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Fuel properties characterization of hydrochars derived from agricultural digestate

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Fuel properties characterization of hydrochars derived from agricultural digestate

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COVER LETTER FOR SUBMISSION OF NEW MANUSCRIPT

Joanna Mikusińska[1*], Klaudia Szkadłubowicz[1], Zuzanna Prus[1], Monika Kuźnia[1], Marcin Gajek[2], Małgorzata Wilk[1]

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Subject: **SUBMISSION OF NEW MANUSCRIPT FOR EVALUATION**

Dear Editor,

We are enclosing herewith a manuscript entitled “Fuel properties characterization of hydrochars derived from agricultural digestate” submitted to a Special Issue of Renewable Energy (VSI:CPOTE 2024) for evaluation.

We would like to emphasize that the Elsevier International Journal RENEWABLE ENERGY and the Organizing Committee of the 8th International Conference on Contemporary Problems of Thermal Engineering - CPOTE 2024 held in Gliwice, Poland based on evaluation of our paper by Scientific Committee and Reviewers had invited us to submit our manuscript in the *Renewable Energy*.

With the submission of this manuscript we would like to undertake that the above mentioned manuscript has not been published elsewhere, accepted for publication elsewhere or under editorial review for publication elsewhere; and that AGH University of Krakow is fully aware of this submission.

In this paper, authors have wanted to present the impact of temperature and residence time, the main parameters of hydrothermal carbonization (HTC), to achieve improved combustible properties of the obtained biofuels (hydrochars) and present its combustion performance.

The paper applies to subject area required to be published in *RENEWABLE ENERGY* an International Journal.

Yours sincerely,

Joanna Mikusińska on the behalf of co-authors

Highlights

- Agriculture digestate was hydrothermally carbonized at 190, 200 and 210°C and 0.5, 1, 1.5, and 2h
- Fuel properties of hydrochar and raw digestate were determined
- Ultimate and proximate analyses confirmed carbonaceous properties of hydrochars
- Stable combustion performance of hydrochar based on TGA were assessed
- Higher temperature and longer residence time of HTC provided carbon-rich material

Fuel properties characterization of hydrochars derived from agricultural digestate

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Abstract

Agricultural digestate is a by–product of biogas plant processes. Its composition is variable and depends on the type of raw feedstock used. Due to its high moisture content the digestate is suitable for hydrothermal carbonization (HTC). The HTC process is performed in a reactor where the feedstock is heated to a high temperature in an aqueous environment. As a result of the reaction, a solid product, process water and a gaseous product are generated. The gaseous product is obtained in trace amounts unlike the process water where the amount is significant. The rich in carbon solid product of HTC process is hydrochar. Hydrochars can be used as an alternative to non-renewable fossil fuels. The aim of this paper was to investigate and characterize hydrochars derived from agricultural digestate at 190 °C, 200 °C and 210 °C and residence times of: 0.5, 1, 1.5, and 2 h. In addition, the fuel properties and combustion performance supported by an activation energy determination were evaluated. In brief, it was found that a higher temperature and longer residence time produced a more carbonaceous biofuel.

Keywords: Hydrochar, Hydrothermal carbonization, Digestate management, Biomass, Biofuels

1. Introduction

In agricultural biogas plants, during the process of anaerobic digestion, the following reactions take place: hydrolysis, acidogenesis, acetogenesis and methanogenesis. In the first phase, biodegradation occurs, resulting in soluble monomers. Short–chain organic acids are then formed, followed by acetic

acid, hydrogen and carbon dioxide. The final product is biogas containing mainly methane and carbon dioxide, which is used in heating and energy industries [1]. In the process of anaerobic digestion a by-product, digestate, is also obtained. It is stored in special tanks in the biogas plants. Digestate is a mixture of solid and liquid phases. Its composition is variable and depends mainly on the feedstock used in the biogas plant. Digestate contains elements such as sodium, magnesium, calcium, potassium and macromolecules such as lipids, carbohydrates and proteins [2,3]. The parameters determining the quality of digestate include pH, nutrient content, dry organic matter content, material homogeneity and concentration of impurities [4]. The economic aspect of digestate management mainly depends on transport and storage costs. The simplest way is to separate it into solid and liquid fractions. The common way to achieve this effect is by using sieves, separators, decanter centrifuges and membrane techniques. As a result, the nutrients from both fractions of the digestate is recovered. Both the liquid and the solid phase can be used in the agricultural industry as fertilizers. During separation, phosphorus goes to the solid fraction, and nitrogen and potassium to the liquid fraction. There are also other methods of digestate management like chemical coagulation and biological composting. The use of various technologies for the treatment of digestate is aimed at its purification and improvement of its quality [5]. Digestate management is a crucial issue, thus, due to its high content of nitrogen and phosphorus, it is primarily used as a fertilizer. Before applying it to the crops analysis is required to check the levels of hazardous substances. Low quality digestate derived during anaerobic digestion may cause a threat to the environment due to the possible presence of heavy metals, pathogens and other contaminants [6]. Biogas plants are usually located in rural areas where there is easy access to biomass and waste from livestock farming. When a biogas plant is located in a remote location, long–distance digestate transportation may cause problems due to its high moisture content and biodegradability. Consequently, this solution can be associated with high costs of transportation [7]. In 2022, 31 Mt of digestate was produced in Europe [8] and, according to estimates, a 500 kW biogas plant can produce about 10,000 tonnes of solid digestate each year [8,9]. Fig. 1. shows the amount of agricultural biogas plants in selected countries around the world. Germany is a leader of agricultural biogas plant ,reaching c.a. 8.300, which is significantly higher amount of biogas installations than in other countries. In comparison, France has 1.271 and the rest of the countries have less than 1.000 installations [10].

