Renewable Energy 178 (2021) 1046–1056

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Hydrothermal co-carbonization of sewage sludge and fuel additives: Combustion performance of hydrochar

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ARTICLE INFO

Article history:
Received 2 March 2021
Received in revised form
27 May 2021
Accepted 23 June 2021
Available online 24 June 2021

Keywords:
Hydrothermal carbonization
Sewage sludge
Biomass
Hydrochar
Combustion

ABSTRACT

Hydrothermal treatment improves dewaterability of sewage sludge, but its solid product (hydrochar) requires enhancement for energy production. Hydrothermal co-carbonization (co-HTC) of sewage sludge and fuel additives could be a successful solution, and in addition boost dewaterability. Thus, sewage sludge with charcoal (10% db), oak sawdust (10% db) and fir sawdust (10% and 20% db) was hydrothermally carbonized. Prior to and after the process, the physical and chemical properties of samples were analyzed and compared. Capillary suction time and filtration tests were conducted in terms of dewaterability. The fuel properties of hydrochars, were determined, namely ultimate and proximate analyses, higher heating values and thermal analysis. Based on the ash composition the operating risk indexes were found. Additionally, the combustion kinetic and comprehensive combustibility indexes were calculated. Concluding, the addition of biomass to the co-HTC process halved the time required for the filtration process and improved dewaterability to 41% moisture content. The higher heating value of hydrochar derived from sewage sludge and 20% fir addition, increased by approximately 6%. Moreover, all additives are believed to provide a more stable combustion process demonstrated by higher values of carbon content (from 34.9% to 37.9%) and lower values of volatile matter (from 56.4% to 40.7%).

1. Introduction

Sewage sludge (SS) is a major waste product generated in the municipal wastewater treatment process and contains not only high organic matter, but also heavy metals, organic contaminants and pathogens. This causes operating difficulties due to its large volume, quantity, high moisture content and unpleasant odour. Currently, it is disposed of in several ways. Among others, the most common ways include: incineration, agricultural application, landfilling and land reclamation [1]. Even though sewage sludge has only 1–3% of total wastewater volume, in Poland in 2019 one thousand tonnes of dry mass sewage sludge was generated. However, over six thousand tonnes had already accumulated in the wastewater treatment plants area, which is over 2 times lower in comparison to the year 2000. Despite the generated problems, sewage sludge can be treated as a potential energy resource as well as a valuable source of nitrogen and phosphorus, especially in terms of the circular economy [2]. A serious problem for sewage treatment plants is the removal of water and neutralization of sludge. One way of dealing with these problems is by conditioning. This is a process that changes the structure and properties of sludge and allows for effective dewatering. It can be carried out using chemical or physical processes such as washing, freezing and thermal conditioning or by the application of various mineral additives [3,4]. The addition of porous material can decrease compressibility and increase permeability acting as a filter aid or as a skeleton builder enhancing the filtration process. Other physical methods use acoustic waves in the sonication process or electrical field. Among the chemical conditioning methods, coagulation, pH variation and advanced oxidation processes can be distinguished. Nevertheless, employing thermochemical methods ensures the complete disinfection of sewage sludge [5,6]. After the successful removal of water to at least 60% of the moisture content, thermal utilization can be used. Pyrolysis, gasification, combustion and co-combustion with other fuels are the most important and widely studied technologies of thermal waste utilization [7–9]. Moreover, legislation rules enforce the development of thermal utilization methods of SS. For the last 20 years, wastewater management and water protection,

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https://doi.org/10.1016/j.renene.2021.06.101
0960-1481/

and protection of air and climate have been the most cost-consuming direction for investment in environmental protection in Poland. Investments in 2019 reached over 6000 million PLN in total. Thus, 56 new wastewater treatment plants were developed providing, at the end of the year, 3278 facilities of this type. Sludge incineration plants are currently being built in Poland, but their number is insufficient for current needs. They require a much larger investment than biomass incineration plants, because sewage sludge requires drying, stabilization and a dewatering process as well as a special pretreatment before the combustion process. Thus, they are mainly located in large cities. Prior to drying the sludge, it is subjected to natural or mechanical thickening. These processes affect changes in the physical and chemical properties of SS and that is why the chemical composition of sewage sludge is not only variable, but also depends on many factors, including the type of treated sludge and the processes applied. This is another reason that is in favour of physical conditioning methods which are less vulnerable to variations in the treated material.

In recent years, efficient methods of waste management and possible routes of sewage sludge utilization have been sought. High moisture content in sewage sludge is one of the biggest economical and logistical obstacles, thus a solution is needed. Wu et al. conducted an extensive review on the dewatering of sewage sludge indicating many important and accurate remarks [3]. Despite the thermal utilization process, water removal from sewage sludge is also carried out in order to decrease sludge volume, ease possible transportation and increase the total efficiency of the disposal process. Problems connected with sludge dewatering originate from highly hydrated colloidal structures of microbial aggregates [10] and also from water in the SS which is bonded in different ways. Four categories can be distinguished: free water, also called moderately mobile water; interstitial water, which is mechanically trapped in the structures of flocs; vicinal water, which is adjoined to the surface of organic compositions; and water of hydration [4]. Among these factors influencing water removal, viscosity, compressibility and porosity should be differentiated from rheological properties. Moreover, other important properties to consider include: particle size, surface charge, micromorphology, and content and composition of extracellular polymeric substances (EPS). The latter builds an exterior layer of microbial aggregates, hence, they interact with water molecules and influence the hydrophobic and hydrophilic properties of flocs.

Hydrothermal treatment may alter the structure of sewage sludge. The removal of hydrophilic functional groups from organic fractions can lead to enhanced dewaterability [5]. HTC of wet sewage sludge is based on complex reactions occurring at elevated temperatures and pressure in an aqueous environment. It converts sludge into a more homogeneous and energy-dense form. The basic parameters of this process concerns temperatures in the range of 150–300 °C with a reaction time from a few minutes to up to 48 h. Pressure is often autogenic and can range from 2 MPa to 10 MPa [5]. Recently, Ruksathamcharoen et al. [11] reported using specific values of pressure to enhance the degradation of feedstock. To assure that the reactions are going to take place similiary throughout the volume of the reactor usually a built in stirrer is used. The application of an elevated temperature and pressure ensures that hydrolysis, dehydration, decarboxylation, polymeric condensation and aromatization occurs [12]. Those reactions do not run separately, but rather mesh with each other [13]. The process of hydrothermal carbonization is widely studied, and there are trials to predict the properties of the products [14–16]. The HTC process creates products in three states of matter. The gas product takes a few percent of input mass and consists mainly of CO_2. The ratio of liquid and solid product depends on the initial moisture content of the sewage sludge and the process parameters. Generally, the mass of solid phase decreases because of the release of water and carbon dioxide as well as the leaching of some compounds into the liquid. As an outcome, the molar ratios of H/C and O/C become lower giving values closer to those of coal [59–61].

