaz et al.,

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[*] Corresponding author.
E-mail addresses: mwilk@agh.edu.pl (M. Wilk), msliz@agh.edu.pl (M. Śliz), kczerwin@agh.edu.pl (K. Czerwińska), malgorzata.sledz@poczta.onet.pl (M. Śledź).

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2020). Latosińska et al. also suggested that the mobility of HMs may cause their harmful effect (Latosińska et al., 2021;2017). Moreover, due to the SARS-CoV-2 pandemic, it appears that thermal treatments, in which sewage sludge can be processed are desirable due to the high temperature that ensures complete disinfection of the sludge, thereby resulting in a minor biological hazard in comparison to sludge that is not subjected to such processes (Hoang et al., 2022). Besides, the thermochemical processing of sewage sludge supports "waste-to-energy" technology and transforms the carbon-rich organic fraction of sewage sludge into valuable energy and fuel (Syed-Hassan et al., 2017).

However, these methods are not as popular because of the high cost related to the initial drying of sewage sludge which contains significant moisture mainly due to the hydrated colloidal structures of microbial aggregates (Schnell et al., 2020). One of the largest economical and logistical obstacles in sewage sludge management is dewatering which causes a significant reduction in volume and hydration of the sludge. Commonly applied dewatering devices do not provide satisfactory results without prior intervention into the structure of sewage sludge. Therefore, to improve sludge dewatering as a pre-dewatering stage, a conditioning process using different techniques and substances is applied. The most popular method is a chemical one using organic flocculants, but due to high costs, risk of toxicity and low effectiveness of water removal some new methods are required (Okolo et al., 2021). As alternative methods for the conditioning of sewage sludge, application at the stage of laboratory tests found, among others: dry ice, water treatment by-products, addition of shells from shellfish, or use of energy waste proved beneficial (Fig. 1). Between the listed methods, hydrothermal carbonization process (HTC) is an exception, as it has already been tested under industrial conditions and provides high temperature conditions in an aqueous environment (Wilk, 2016). Furthermore, it enhances the dewaterability of sewage sludge (Román et al., 2021), generates hydrochar (solid product) and post-processing liquid with adequate properties necessary for energy production (Wang et al., 2019), reduces significantly the volume of sewage sludge leading to the omission of the drying process, which requires a substantial amount of energy (Zhao et al., 2014). Furthermore, the addition of different organic origin additives including lignocellulosic, municipal solids, agricultural or food waste to sewage sludge prior to hydrothermal treatment greatly improves the dewaterability of sewage sludge and fuel properties of hydrochar (Wilk et al., 2021). Consequently, the hydrothermal carbonization process appears to be an appropriate thermal treatment of sewage sludge which is urgently required in order to improve sewage sludge properties, its hygienization, and further sewage sludge management (Czerwińska et al., 2022). Unfortunately, the process water from the HTC of sewage sludge, also called the aqueous phase, post-processing liquid or wastewater, contains many harmful compounds. It primarily contains organic acids (short-chain), fatty acids and various organic products from the conversion of many inorganic substances during the HTC process. For this reason adequate treatment is required before its further disposal including advanced selected processes based on membrane filtration, coagulation, ultrasonication and chlorination (Czerwińska et al., 2023a,b). From another point of view, the process water from hydrothermally treated sewage sludge contains enough organic compounds that can be used in energy production. For instance, Aragón-Briceño et al. proved that anaerobic digestion of the post-processing water derived from the HTC of digested sewage sludge is a suitable option for biomethane production (Aragón-Briceño et al., 2017). Moreover, according to Oliveira et al. hydrothermal carbonization can be integrated into the aqueous phase, reforming the generated process water from sewage sludge and providing hydrochar with improved fuel properties as well as a high yield of hydrogen produced from the post-processing liquid by using the bimetallic Pt/Rh catalyst (Oliveira et al., 2022). Xu et al. pointed out that the recycling of the aqueous phase after the HTC of sewage sludge was favourable for energy recovery from this phase and caused improvements in the combustion properties of the hydrochar (Xu et al., 2019). This concept as well as the aqueous phase properties was also carefully reviewed taking into account the industrial scale of the HTC process (Xu et al., 2022). Although it is a very promising technology, it does not resolve the HMs problem. (Chanaka Udayanga et al., 2018). Consequently, the optimal parameters of the HTC process, such as the process temperature, its duration, the addition of a catalyst or other biomass, may influence the physicochemical properties of the sludge, e.g. the amount of heavy metals and their chemical form (Lu et al., 2021). For instance, Shi et al. studied the fate and environmental risk of heavy metals by proving that the synergistic effect of rice husk addition to sewage sludge treated by hydrothermal carbonization reduces the risk of HMs (Shi et al., 2013). Zhai et al. (2016) studied the influence of the pH of the feedwater on the HMs stabilization in the hydrochars. According to (Zhai et al. the pH of the feedwater has a significant impact on the accumulation of lead, nickel, cadmium and zinc in both acidic and alkaline environments (Zhai et al., 2016). In the case of copper and chromium, the alkaline environment promotes stabilization, while the alkaline environment shows the opposite (Reza et al., 2015). It was indicated that an alkaline pH (e.g. pH of 12) resulted in the lowest level of heavy metal contamination in the hydrochar. Reza et al. (2015) investigated the influence of the pH of the feedwater with the use of acetic acid and potassium hydroxide on the hydrothermal carbonization process of wheat straw. It was found that both the hydrochars and the liquid phase after the hydrothermal carbonization process are acidic, regardless of the pH of the feedwater used. The remaining indicators depended on the composition of the biomass used for the hydrothermal carbonization process. Wilk et al. studied heavy metals in the solid and liquid products derived from the hydrothermal carbonization of sewage sludge performed at 200 and 220 °C. Additionally, in this study, distillation was applied for the treatment of the post-processing water. Therefore, the filtrates and distillates were analyzed in terms of HMs content to assess the possibility of using both liquids for soil reclamation or agricultural use (Wilk et al., 2023). In both cases, heavy metals greatly decreased after the treatments, achieving the requirements for these applications. They also compared the HMs content in hydrochars derived at 200 and 220 °C to those in sewage sludge and observed a slight increase of Pb (lead), Cu (copper), and Zn (zinc) compounds, and a decrease in the contents of Cr (chromium) and Ni (nickel) compounds. Wang et al. studied HTC of SS in terms of heavy metals and phosphorus (P) conversion and distribution