The features of this process essentially distinguish it from the biological processes of methane or alcohol fermentation, which depend mainly on the action of microorganisms. Due to the high water content in sewage sludge, HTC technology seems to be an adequate method of pretreatment. The great advantage of HTC is its lower energy consumption rather than the pre-drying of sewage sludge in a conventional incineration plant, which is more costly. In addition, the water separated from the sludge can be returned to the wastewater treatment plant, and not be irreversibly evaporated when drying. The hydrochar produced in HTC installations can be used for further thermal conversion in order to obtain energy: either through direct combustion or the gasification process [62]. The hydrochar can also be used as a fertilizer [17]. Despite many investigations concerning sewage sludge hydrothermal carbonization [18–20], new studies have been conducted on the combustion of hydrochars derived from sewage sludge [21,22]. The research [21] is focussed on co-carbonization of sewage sludge with agriculture residue, whereas [22] concerns the HTC of dried SS.

Recently, a new trend has been observed which indicates an enhancement in the positive results of the hydrothermal process by mixing sewage sludge with different additives. Many researchers focus on the fuel properties of the received hydrochars [21,23,24]. The addition of biomass is characterized by a higher carbon and lower ash content which may improve the overall composition of the produced hydrochars. Moreover, after the hydrothermal process, supported by the additives, higher calorific values and energy yields of the produced hydrochars were reported [25,26]. Other researchers investigated the movement of heavy metals after conditioning while only a few examined changes in the dewaterability of hydrothermally treated sludge (HTTS). Recently published research is summarized in Table 1.

According to He et al. [21] and Azzaz et al. [31] it can be stated that the organic additives were indeed found to increase carbon content and a higher heating value of derived hydrochars while, and simultaneously, the combustion process became more stable. Heavy metals were reported to be trapped in solid fraction in a more immobilized form after the hydrothermal process [27]. Thus, providing an easier liquid phase purification. The recovery of phosphorus is also an important aspect, taking into account the depletion of natural resources such as phosphate ore [2]. Due to hydrothermal treatment, nitrogen release pathways are altered, which leads to the release of a volatile nitrogen during the combustion of hydrochars e.g. NH_3. This facilitates a reaction between NH_3 and NO, which decreases the risk of NO_x emissions [5]. Moreover, comprehensive studies on dewaterability enhancement of sewage sludge may help in the transition from laboratory to commercial scale as well as find the optimal conditions for maximal energy and resource recovery. At the same time it will allow a decrease in the number of troublesome by-products of wastewater treatment plants' processes.

To the authors' best knowledge, the dewaterability and combustion properties of hydrothermally co-carbonized sewage sludge and biomass have not been widely studied. This is the reason why the authors wish to undertake research which focusses on both issues: dewaterability and the fuel properties of hydrochars. HTC of sewage sludge and biomass additives, charcoal (10% db), oak sawdust (10% db) and fir sawdust (10% and 20% db) were conducted, respectively. Prior to and after the HTC process, the physical and chemical properties of solid materials were analyzed to examine the hydrochars and discuss their perspective in the energy production sector. Moreover, the dewatering performance

Table 1
Selected additives applied to sewage sludge in hydrothermal treatment.

Additives	Temp., °C	Time, h	Volume, ml	Main focus	Authors	Ref.
fruit and agricultural waste	220	12	100	fuel properties	He et al., 2019	[21]
food waste	180, 230, 280	1	250	fuel properties	Zheng et al., 2019	[23]
phenolic wastewater	140, 170, 200, 230, 260	2, 4, 6, 8, 10	250	fuel properties	Wang et al., 2020	[24]
rice husk	200	1	200	heavy metals immobilization	Shi et al., 2013	[27]
lignocellulosic biomass	220	1	–	fuel properties and heavy metal content	Lu et al., 2021	[28]
sawdust, corncob, cornstalk, rape straw	220, 260, 300	1	500	dewaterability	Zhai et al., 2017	[29]
sawdust	120, 150, 180, 210, 240	0.33	250	dewaterability and fuel properties	Wang et al., 2020	[30]
hydrochloric acid	170	0.5	250	recovery of phosphorus	Shi et al., 2019	[2]

supported by capillary suction time and filtration tests were determined to confirm the advantages of the hydrothermal treatment process.

2. Materials and methods

The sewage sludge used in this study was collected from the Central Sewage Treatment Plant Radzionków, Poland, in July 2019. It was digested and pre-concentrated to 82.8% of moisture content. It was rather solid in consistency and required dilution prior to the hydrothermal process. The addition of distilled water was needed to increase the moisture content to 89.4% in order to provide effortless stirring of the sewage sludge. In the meantime, SS was stored at 4 °C to prevent changes in its physical and chemical properties.

In the following tests, different additives were used in order to find out which one would best enhance the dewaterability and combustion properties of the produced hydrochars. Two types of lignocellulosic biomass and charcoal were used. Oak sawdust, as an example of a deciduous tree, was applied and fir, as an example of a coniferous tree, was tested. Commercially available charcoal was used after being ground in a roller mill to an analytical state below 0.2 mm. Oak sawdust, with a particle size of below 1 mm, was collected from a sawmill in Libertów, Poland. Fir was supplied in the form of branches and was shredded by an electric planer into chips. Subsequently, it was milled to below 1 mm using a knife mill LN-100 Testchem available at the Centre of Energy, AGH UST. The biomass was air dried at room temperature and stored in open containers prior to further tests.

2.1. Hydrothermal carbonization

The experimental set up for hydrothermal carbonization consists of a Zipperclave Stirred Reactor, Parker Autoclave Engineers, USA. The reactor has a built-in stirrer, a cooling coil inside and an electric heating mantle on the exterior. It is capable of operating at a pressure up to 15.1 MPa and at a temperature up to 232 °C. Both temperature and stirrer speed can be set on the control panel. The schematic diagram of the test stand is shown in Fig. 1.

At the beginning, 700 ml of diluted sewage sludge was inserted into the reactor. The parameters of the hydrothermal carbonization process were fixed and set to a temperature of 200 °C and a residence time of 2 h with the stirrer at 150 RPM. The only variable was the composition of the feedstock. Firstly, sewage sludge without any addition was processed. Then, different additives were used: 10% charcoal, 10% oak sawdust, 10% and 20% fir sawdust (dry basis was taken into account). The result of the addition of fir to sewage sludge provided the most repeatable and satisfactory filtration results and that is why it was also tested at a higher concentration. At the end of the reaction time, the heating was turned off, the heating mantle was removed, and the reactor was cooled down to room temperature. Afterwards, the received slurry was stored in sealed

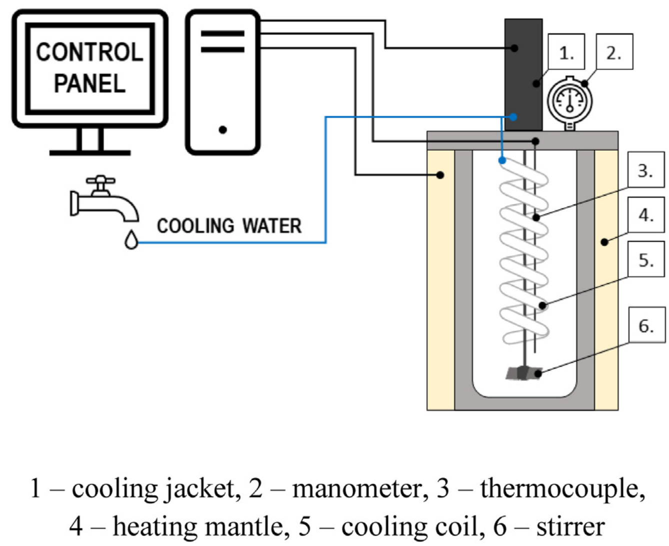

Fig. 1. Schematic diagram of HTC apparatus [32].

containers before further testing.

Untreated sewage sludge and the received hydrothermally treated sludge from each run was subjected to capillary suction time tests (CST) and filtration tests to investigate changes in dewaterability. CST was conducted according to EN 14701-1:2006 with a CST meter. A cylinder with a diameter of 18 mm and height of 25 mm was placed on filtration paper and filled with sludge. Water from the sludge travelled through the paper by capillary action and the time was recorded between sensors at circles of diameters 32 mm and 45 mm, which gave the results for the test. When water had a small affinity with the sludge, the recorded times were much shorter.

For filtration tests a hydraulic pressure unit was used and two different approaches were employed. In the first one, the conventional three-step filtration was used (I-filtration, II-pressing, III-blowing) to achieve the lowest moisture content. The second one consisted of a one-step filtration with constant pressure to investigate the ease of the dewatering process. The moisture content of the received filter cakes was measured by using the moisture analyzer AXIS BTS, then the hydrochars were dried at 105 °C and stored for further analysis. Similarly, the filtrate was collected and stored in sealed containers for analysis.

2.2. Analytical methods

The additives and produced hydrochars underwent detailed analysis in order to assess their influence on the properties of sewage sludge.

Proximate analysis was conducted to determine moisture, ash and volatile matter contents. All analyses for sewage sludge, biomass and charcoal were carried out in accordance with applicable standards. The moisture content was measured according to EN ISO 18134-2:2017. Determination of the moisture content prior to and after hydrothermal carbonization and after the filtration process allowed mass yield and water removal efficiency to be calculated, thus, the dewaterability was estimated. Ash and volatile matter content were determined according to EN ISO 18122:2015 and EN ISO 18123:2015, respectively. They are very important parameters which influence the combustion process, hence, the need for control.

Ultimate analysis was performed using the Truespec LECO CHNS628 Analyzer, according to PKN-ISO/TS 12902:2007. The analysis of carbon, hydrogen and nitrogen consists of complete and total combustion of the tested sample (0.1 g) at 950 °C in oxygen, while the analysis of sulphur content was conducted at 1350 °C. The oxygen content of the samples was calculated on dry basis as the difference between 100% and the sum of ash content and other determined elements. Based on the C, H, N and S elements, the calculations of atomic ratios (H/C and O/C) were carried out in order to investigate the decarboxylation, dehydration, and demethanation processes of hydrothermally treated sludge.

The high heating value (HHV) was determined in a Leco AC500 isoperibolic calorimeter. All analyses were performed on dried samples. Changes found in HHVs provide the most basic information regarding the energy potential of the studied material.

XRF analysis of dried sewage sludge and ashes from sewage sludge, oak and fir was performed on a WD-XRF ZSX Primus II Rigaku spectrometer (Rh lamp) by the X-ray fluorescence method (WD-XRF). A qualitative spectrum analysis was executed by identifying spectral lines and determining their possible coincidences. Based on this, analytical lines were selected. Semi-quantitative analysis was developed using the SQX Calculation software (a method of determining fundamental parameters). The analysis was carried out in the fluorine - uranium (F-U) range, and the content of the determined elements was normalized to 100%. Analysis of the ash composition may allow the exploitation risks, connected with the combustion of the sludge, to be established. Therefore, based on the identified oxides in ash, the following indexes were determined: S_R - viscosity index, R_S – slagging index, F_u - fouling index.

In order to study the migration of heavy metals, post-processed water was collected after filtration and examined at the accredited laboratory of Kraków Waterworks. The following tests were performed: pH chemical oxygen demand (COD), total organic carbon (TOC), ammoniacal nitrogen, Kjeldahl nitrogen, total nitrogen, total phosphorus, electrical conductivity, detection of metals: arsenic, zinc, cadmium, copper, nickel, lead, general chromium and mercury. In addition, kinematic viscosity tests of filtrates were performed using Ubbelohde viscometers placed in a water bath at 25 and 60 °C. Density was measured as well by weighing the volumetric flask with filtrate.

The specific surface area of the materials was measured by the BET (Brunauer-Emmett-Teller) multipoint adsorption method using the ASAP 2010 apparatus (Micromeritics Inst.). Measurements were made at 77 K using nitrogen as the adsorbate. Before the measurements were calculated, the samples were degassed at 200 °C for 24 h.

Thermogravimetric analysis of dried sewage sludge and hydrochars was performed using the Mettler Toledo analyser, STAR System TGA/DSC 3 HT 1600. About 5 mg of sample was combusted in an air atmosphere with a flow rate of 50 ml/min and varied heating rates of 5, 10 and 20 K/min. During the linear temperature increase, the weight change in the form of TG curves (thermogravimetry) and thermal effects in the form of the DSC curve were recorded continuously. DTG curves were obtained as a result of mathematical transformations (differentiation of the TG curve as a function of temperature). The DTG curve facilitates the discrimination and separation of mass losses occurring in similar conditions, which on the TG curve may be unnoticed. The results of thermogravimetric analysis were used to calculate the combustibility indexes as well as kinetic parameters such as activation energy and pre-exponential factor.

2.3. Kinetic analysis

Significant parameters of kinetic study in the combustion process (activation energy, *Ea*, and pre-exponential factor, *A*) were estimated by three model-free methods: Friedman, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) [33–36]. The ratio of solid-state reaction rate was described by eq. (1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where t and T depict the time and temperature of the process. And α shows the conversion rate of the sample given by eq. (2):

$$\alpha = \frac{m_{i0} - m_a}{m_{i0} - m_f} \tag{2}$$

where m_{i0}, m_a, and m_f depict the initial mass of the sample, the actual mass, and mass after combustion, respectively. The Arrhenius equation defined the rate constant k determined by the temperature and is presented as:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where R depicts a gas constant, A - a pre-exponential factor, and E_a - an activation energy. Based on the TGA results the reaction rate in analytical methods was calculated by:

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

For non-isothermal TG experiments, in which a sample was heated at a constant rate, and $\beta = \frac{dT}{dt}$ was the heating rate of the combustion, the conversion of material during the temperature change was given by:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

The integration of this equation is expressed as:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \tag{6}$$