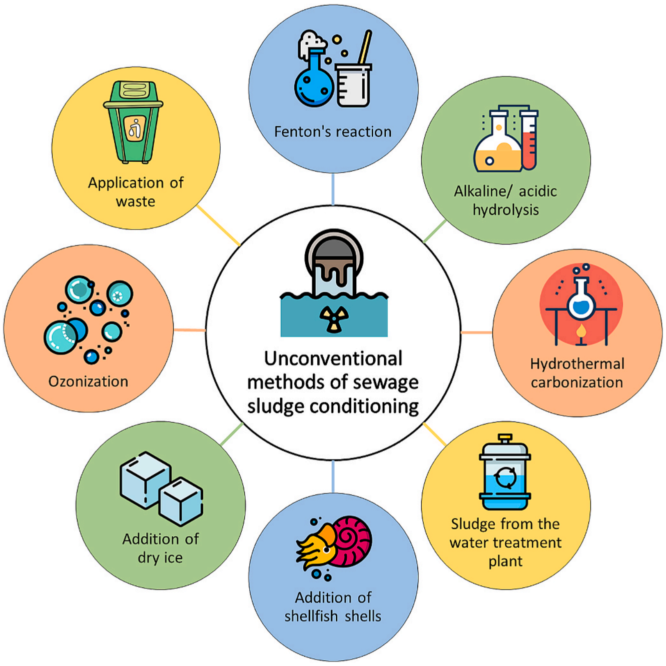

Fig. 1. Unconventional treatments of sewage sludge.

under acidic conditions. They confirmed the low ecological toxicity of HMs, which were immobilized and concentrated in hydrochar. More importantly, they discussed how organic phosphorous transformed into inorganic and how the apatite phosphorous converted to non-apatite inorganic phosphorous in hydrochar (Wang et al., 2020). Regarding HMs migration, Huang and Yuan confirmed that as the temperature of the HTC process increased, the total heavy metal content increased and accumulated in the hydrochar. Overall, hydrothermal carbonization causes the transformation of heavy metals due to undergoing a different complex process. It was also suggested that the migration and transformation behaviours of heavy metals during the hydrothermal treatment of sewage sludge might depend on the catalyst used (Huang and Yuan, 2016). Accordingly, in this study, an acid catalyst, i.e. sulphuric acid (VI), was applied and its effect on solid and liquid products resulting from the hydrothermal carbonization process was investigated with a special regard towards the migration of phosphorous and HMs from the solid to liquid phase. Based on recent studies, it was observed that the majority of sewage sludge applied to the hydrothermal treatment was previously anaerobically digested. However, there are a number of small wastewater treatment plants without anaerobic digestion treatment which require modernization and investment. Therefore, there is a great need on the market for newly developed technologies to be installed in order to improve dewaterability, disposal and recovery of nutrients from non-anaerobic digestated sewage sludge. Information concerning ongoing reactions, changes in properties and structure, and the recovery of valuable nutrients from non-anaerobic digested sewage sludge is incomplete and this knowledge gap should be filled to provide new insights for potential investors who are interested in this field. Hence, the novelty of this study concerns aerobic treated sewage sludge, its transformation, changes in the physical and chemical properties and structure as well as the migration of various elements including P and HMs during hydrothermal carbonization with the addition of different amounts of acid catalyst. For this reason, multicriterial analysis and various instrumental techniques were employed.

2. Material and methods

2.1. Material

Dewatered excess sewage sludge was collected from the Wastewater Treatment Plant, Lubin, in the Lower Silesian region of Poland. The treatment of sewage sludge mainly consisted of mechanical and gravitational thickening, fermentation in an open digestion chamber, and mechanical dewatering of pretreated sewage sludge. The material was stored at 4 °C in sealed containers before the tests. Then, the solid mass in the sewage sludge was determined (17%). A portion of the sewage sludge was dried at 105 °C for 24 h, then ground, sieved and stored for further analytical tests. For the hydrothermal carbonization process, sewage sludge (SS) was mixed with distilled water resulting in a moisture content of 89.9% to ensure the homogeneity of the feedstock. Sulphuric acid (VI), 30%, was used to adjust the pH of feedstock. The mixture of sewage sludge and sulphuric acid (VI) before hydrothermal carbonization was prepared to provide an acidic environment. Therefore, 3, 7 and 10 ml of acid were added to the sewage sludge and vigorously mixed to provide homogeneous solutions which resulted in pH = 5, 3.5, and 2, respectively. Then, four samples were investigated under the hydrothermal carbonization process and labelled according to their pH values, namely HTC (no acid addition), HTC_pH 2, HTC_pH 3.5, and HTC_pH 5, respectively.

2.2. Methods

2.2.1. Hydrothermal carbonization procedure

The hydrothermal carbonization set-up consists of a batch type Zipperclave® Stirred Reactor (Parker Autoclave Engineers) with a volume of 1000 ml, a heating system, a cooling system and a temperature controller, pressure and mixing speed. The in-line magnetic stirrer is inside a 316 stainless steel reactor. The electric heating cover can be removed for the cooling process. The hydrothermal carbonization procedure was divided into a few steps. Firstly, 650 g of feedstock was loaded into the reactor. Secondly, the reactor was adequately isolated by a low pressure spring closure, which was designed to reduce the time required to open and close a pressure vessel. Then, the temperature programme was set at 200 °C and maintained for a residence time of 2 h and the feedstock vigorously stirred at the speed of 150 rpm. The autogenous pressure rose to 2.5 MPa. Once the residence time was over, the heat was turned off, the heating cover was removed and the reactor was cooled down by cold water via a cooling coil to room temperature. During the process, the temperature and autogenous pressure in the reactor was recorded on-line and the results depicted on the screen. Finally, the stirrer was turned off and the hydrothermal carbonized products were ready to be evacuated from the reactor. At the beginning, gaseous products were released and a gas sample trapped in a Tedlar bag for composition analysis. After opening the reactor, the slurry was evacuated from the vessel. Vacuum filtration was used to separate the process water (liquid) and hydrochar (solid product) which were precisely weighed to assess HTC product distribution and mass yield. The hydrochar was oven dried at 105 °C for 24 h, pulverized, sieved and stored into plastic containers, whereas process water was poured into glass containers and kept at 4 °C for further analysis.

2.2.2. Fuel characteristics of solid material

Ultimate analysis of solid samples were tested by means of the Elemental Analyzer Truespec Leco CHNS628 under standard PKN–ISO/TS 12902:2007. The oxygen content was calculated as a difference between 100% wt. And measured carbon, hydrogen, nitrogen, and sulphur contents in % wt. Proximate analysis, including moisture, ash and volatile contents, were determined under: PN EN ISO 18134–2:2017, and PN EN ISO 3 standards. The higher heating value was determined by a Leco AC500 isoperibolic calorimeter following DIN 51900 and ISO 1928 standards.

2.2.3. X-ray fluorescence method

The X-ray fluorescence method (WD-XRF) was employed for heavy metal and other element oxide concentrations. The WD-XRF ZSX Primus II Rigaku spectrometer (Rh lamp) was employed under the fluorine - uranium (F–U) range using SQX Calculation software. Based on the XRF analysis and literature, the slagging and fouling indices have been determined including R_B - the percentage of basic constituents in ash, $R_{B/A}$ - the ratio of basic oxides to acid oxides, S_R - viscosity index, R_S - slagging index, F_u - fouling index, LF - ash viscosity index, and slagging ability (Table S1).

2.2.4. Thermogravimetric analysis

The Mettler Toledo analyzer, STAR System TGA/DSC 3 H T 1600 calibrated with indium, zinc and aluminium with accuracy of 10^{-6} g was applied to conduct the combustion process. Accordingly, the solid samples, inserted in an alumina crucible, were heated by 10 °C/min in an air atmosphere with a flow rate of 50 ml/min up to 800 °C. The combustion process was depicted in the form of thermogravimetry (TG), and a weight loss rate of the sample by derivative thermogravimetry (DTG) to assess the thermal characteristics of the fuel samples. Based on the TGA analysis, the following combustion indices have been determined: burnout temperature (T_b), burnout index (D_b), ignition temperature (T_i), ignition index (D_i), combustion comprehensive index (S) and combustion stability index (H_f).

2.2.5. Structural analyses

The analysis of particles was performed using the FEI Inspect S50 microscope employing a low vacuum and an accelerating voltage of 1 kV. Changes in the functional bonds were performed using the Fourier Transformation Infrared Spectroscopy and employing the Bruker spectroscope within the range: 400–4000 cm^{-1}. The multipoint adsorption method using an ASAP 2010 apparatus (Micromeritics Inst.) was employed to measure the specific surface area (SSA) of solid samples by the Brunauer–Emmett–Teller (BET) method.