If x is given by E_a/RT and integration limits, the transformed equation (6) becomes:

$$g(\alpha) = \frac{AE_a}{\beta R}\int_0^\infty \frac{\exp(-x)}{x^2} dx = \frac{AE_a}{\beta R} p(x) \tag{7}$$

Integral $p(x)$ must be approximated [37]. Different approximation formulas and a variety of methods were applied to calculate the activation energy [38–42]. Among them the earliest isoconversion method was the Friedman method [43] in which:

$$\beta \frac{d\alpha}{dT} = A \cdot e^{\frac{-E_a}{RT}} f(\alpha) \tag{8}$$

transformed to:

$$\ln\left[\beta \frac{d\alpha}{dT}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_{a,\alpha}}{RT_\alpha} \tag{9}$$

The Kissinger-Akahira-Sunose method is also frequently applied [42,44] and based on the Coats-Redfern approximation of the *p(x)* [38]:

$$p(x) = \frac{e^{-x}}{x^2} \tag{10}$$

where the plot of *ln[βdα/dT]* versus *1/T* at each α formed a straight line by fitting the data achieved at several heating rates and thus E_a was calculated through the slope of the plot resulting in

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{E_{a,\alpha} g(\alpha)}\right) - \frac{E_{a,\alpha}}{RT_\alpha} \tag{11}$$

with the apparent activation energy being obtained from a plot of $ln(\beta/T_\alpha^2)$ versus *1/T* for a given value of conversion α, where the slope is equal to $-E_a/R$. Whereas, the Flynn-Wall-Ozawa method is based on Doyle's approximation of *p(x)* [39]:

$$\log p(x) = -2.315 - 0.4567\ x \tag{12}$$

which results in the following equation:

$$ln\beta = \ln\left[\frac{0.0048E_a}{Rg(\alpha)}\right] - 1.0516\frac{E_a}{RT} \tag{13}$$

The activation energy was determined by measuring the temperatures corresponding to the fixed values of α from experiments conducted at different heating rates from the slope of the plot of *ln β* vs. *1/T*.

3. Results and discussion

3.1. Proximate and ultimate analysis of feedstock and hydrochars

Raw sewage sludge, delivered to the laboratory, contained 82.8% moisture, which was then diluted (in order to obtain an easily mixable consistency) before using the HTC process to obtain a moisture content of 89.4%. However, after the HTC process, the moisture content in the hydrothermally treated sludge (HTTS) increased to 92%. In other words, the dry matter content in the sludge decreased from 10.6% to 8% which was a drop of 24.5%.

The results of ultimate and proximate analyses, supported by high heating values are presented in Table 2. The moisture content for hydrothermally treated sludge was measured directly after filtration. Other parameters were examined after proper drying of the samples. Hydrothermal carbonization caused an increase in the ash content from 36.49% to 52.04%, but the presence of the additive moderated that unwanted effect, namely 44.58% ash content for HTTS+20% fir, was found. Generally, during the biomass degradation under hydrothermal carbonization, the inorganic elements are released and dissolved in the processing solution, thus, a lower ash content in hydrochar is found than in raw biomass [31]. In the case of sewage sludge, the opposite results have been found [13,28]. Due to the excess loss of volatile matter, retention of minerals and degradation of organic substances, an increase of ash in the hydrochar is observed [2,27]. The volatile matter content decreased after conditioning from 56.39% to 47.67% for sludge without an additive and further to 40.66% for sludge conditioned with 10% charcoal. Minor changes in the elemental composition of the received hydrochars were observed. The carbon content increased by 3% points moving up from 34.9% and achieving the highest value after treatment with charcoal. The highest high heating value was measured for HTTS+20% fir − 16 MJ/kg, in contrast to untreated, dried sewage sludge − 15 MJ/kg. A slight decrease in the higher heating content of the HHTS product after hydrothermal carbonization of the dried SS is probably due to dissolution of biopolymers. According to Wang et al. [2] it can be caused by extraction of oxygen-rich substances and the hydrolysis of compounds with low higher heating values. Another hypothesis proposed by Wang et al. [2] is the leaching of some organic compounds to post-processing water or changes in the chemical composition of products caused by filtration conditions e.g. applied membrane or lack of washing of the separated solid part. Altogether, higher HHV, C and FC contents, supported by lower VM content, led to a more favourable combustion performance, which can be confirmed by the combustion index values.

Hydrothermal treatment slightly alters the carbon content in sewage sludge, but the addition of biomass significantly increases its content, namely from 34.9% to 37.9%. The nitrogen content decreases after HT conditioning by about 11% from 4.28 to 3.80%, and even as much as 50% after co-carbonization, namely to 2.15%. The trends noticed in Table 2 were also reported in other studies. Zheng et al. pointed out that it may be connected with the stopping of Maillard's reaction and the occurrence of denitrification [23]. The results concerning the increase in fixed carbon and the decrease in volatile matter are consistent with those reported by Wang et al. [24] and He et al. [21]. The decrease in VM content proves that the devolatilization process has taken place [45]. It is also connected with an increased ash content due to retained minerals after devolatilization [46].

Table 2
Results of ultimate, proximate and HHV analyses.

Material	M^{ar}	A^{db}	VM^{db}	FC^{db}	C^{db}	H^{db}	N^{db}	S^{db}	O^{db}	HHV^{db}
	%	%	%	%	%	%	%	%	%	kJ/kg
Dried SS	3.4	36.49	56.39	7.12	34.9	5.04	4.28	2.53	16.76	15,088
Fir sawdust	4.7	1.75	82.41	15.84	47.5	6.52	0.00	0.00	44.08	18,287
Oak sawdust	4.6	1.11	84.90	13.99	47.3	6.37	0.19	0.00	44.83	18,264
Charcoal	3.3	3.14	27.49	69.37	77.8	3.69	0.66	0.06	15,13	30,491
HTTS	47.9	52.04	47.67	0.29	35.6	4.70	3.80	3.11	0.75	14,347
HTTS + 10% fir	44.1	47.05	43.79	9.16	35.1	4.35	2.23	2.93	8.34	15,313
HTTS + 10% oak	41.2	46.01	40.89	13.10	36.9	4.24	2.15	2.95	7.75	15,440
HTTS + 10% charcoal	41.5	45.90	40.66	13.44	37.9	4.18	2.17	2.87	6.98	11,566
HTTS + 20% fir	44.0	44.58	44.48	10.94	36.6	4.48	2.18	2.62	9.54	16,038

M − moisture, A − ash, VM − volatile matter, FC − fixed carbon, C − carbon, H − hydrogen, N − nitrogen, S − sulphur, O − oxygen, HHV − high heating value, ar − as received, db − dry basis.