2.2.6. Analytical methods for post-processing water

Post-processing water characteristics included ultimate analysis following the standards and on the device described above for solid samples. In addition, pH values and conductivity were conducted by means of the Multifunction Laboratory Meter CX-461 ELMETRON. Elements including: heavy metals (cadmium, chromium, copper, iron, lead, mercury, nickel, zinc), and alkali metals (sodium), alkali earth metals (calcium and magnesium) and nonmetal (phosphorous) in a liquid phase, were investigated using two inductively coupled plasma methods (ICP): ICP-MS by means of Thermo Scientific iCAP RQ ICP-MS Spectrometer, and ICP-OES using the Optima 7300 dv PerkinElmer Spectrometer, according to standards PN-EN ISO 17294–2:2016-11 and PN-EN ISO 11885:2009, respectively.

3. Results

The SS characteristics are summarized in Table 1. The ultimate analyses were as follows: carbon content – 39.20%, hydrogen – 5.73%, nitrogen – 6.48%, and sulphur – 1.35%. The ash content (22.78%) and volatile content (66.45%) were used for oxygen and fixed carbon determination, resulting in 24.46% and 10.76%, respectively. The higher heating value was at the level of 17.72 kJ/kg. The ultimate and proximate analyses of sewage sludge slightly differed between the previously studied samples (Wilk et al., 2022) probably because the material was pretreated in an open digestion chamber. Moreover, they corresponded well with the samples studied by Magdziarz and Werle (2014).

The hydrothermal carbonization process of sewage sludge greatly improved its dewaterability and sedimentation. Both processes were studied for feedstock only without catalyst addition. The vacuum filtration process, performed at 0.4 MPa, during the first 5 s resulted in 100 ml of post-processing water and filtration cakes with 52–56% of dry mass as opposed to the non-effective filtration of wet sewage sludge. The sedimentation of slurry was studied for 7200 s. After the first 300 s the clear line between post-processing water and solid particles could already be observed and it completely stabilized after 2400 s. Table 1 presents the main characteristics of dried solid samples (in dry basis), which were determined before and after the hydrothermal carbonization process without and with catalyst addition, represented by the following labelled samples: SS (sewage sludge), HTC (hydrochar produced without acid addition to sewage sludge), and hydrochars produced with acid addition, namely HTC_pH = 5, HTC_pH = 3.5, and HTC_pH = 2. Regarding ultimate analysis, hydrothermal carbonization slightly increased the carbon content of sewage sludge by 1%, and decreased hydrogen by 11%, nitrogen by 60%, sulphur by 74% and oxygen by 50%, respectively.

Table 1

Ultimate and proximate analyses, energy parameters of sewage sludge and hydrochars supported by hydrothermal carbonization product distribution, db.

	SS	HTC	HTC_pH = 5	HTC_pH = 3.5	HTC_pH = 2
Ultimate analysis					
C, %	39.20	41.20	41.18	41.57	41.32
H, %	5.73	5.16	5.09	5.09	4.89
N, %	6.48	3.90	4.04	4.19	4.51
S, %	1.35	1.00	1.38	2.20	2.93
O, %	24.46	12.16	12.22	11.86	12.82
Proximate analysis					
VM, %	66.45	51.21	52.38	54.87	56.49
Ash, %	22.78	36.58	36.09	35.09	33.53
FC, %	10.76	12.21	11.53	10.04	9.98
Energy parameters					
HHV, MJ	17.72	19.04	18.79	18.96	18.72
EY, %	–	45.89	44.80	66.65	59.41
MY, %	–	43.41	41.82	61.43	55.24
EDR	–	1.06	1.07	1.09	1.08
Specific Surface Area, m^2/g	0.4	3.6	5.5	5.8	6.2
Product distribution					
Solid, %	–	4.38	4.22	6.20	5.57
Liquid, %	–	90.65	90.08	89.31	90.16
Gas and losses, %	–	4.97	5.70	4.49	4.27

The addition of sulphuric acid (VI) affected the carbon content in hydrochars only for HTC_pH = 3.5 b y 1%. The hydrogen content decreased when the catalyst volume increased in the feedstock up to 5%, for sample HTC_pH = 2. The nitrogen content gradually increased by 3.6, 7.4, and 15.7% along with a higher catalyst addition, respectively. Consequently, when sulphuric acid was applied as a catalyst, the sulphur contents in hydrochars also increased.

The chemical changes represented by H/C and O/C molar ratios are depicted in the van Krevelen diagram (Fig. 2). Hydrochars underwent dehydration, decarbonization followed by demethanation and are shifted to the left side of the diagram. These results are consistent with previous literature (Gao et al., 2019; Wilk et al., 2022).

As for proximate analysis after hydrothermal treatment, volatile matter decreased by 30%, whereas ash content increased by c. a. 61%. The proximate analysis was also affected by the catalyst addition. Volatile matter gradually increased in hydrochars with an increase in the amount of acid in sewage sludge by 2.3, 7.15 and 10.21% and ash content progressively decreased by 1.4%, 4.2% and 9%. This behaviour was due to decomposition and transformation of organic compounds which occurred during the hydrothermal carbonization process and was responsible for a decrease in the sample weight (mass yield) and an increase in ash content. It was noticed that the ash content increased in hydrochar due to an excess loss of volatile matter. According to Zhang et al. the organic matter dissolved into the liquid phase and inorganic salts and heavy metals were deposited on the surface of hydrochar (Zhang et al., 2014). Whereas, when the catalyst content increased the ash content was slightly lower in the resulting hydrochars due to the leaching process caused by the acidic environment. Consequently, the fixed carbon successively decreased by 6, 17, and 18.3%.

HTC enhanced the higher heating value by 13%. The mass and energy yields for HTC hydrochar achieved c. a. 45%, whereas an acidic catalyst addition to the energy yield increased to a peak value of 66.76% at pH = 3.5, which corresponded with the highest higher heating value and mass yield. Furthermore, this correlated with the highest value of energy densification ratio and solid fraction in hydrothermal products.

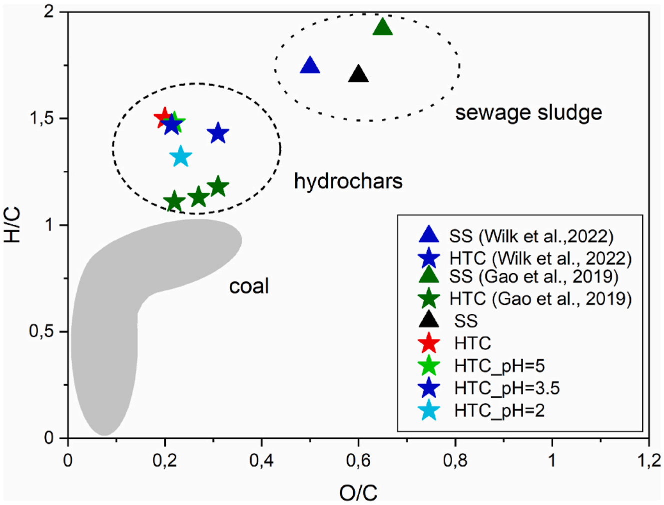

Fig. 2. Van Krevelen diagram.

Additionally, the distribution of hydrothermal products summarized in Table 1 indicate that in the case of HTC_pH = 3.5, the main product was in a liquid phase c. a. 90%.

The results of specific surface area analysis are also summarized. The catalyst only slightly enhanced the porosity of samples. In the case of a low acid value (at pH = 2), the specific surface area increased 20 times.

The addition of sulphuric acid resulted in changes of colour to the feedstock. A higher volume of catalyst caused a more acidic environment and more intensive brightness in colour. This trend was confirmed after hydrothermal carbonization and resulted in the following pH value of post-processing water: 5.35, 5.14 and 4.82 (Table 2).

The thermal behaviour of hydrochars versus sewage sludge are depicted in Fig. 3. Typically, the combustion profiles of sewage sludge and hydrochars are divided into three stages. The first is dedicated to moisture release, which was almost invisible because the samples were dried after the filtration process. Then, the volatile matters were released and combusted. At the end, the chars were combusted. In this case, the combustion of sewage sludge significantly differed from hydrochars. Sewage sludge started to combust earlier (c.a. 200 °C) and finished later (c.a. 550 °C) supported by two DTG peaks at c. a. 270 °C and 520 °C. Hydrochars followed almost the same trends and shapes. However, HTC, represented by a red line, indicated a slight shift to higher temperatures, as it started to combust at c. a. 225 and finished at c. a. 480 °C with two peaks of mass loss c. a. 310 and 430 °C. The two peaks of DTG curves enabled a slight difference between the samples to be distinguished and confirmed that the combustion of HTC was followed by HTC_pH = 5, then HTC_pH = 3.5 and HTC_pH = 2, respectively. At c. a. 220 °C there existed a small peak initializing ignition of combustion and resembling the fluctuation found in sewage sludge at 200 °C. A similar observation was found in other research (He et al., 2013; Merzari et al., 2020; Zhuang et al., 2018). For instance, Zheng et al., 2019 suggested that it was a small quantity of organic compounds which was relatively stable and required higher temperatures, above 280 °C, for hydrolyses. The first peak for hydrochars differed from sewage sludge and was shifted towards a higher range of temperatures from sewage sludge and was found in the range 220 °C–375 °C. This was assigned to the release and combustion of volatile matters from decomposition and solubilization of organic compounds contained in sewage sludge such as debris, colloid, bacteria and others (Zdybel et al., 2018). The second was found earlier than in the case of sewage sludge and was in the range 380–490 °C. The TGA results are consistent with the proximate analysis confirming that after the combustion process of char, the resulting residue for sewage sludge was almost 47% less than in the case of hydrochars. Later, the hydrothermal carbonization mineral matter cumulated, caused by degradation of the material and reactions which occurred under temperature and pressure in an aqueous environment.

Based on TG/DTG/DSC data (Figs. S1–S5) the key combustion parameters including characteristic temperatures T_i, T_1, and T_b, and indices such as D_i, D_b, S and H_f were determined and summarized in Table 3. Hydrothermal carbonization slightly enhanced T_i, which is a critical factor due to potential fire hazards when using hydrochar as solid fuel (Zheng et al., 2019), suggesting a slightly higher difficulty regarding its ignition. T_i increased due to the decrease of volatile matters in hydrochars. However despite the fact that volatile matters significantly reduced it increased by only c. a. 25 °C, which is probably because of the catalysis effect of inorganic matter (higher ash content in hydrochars than in sewage sludge) on combustion reactivity (He et al., 2013). After hydrothermal carbonization T_b decreased by approximately 50–70 °C.

Table 2
Characteristics of post-processing water.