3.2. Chemical composition of ash and operating risk indexes

The results from X-ray fluorescence analysis are summarized in Table 3. The combustion process slightly altered the oxide composition in sewage sludge and its ash. Contents of sodium, magnesium, aluminium and phosphor oxides increased while contents of sulphur, potassium, calcium and iron oxides decreased. The distribution of identified oxides in dried SS can be organized from the highest to the lowest values: Fe > Si > Ca > P > S and for ash derived from SS Si > P > Fe > Ca > Al. Taking into account the dewaterability performance, high values of CaO and SiO_2 in additives are preferable. XRF analysis confirmed that there was a high content of Ca in the applied additives. Based on detailed analysis of the ash composition from sewage sludge and hydrochar, the typical indexes which make it possible to predict operating problems were determined. They characterized the ash behaviour and its deposition tendencies during the combustion process. The transformation of inorganic matter contained in sewage sludge may cause corrosion, fouling and slagging. Thus, the following indexes were calculated: S_R - viscosity index, R_S – slagging index, F_u - fouling index [47,48] and are presented in Table 4. For the slagging index, there was an inclination toward an extremely high tendency for slagging in both ashes derived from sewage sludge and hydrochar ($R_S > 2.0$), respectively. Similar conclusions were drawn when taking into account the viscosity index ($S_R < 65$). Whereas, the fouling index presented a high inclination to sintering and fouling ($0.6 < F_u < 40$). Ratios of Fe_2O_3 to CaO were found to be in the range of 0.3–3.0. This suggested that eutectics might be present which promote slag formation. Therefore, it was difficult to assess a simple statement about the influence of hydrothermal conditioning on ash properties of treated sludge due to the fact that values did not follow the known trends; some indexes decreased (S_R, F_u) while others increased (R_S, Fe_2O_3/CaO). Therefore, the study of exploitation problems should be taken into consideration and other complementary, more advanced techniques should be applied to obtain a clear-cut answer.

3.3. Specific surface analysis

The results of specific surface analysis (SSA) (Table 5) showed that hydrothermal carbonization of sewage sludge increased the specific surface area c.a. 3.5 times compared to SSA values of dried sewage sludge. Moreover, the addition of biomass led to a further increase giving 16.6 m^2/g (HTTS+ 10% fir), 8 times higher than the initial value for dried sewage sludge, which was 2.2 m^2/g. Despite the observed increase in SSAs, they are still relatively small values [49]. Nevertheless, after further activation hydrochars may be used as a source of activated carbon. Bernardo et al. used potassium hydroxide as the activation agent for hydrochars derived from biogas digestate and the investigated recovery of phosphate by porous carbon [50]. It is also possible to achieve surface areas up to 1300 m^2/g and employ the derived material as an adsorbent in gas phase applications. For example, the upgrading of raw biogas to biomethane due to a higher affinity of hydrochars towards carbon dioxide in comparison to methane [51].

Table 4
Slagging and fouling indexes.

Material	R_b	$R_{b/a}$	S_R	R_S	F_u	Fe_2O_3/CaO
Ash from SS	35.29	0.99	42.96	2.50	2.61	1.06
HTTS+20% fir	38.65	1.32	34.60	3.45	1.94	1.15

R_B - basic constituents; $R_{B/A}$ - (base-to-acid) characterizes the ash fouling tendency.

Table 5
Results of specific surface area analysis.

Material	SSA m^2/g
Dried sewage sludge	2.1842
Fir	0.7234
Oak	0.9757
Charcoal	0.4225
HTTS	7.0720
HTTS + 10% fir	16.5572
HTTS + 10% oak	10.4111
HTTS + 10% charcoal	10.3204
HTTS + 20% fir	13.4297

3.4. Liquid phase characteristics

The results of filtrate analysis showed highly exceeded values in chemical oxygen demand, total organic carbon, total nitrogen and total phosphorus (Table 6). Those values indicate the great challenge posed by the purification of post-processed water. According to Polish legislation, water returned from wastewater treatment

Table 6
Results of filtrate detailed analysis.

Test	Result
pH, -	7.6 ± 0
Kinematic viscosity, mm^2/s	T = 21.5 °C 1.102 ± 0.007 T = 50 °C 0.609 ± 0.003
Density, kg/dm^3	1 ± 0.01
Chemical oxygen demand, mg O_2/l	41,600 ± 3952
Total organic carbon, mg/l	11,624 ± 1627
Ammoniacal nitrogen, mg/l	1480 ± 89
Kjeldahl nitrogen, mg/l	10,400 ± 780
Total phosphorus, mg/l	122 ± 6
Specific conductance (at 25 °C), μS/cm	10,580 ± 317
Arsenic, mg/l	0.0039
Zinc, mg/l	0.42 ± 0.09
Chromium, mg/l	0.65
Cadmium, mg/l	<0.04
Copper, mg/l	<0.06
Nickel, mg/l	0.23 ± 0.04
Lead, mg/l	<0.2
Mercury, mg/l	<0.001

Table 3
Results of XRF analysis.

Material	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	PbO	ZnO
	%	%	%	%	%	%	%	%	%	%	%
Dried SS	0.19	2.44	8.30	19.04	15.04	14.95	1.73	15.49	19.14	0.11	1.29
Ash from SS	0.95	3.63	11.20	24.58	16.83	9.62	1.70	14.09	14.92	0.09	1.06
HTTS+20% fir	0.35	2.54	9.64	19.67	15.70	13.03	1.12	16.10	18.54	0.11	1.30
Ash from fir	1.28	5.59	6.39	8.16	9.68	4.21	20.00	28.90	10.37	1.15	0.67
Ash from oak	0.10	2.62	0.36	1.47	1.33	0.70	7.01	83.87	0.85	–	0.02
Ash from charcoal	1.18	4.80	1.29	7.22	5.80	4.06	8.02	49.75	14.51	0.01	0.19

plants to the environment should not exceed the following values: 125 mg O_2/l for COD, 30 mg C/l for TOC, 30 mg N/l for total nitrogen, 1 mg P/l for total phosphorus [19]. Heavy metals (HMs) do not transfer to the liquid phase in amounts that would cause a significant problem. Furthermore, it is reported that hydrothermal treatment has a positive effect on HMs immobilization in the solid fraction of the products. After the HT conditioning process, heavy metals become stable in the hydrochars, which reduces environmental risks and toxicity. Those effects can be enhanced by the proper pH of feed-water. Zhai et al. reported the positive aspects of an alkaline environment, by which a pH equal to 11 resulted in the lowest pollution level [52]. Shi et al. found a synergistic effect after the addition of rice husk to sewage sludge during the HTT process. Rice husk possesses a binding capacity which allows for the elimination of eco-toxicity and leaching toxicity of hydrochars at appropriate ratios [27].

A viscosity test (Table 7) presented a significant dependence on temperature, thus, filtration tests and capillary suction time tests were conducted using samples heated up to 50 °C in a water bath. Elevated temperatures of the tests can also be justified from an economical point of view. On a commercial scale, HTTS should not be cooled down to an ambient temperature to reduce energy losses. Gao et al. even proposed an in-situ mechanical compression to further enhance water removal from HTTS [6]. The hydrothermal carbonization process greatly altered the behaviour of the sludge. This was confirmed by the CST values – with over 30 times shorter capillary suction time achieved for the HTTS+20% fir sample in reference to untreated sludge. It was also noticeable during experiments; over a short time, water from HTTS partially separated from the sewage sludge. For untreated SS, even after dilution, the sedimentation was not observed, which demonstrates a high affinity of raw sewage sludge to water. It creates a grease-like homogenous mixture, which is black in colour and has an unpleasant and specific odour. After HT conditioning and water separation the colour becomes lighter, rather dark grey. The odour, also, was altered and became less intense. These changes may be connected with the occurrence of Maillard's reaction between amino acids and reducing sugars [3].

In order to perform filtration tests, 150 ml of sludge was introduced to the filtration chamber. At first, the untreated sewage sludge was filtrated, but over a period of 600 s only 10 ml of filtrate was collected, proving that sewage sludge is difficult to filtrate and providing a convincing point of view to the debate on the importance of dewaterability improvements. Hydrothermally treated sludge presented much better results (Fig. 2): 120 ml of filtrate was collected. The moisture content after the filtration tests was 47.9%, which is a rather satisfactory result but it still could be improved. The additives slightly increased the dewaterability of hydrothermally treated sludge; 130 ml of filtrate was collected in every test, resulting in a moisture content reduced to the level of 41.2–44.1%. The most important advantage, and a reason for considering the use of additives, is a decrease in the filtration process time; from 600s to 240s for HTTS+10% oak. However, the tests conducted at constant pressure proved that the addition of fir provided more repeatable and suitable results. An increase in the fir concentration allowed a decrease in the filtration time from nearly 240s to almost 120s (at constant pressure).

Table 7
Results of kinematic viscosity analysis for filtrates and capillary suction time test for sludges.

Material	viscosity at 21.5 °C	viscosity at 50 °C	CST at 50 °C
	mm^2/s	mm^2/s	s
untreated SS			910.6 (at 20 °C)
HTTS	1.102 ± 0.007	0.609 ± 0.003	49.27
HTTS + 10% fir	1.069 ± 0.007	0.609 ± 0.003	34.56
HTTS + 10% oak	1.063 ± 0.002	0.614 ± 0.003	33.30
HTTS + 10% charcoal	1.068 ± 0.004	0.609 ± 0.003	41.94
HTTS + 20% fir	1.050 ± 0.004	0.609 ± 0.007	**26.46**

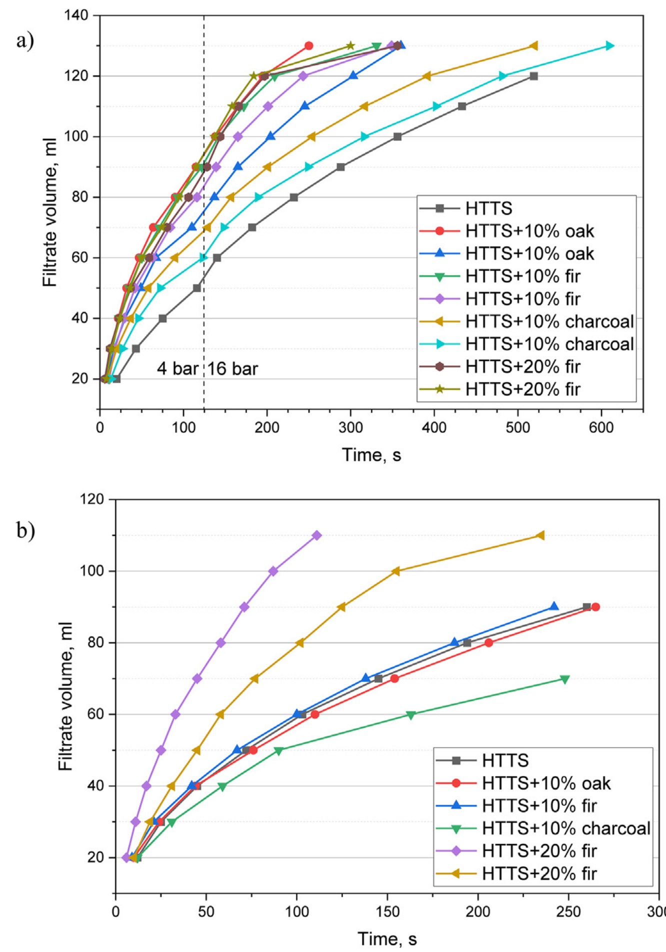

Fig. 2. Filtration curves for sludge produced with different additives.

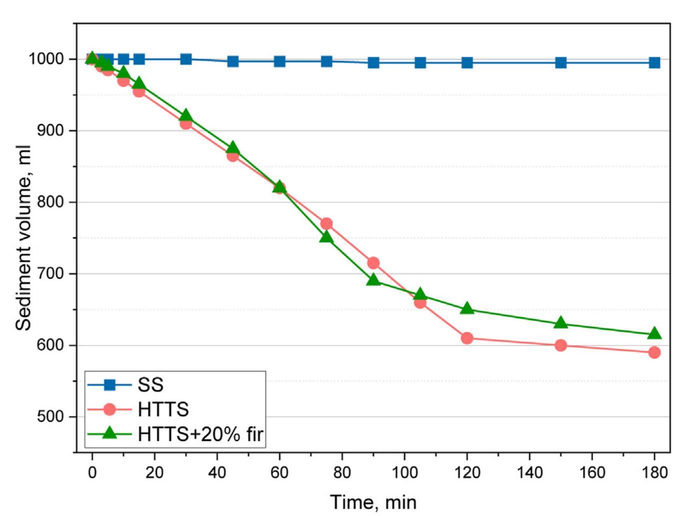

Fig. 3. Sedimentation curves for hydrothermally treated sludge.