	HTC	HTC_pH = 5	HTC_pH = 3.5	HTC_pH = 2
Ultimate analysis				
C, %	2.84	2.76	2.56	2.59
H, %	10.10	9.66	9.72	9.40
N, %	0.58	0.57	0.56	0.57
pH	5.93	5.35	5.14	4.82
Conductivity, mS/cm	7.32	8.51	6.67	13.02

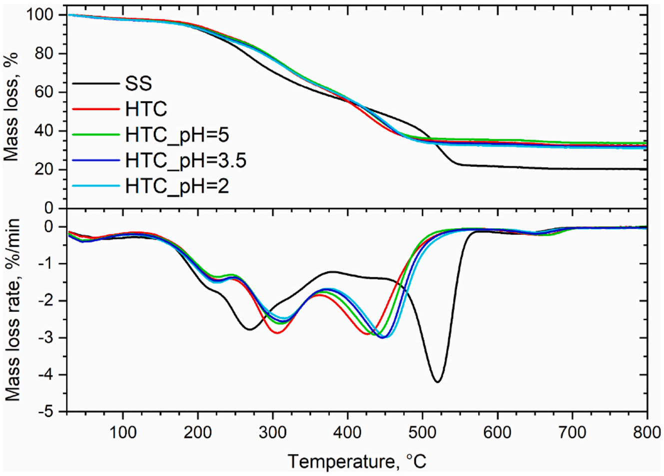

Fig. 3. TG and DTG curves for sewage sludge and hydrochars conducted by thermal analysis (heating rate 10 °C/min, air atmosphere, heated up to 800 °C).

Table 3
The combustion characteristics' parameters determined for SS and hydrochars.

	SS	HTC	HTC_pH = 5	HTC_pH = 3.5	HTC_pH = 2
T_i,°C	200	226	225	223	222
t_i, min	17.60	20.17	20.08	19.92	19.78
T_b,°C	547	482	477	485	493
t_b, min	52.27	45.57	45.63	46.05	46.83
T_1, °C	270	308	307	313	319
t_1, min	24.35	28.20	28.07	28.67	29.27
DTG_1, %/min	−3.174	−3.198	−2.925	−2.805	−2.823
T_2, °C	520	427	437	445	455
DTG_2, %/min	−4.815	−3.414	−3.249	−3.321	−3.429
DTG_{mean}, %/min	1.027	0.872	0.854	0.879	0.888
D_i, $\%/min^3 \cdot 10^{-2}$	0.74	0.56	0.52	0.49	0.49
D_f, $\%/min^4 \cdot 10^{-4}$	1.23	1.12	0.97	0.92	0.87
S, $\%^2/(min^2 \cdot {}^\circ C^3)$ 10^{-8}	14.9	11.3	10.3	10.2	10.3
H_f, °C	805	998	1019	1024	1046

The combustion performance was evaluated by the comprehensive combustion index S which reflects ignition, combustion and burnout properties. A greater value was found for sewage sludge, because it contained a higher content of volatile matter than hydrochars. Index D_i measured the ease of the volatile matter release: the lowest values after the HTC process ($0.0049\% \cdot min^{-3}$) were determined for hydrochars with the longest burnout temperature, e.g. HTC_pH = 3.5 and HTC_pH = 2. The H_f index reflects the quality of the combustion process: its rate and intensity. Lower values of H_f index indicates a more stable combustion process. Although the results suggest that sewage sludge has a better combustion performance, the high volatile matters may cause significant heat loss by destabilized flame and turbulent combustion. For this reason, the combustion performance of hydrochars is expected to perform a relatively better combustion than sewage sludge (He et al., 2013).

Fig. 4 presents the functional groups in sewage sludge and hydrochars provided by FTIR analysis. Generally, the curves depicting the functional groups for solid samples resembled each other with the exception of sewage sludge. An O–H stretching vibration band was found between 3100 and 3400 cm^{-1} as a result of the dehydration process caused by the hydrothermal process. Peaks at 2923 and 2853

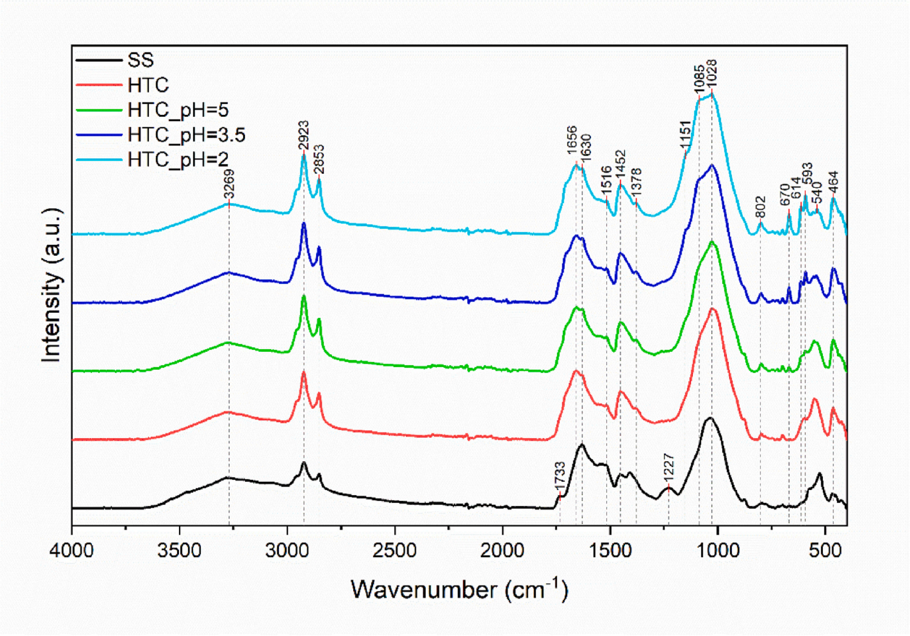

Fig. 4. FTIR results.