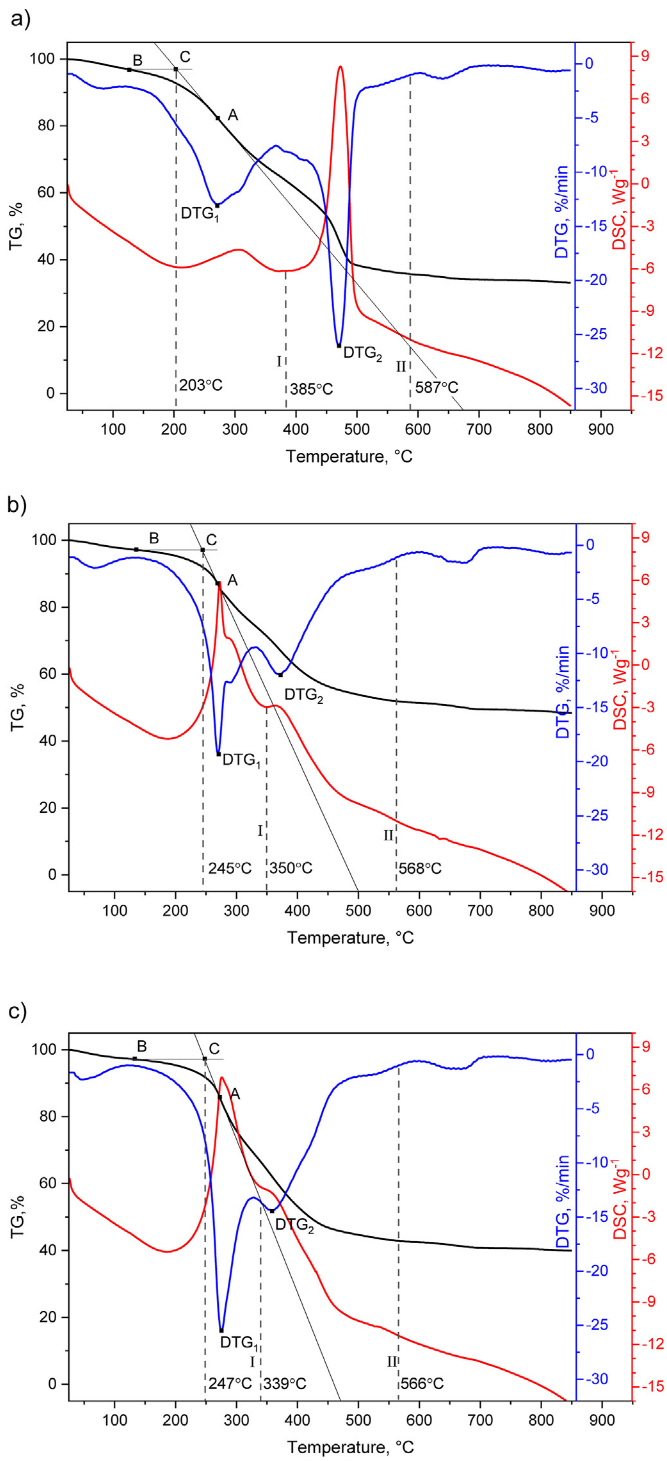

Fig. 4. Combustion of (a) sewage sludge, (b) hydrothermally treated sewage sludge and (c) hydrothermally treated sewage sludge with 20% fir addition, represented by TG/DTG/DSC curves.

The removal of water from sewage sludge is a well-known problem and some solutions looking to improve the efficiency of this process are already being sought [3,10]. Different approaches were proposed to enhance the dewaterability of sewage sludge: it can be achieved, for instance, by breaking the structures of extracellular polymeric substances and cell membranes [53] while simultaneously improving the permeability of sludge by the addition of skeleton building substances [54,55]. Guo et al. [53] in research similar to that presented by Wójcik et al. [54] achieved a moisture content of around 60% by conditioning the sludge with corn-core powder and biomass ash with polyelectrolyte, respectively. Nevertheless, the best results can be achieved by combining a thermochemical treatment with suitable additives. Zhai et al. [29] as well as Wang et al. [30] have already investigated the hydrothermal process of sewage sludge blended with biomass. Zhai et al. achieved comparable results to this study with moisture contents around 47–48% but at much higher processing temperatures (260–300 °C) for different types of biomass and with a higher sludge to biomass ratio equal to 1:1 (dry mass basis). Wang et al. studied a wide range of temperatures but also used a higher ratio of sludge to water equal to 1:0.3, which fructified with very satisfactory results. In this study, lower biomass ratios were employed to further optimize efficiency and investigate potential benefits. As stated before, the achieved moisture content and the significant decrease in filtration time are more than optimistic results. Conducted sedimentation tests proved that the hydrothermal process alone introduces changes to the sludge, facilitating a spontaneous separation of the liquid and solid phases (Fig. 3).

3.5. Combustion performance

Hydrothermal carbonization also modified the combustion process of the sewage sludge. Based on TGA analysis (Fig. 4), categories of temperature were determined and combustibility indexes were calculated. The ignition temperature (T_i) was determined by the intersection method. The burnout temperature (T_b) was found at the point where mass stabilization occurs [56]. Ignition index (D_i), burnout index (D_b), combustion index (S) and combustion stability index (H_f) were calculated by the methods described in Refs. [57,58]. The results are presented in Table 8. Concerning the SS combustion process, ignition occurred at 203 °C, with the first stage lasting until a temperature of 385 °C was achieved, and burnout occurred at 587 °C. In the second stage, where char is combusted, the highest combustion rate was achieved (26.03%/min) compared to the I stage (12.99%/min). For hydrothermally treated sludge, the combustion process was shortened. Ignition occurred at 245 and 247 °C, while burnout was found at 568 and 566 °C, for HTTS and HTTS+20% fir samples, respectively. Also, the HTC process ensured

Table 8
The combustion characteristics' parameters of different types of sludge.

	SS	HTTS	HTTS+20% fir
T_i (°C)	203	245	247
t_i (min)	17.80	22.00	22.20
T_b (°C)	587	568	566
t_b (min)	56.22	54.30	54.07
$t_{0.5}$ (min)	18.95	22.78	23.43
t_1 (min)	24.60	24.47	25.03
T_1 (°C)	271	270	275
DTG_1 (%/min)	12.99	19.24	25.54
T_2 (°C)	470	371	359
DTG_2 (%/min)	26.03	11.94	14.425
DTG_{mean} (%/min)	4.86	3.75	4.36
D_i (%/min^3·10^{-3})	29.7	35.7	46.0
D_b (%/min^4·10^{-5})	49.6	63.6	80.5
S (%/(min^2·°C^3) ·10^{-8})	261.0	211.6	322.5
H_f (°C·10^3)	0.37	0.49	0.46

DTG_{mean} – mean combustion rate.
DTG_1 – maximum combustion rate.
$D_i = DTG_1/(t_1 \cdot t_i)$, t_1 – corresponding time for DTG_1.
t_i – ignition time; t_b – burnout time.
$D_b = DTG_1/(t_1 \cdot t_b \cdot t_{0.5})$; $t_{0.5}$ - time range of $DTG/DTG_1 = 0.5$.
$S = (DTG_1 \cdot DTG_{mean})/(T_i^2 \cdot T_b)$.
$H_f = T_1 \cdot \ln(t_{0.5}/DTG_{mean})$.

Table 9
The combustion characteristics' parameters of different type of sludge.

Material	Friedmann		FWO		KAS	
	Ea, kJ/mol	A, 1/s	Ea, kJ/mol	A, 1/s	Ea, kJ/mol	A, 1/s
untreated SS	122,592	4,274E+11	132,462	2,153E+12	129,354	1,870E+12
HTTS	119,554	3,340E+11	124,666	1,756E+12	121,112	1,533E+12
HTTS + 10% fir	137,517	2,400E+11	128,157	8,746E+12	124,212	8,577E+12
HTTS + 10% oak	111,989	4,294E+09	124,365	6,527E+09	121,598	3,848E+09
HTTS + 10% charcoal	134,164	1,559E+18	131,223	1,740E+15	127,588	2,284E+15
HTTS + 20% fir	133,032	1,710E+12	135,701	9,813E+10	132,736	6,997E+10

that the highest combustion rate for hydrochars was achieved in the first stage. The ignition index determines the ease of separation in fuel volatile compounds. Higher D_i values were indicative of the easier release of volatile matter and easy combustion of fuel at an early stage. The combustion index (S) reflects the ignition, combustion and burnout properties of the sample. Despite raw SS having the highest volatile matter content, an increase in the combustion index was found for hydrothermally treated samples. The combustion stability index (H_f) certifies the rate and intensity of the combustion process. An increase of H_f values for HTTS was observed which suggests a lower rate and intensity of the combustion process.