cm^{-1}, are associated with C–H stretching in cellulose confirming that aliphatic compounds were created during the hydrothermal carbonization process (Peng et al., 2016). The peak at around 1656 cm^{-1} signifies a protein vibration. The peak at 1516 cm^{-1} probably indicates that the carboxyl group (C═O) is a result of a decarboxylation reaction. The peak located c. a. 1500 $cm^{-1}$is a SiO_2 vibration whereas at 1000 cm^{-1} alkanes, alcohols or phenols appear due to the vibration of C–C skeleton or stretching of C–O bond (Su et al., 2019; Wang et al., 2019; Zhang et al., 2014).

X-ray fluorescence results are summarized in Table 4. The hydrothermal carbonization process resulted in a decrease in phosphorus oxides, and potassium oxide in comparison to sewage sludge. A higher amount of acid catalyst in feedstock provided a further reduction in phosphorus oxides. These results are contrary to those presented by Wang et al. who found an accumulation of phosphorous in the hydrochar under the acidic condition of HTC (Wang et al., 2020). In other words it was proven that aerobic sewage sludge during hydrothermal carbonization causes reactions. An increase in magnesium oxide, aluminium oxide, calcium oxide and iron oxide were found for hydrothermally treated samples. Whereas the addition of the acid catalyst caused their decrease. Sulphur oxide increased because of the addition of sulphuric acid. The hydrothermal carbonization process also affected the heavy metal contents of sludge, because the acidic environment caused their transfer into the process water. For instance, a higher amount of copper, lead, and zinc and lower amount of chromium and nickel oxides were detected in hydrochars.

Table 4
XRF results for a) SS b) HTC c) HTC_pH = 2 d) HTC_pH = 3.5 e) HTC_pH = 5.

Compounds	SS	HTC	HTC_pH = 5	HTC_pH = 3.5	HTC_pH = 2
Na_2O	0.8153	0.5066	0.4746	0.4443	0.4904
MgO	4.6777	4.8100	4.6763	4.4601	3.9290
Al_2O_3	5.4761	6.4932	6.4865	6.5979	6.3721
SiO_2	20.4600	21.3478	21.1093	21.2750	20.9872
P_2O_5	29.5347	26.8832	26.6472	24.0831	22.3130
SO_3	2.5372	2.8503	4.4213	8.9990	12.8801
Cl	0.0404	0.0245	0.0180	0.0111	0.0126
K_2O	3.1679	1.4399	1.2809	1.4090	1.5127
CaO	20.0260	21.1726	20.4536	18.1619	17.9915
TiO_2	1.0982	1.2987	1.2565	1.2992	1.2222
V_2O_5	0.0188	0.0161	0.0122	0.0173	0.0079
Cr_2O_3	0.0809	0.0808	0.0646	0.0727	0.0848
MnO	0.6101	0.6860	0.6532	0.6422	0.5984
Fe_2O_3	10.5483	11.3501	11.3947	11.4543	10.5562
NiO	0.0163	0.0132	0.0146	0.0130	0.0128
CuO	0.1568	0.1943	0.1806	0.1863	0.1978
ZnO	0.3586	0.4320	0.4344	0.4362	0.4149
Br	0.0181	0.0035	0.0062	0.0019	0.0020
SrO	0.0517	0.0585	0.0561	0.0535	0.0518
ZrO_2	0.0521	0.0546	0.0572	0.0534	0.0475
SnO_2	0.0121	0.0172	nd	0.0085	0.0112
BaO	0.1882	0.1947	0.2362	0.2445	0.2388
PbO	0.0526	0.0631	0.0613	0.0490	0.0563

nd – no data.

High and medium tendencies for slagging are determined based on oxide contents in sewage sludge and hydrochars, which enable operational risks to be defined (Table S2). Both sewage sludge and hydrochar, and hydrochars produced with an altered pH, have a very high slagging tendency and form impurities, which result from very high S_R and F_u indices. This occurs because the amount of alkali metal oxides is much smaller than that of SiO_2, Fe_2O_3 and Al_2O_3. Additionally, the value of Fe_2O_3/CaO, which is in the range of 0.3 ÷ 3.0 for all samples, suggests that the eutectics and consequently high quantities of slag may be formed The parameter R_s for sewage sludge and hydrochar indicates a high or medium slagging tendency. For hydrochar without a pH change and hydrochar pH 5, this parameter decreases slightly. Therefore, it is difficult to evaluate the influence of hydrothermal carbonization and the pH changes during the process on ash slagging (Magdziarz et al., 2018; Parmar and Ross, 2019; Syed-Hassan et al., 2017).

Table 5 summarizes the results from ICP-OES and ICP-MS analyses of element compositions in post-processing water. In general, the acid catalyst caused an increase in phosphorous, magnesium, calcium, and zinc. However, the iron content was significantly decreased. HMs, represented by chromium, mercury, and nickel, decreased due to the positive effect of the acid catalyst. For more detailed analyses the fractionation procedure is required (Liu et al., 2018; Latosińska et al., 2021). An increase in the migration of P to post-processing water under more acidic conditions is very promising for phosphorous recovery, e.g. by struvite precipitation. The direct recovery of P from sludge is a significant problem because of contamination by harmful substances. Therefore, hydrothermal carbonization provides an opportunity for the safe recycling of this critical element in a sustainable way ensuring its

Table 5
Elements found in post-processing water after the hydrothermal carbonization process.

Elements ml/g	Post-processing water			
	HTC	HTC_pH = 5	HTC_pH = 3.5	HTC_pH = 2
Cd	<0.0003	<0.0003	<0.0003	<0.0003
Cr	0.789	0.612	0.496	0.457
Cu	<0.001	<0.001	<0.001	<0.001
Fe	46.76	40.42	33.39	34.93
Pb	<0.0001	<0.0001	<0.0001	<0.0001
Hg	0.0016	0.0002	0.0002	0.0002
Ni	0.271	0.193	0.194	0.215
Zn	0.349	0.342	0.512	0.838
Na	103.3	91.1	96.2	108.1
Ca	106.1	275.2	467.2	592.7
Mg	91.9	101.2	149.7	243.9
P	452.2	487.4	698.8	862.2

use as a fertilizer (Wang et al., 2020). Accordingly, the assessment of optimal conditions for the migration of phosphorous from hydrochar to postprocessing is a crucial issue. In this case, it was found that a pH = 2 of feedstock was the most effective for leaching P from aerobic sewage sludge to HTC post-processing water resulting in an almost two times higher amount of P when compared to post-processing liquid from hydrothermal carbonization without any acidic catalyst.

Figs. S6–S10 show the SEM results combined with the EDS analysis for sewage sludge and hydrochar. It was observed that the sewage sludge consisted of variously sized particles and shapes. It was further noted that the HTC process and the addition of acid affected the particles structure providing more homogeneous and fragmented material. The EDS method identified the following elements: C, O, Na, Mg, Al, Si, P, K, Ca, Mn and Fe, between which carbon was the dominant element. The ashes of sewage sludge and hydrochars were also analyzed by the SEM-EDS technique (Figs. S11–S15). According to the results, smaller particles and a lower amount of carbon was detected in ash derived from hydrochars than in ash from sewage sludge (Gaur et al., 2020; Wilk et al., 2022).

4. Conclusion

The carbon content, higher heating value, and fixed carbon proved that the fuel properties of hydrochars were slightly enhanced in comparison to sewage sludge pretreated in open digestion chambers. Moreover, thermal analysis indicated that hydrochars could be combusted earlier at a higher temperature in a shorter period of time. The addition of an acidic catalyst to the feedstock did not significantly affect those properties. However, regarding the specific surface area, it was found that hydrochars, modified by the highest content of sulphuric acid (VI), were 20 times higher than in the case of sewage sludge. This was mainly caused by degradation and transformation of feedstock identified by FTIR results. The XRF spectrometry indicated that the catalyst addition caused an increase in zinc, copper, and lead oxides, and a decrease in chromium and nickel compounds in hydrochars. In the post-processing water, the ICP-OES and ICP-MS analyses identified heavy metals proving that during the hydrothermal carbonization process, migration of those elements occurred. It was found that the addition of the acid catalyst caused a decrease in the heavy metals including mercury, chromium, and nickel contents and an increase in phosphorous, magnesium, calcium, and zinc. The most promising condition for phosphorous recovery from post-processing water was found for feedstock with pH = 2, where phosphorus content was almost two times higher than in the case of hydrothermal treatment without any catalyst.

Credit author statement

Authors confirm their following contribution in the preparation of the manuscript:

1. Małgorzata Wilk - corresponding author, conceptual design and idea of investigations concerning the detailed description of hydrothermal carbonization products and raw material, development and design of methodology of hydrothermal carbonization, conducting a research and HTC investigation process, specifically performing the experiments, and data collection, analysis of results, preparation of manuscript, writing – original draft preparation, writing – original draft review and editing, funding acquisition, supervision, Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Writing - original draft, Visualization, Writing - review & editing, Funding acquisition, Project administration, Supervision.2. Maciej Śliz - conducting a research and HTC investigation, specifically performing the experiments, and data collection, analysis of results, preparation of manuscript, Formal analysis, Data collection, Investigation, Resources, Validation, Visualization. 3. Klaudia Czerwińska - development and design of methodology of post-processing water investigation, specifically performing the experiments, and data collection, analysis of results, preparation of manuscript, Formal analysis, Data collection, Investigation, Methodology, Resources, Validation, Writing - original draft, Visualization.4. Małgorzata Śledź - specifically performing the experiments, and data collection, analysis of results Investigation, Data collection, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data are available in https://doi.org/10.58032/AGH/0GLKOG.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.118820.

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