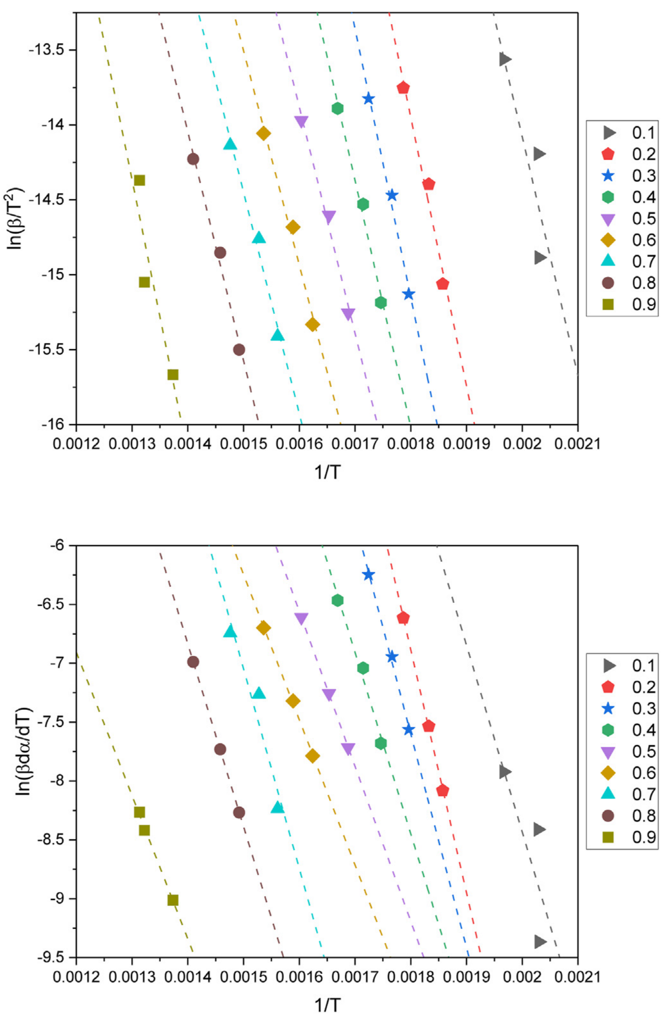

Fig. 5. Fitting to kinetic model proposed by a) Kissinger-Akahira-Sunose and b) Friedman under non-isothermal conditions for various conversion rates corresponding to the combustion of hydrochar HTTS+20% fir represented by TG/DTG/DSC curves.

3.6. Kinetic analysis

Based on kinetic analysis, it was observed that hydrothermal treatment did not have a strong influence on the activation energy of the sludge; it was slightly decreased by 10 kJ/mol (Table 9). KAS and FWO methods present the same trends of change, whereas the Friedman method is consistent with them only for conversion rate between 0.1 and 0.7 (Figs. 5 and 6). The type of additive used had a strong impact on the results of the kinetic study. The addition of fir and charcoal caused a significant increase in the activation energy while oak, in contrast, showed a decrease. During the combustion process, this parameter differed depending on the conversion rate. Also, for the oak additive the calculations were deemed the least accurate due to the fact that a few results did not fulfil the requirements of Doyle's approximation of an exponential integral.

4. Conclusions

Hydrothermal co-carbonization of sewage sludge and fuel characteristic additives were investigated. The HTC process proved to be a suitable pretreatment method for SS by significantly improving its dewaterability. Moreover, the addition of three kinds of biomass led to a further decrease in the moisture content of hydrochars and allowed effortless filtration. Hydrothermal co-carbonization led to an increase in the high heating value, carbon and fixed carbon contents. As a result, 20% of fir was chosen as the best additive used in the HTC process as it improved dewaterability and provided optimal fuel properties. The combustibility indexes confirmed easier and more stable combustion compared to hydrothermally treated sludge without an additive. Moreover, the

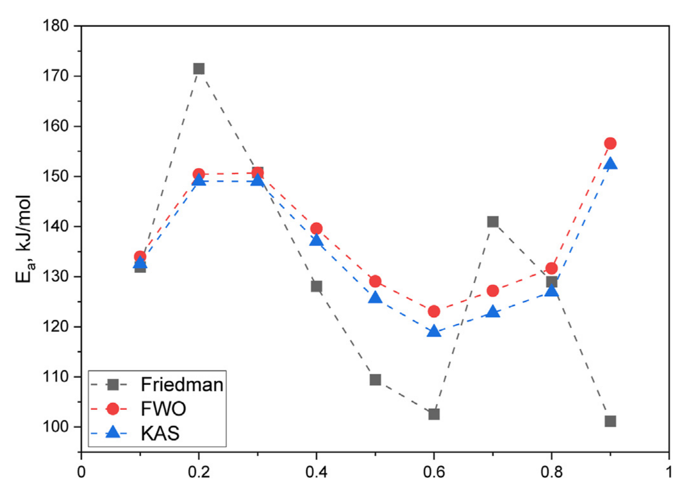

Fig. 6. Comparison of activation energy (E_a) estimated using Friedman, FWO and KAS methods for combustion of hydrochar HTTS+20% fir.

addition of fir significantly decreased the capillary suction time (c.a. 47%) as well as the time required for the filtration process (almost 2 times). Thus, it further enhanced the hydrothermal treatment effect on dewaterability. XRF analysis of the oak sawdust ash presented a high calcium oxide content (over 80%) which is very beneficial for enhancing sewage sludge dewatering, yet the addition of fir was proved to be a more suitable additive. One problem, the purification of post-processed water should be considered as a potential individual research topic. An insight into the dewatering performance, migration of compounds between liquid and solid phases and the combustion properties of the received products will provide a better understanding of the thermal conversion process. Furthermore, the derived hydrochars are expected to create a more environmentally friendly fuel in energy applications.

CRediT authorship contribution statement

Małgorzata Wilk: Conceptualization, Investigation, Resources, Writing – review & editing, Supervision, Funding acquisition. **Maciej Śliz:** Investigation, Writing – original draft, Visualization. **Bogusław Lubieniecki:** Conceptualization, Investigation, 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.

Acknowledgements

The authors are grateful to Ekoprod Ltd. for financial support under contract no. 5.5.110.668. Some of the work was realized as a part of fundamental research co-financed by the Ministry of Science and Higher Education, Poland [grant AGH UST no. 16.16.110.663].

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