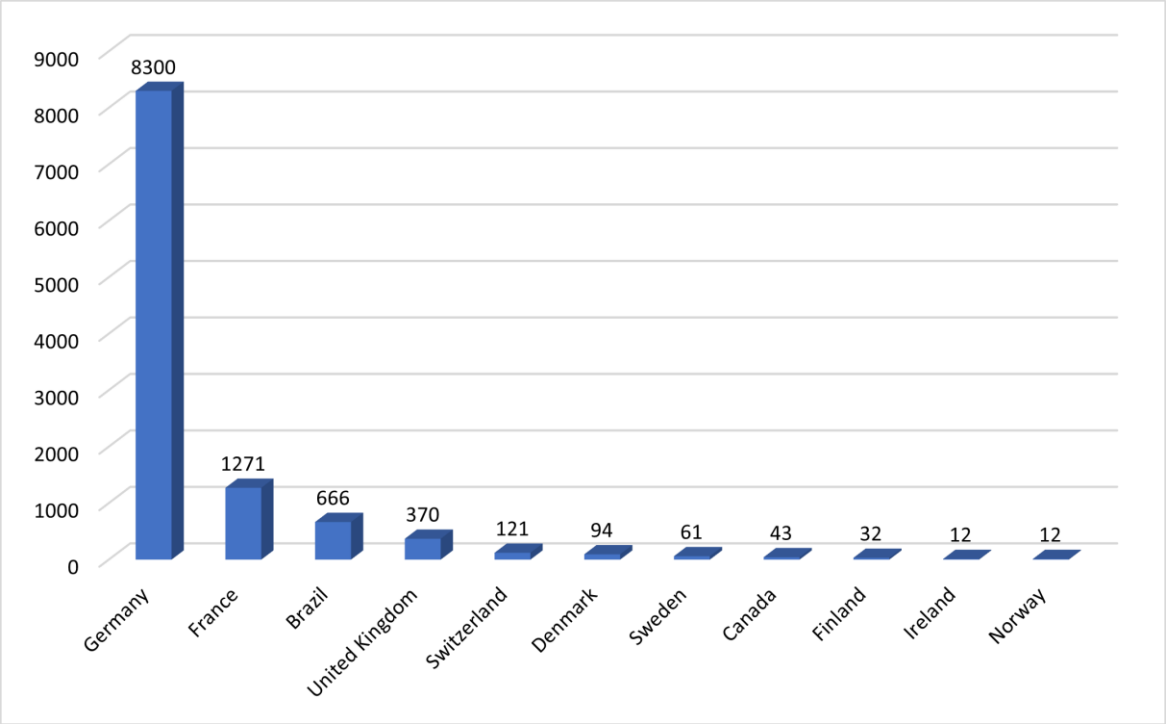

Fig. 1. Number of agricultural biogas plants in selected countries around the world according to IEA Bioenergy [10].

As a consequence of the growing popularity of biogas plants as well as the increase in digestate production, new solutions for its management are being sought. One of the most common methods is hydrothermal carbonization (HTC), which can be applied to feedstock with a high moisture level. Temperature and residence time are crucial parameters that affect the properties of the final products. In the HTC process, a gaseous product and a post–process mixture are attained, which are then separated into solid and liquid products [11]. Pre–drying of the raw material is not required, which reduces the energy consumption of the process. The feedstocks used in HTC are mainly biomass, sewage sludge and food waste. They are heated to a temperature in the range of 160 – 280 °C in an aqueous environment and at autogenous pressure [12,13]. Three products are acquired from the HTC process: hydrochar, process water, and a gaseous phase. The amount of each fraction depends on the type of feedstock used and the conditions of the process, mainly temperature and residence time. Process water is obtained in the largest volume during the HTC process and it contains dissolved organic substances. The mass of hydrochar decreases due to the release of water and carbon dioxide. This is also influenced by the transfer of some of the chemical compounds into the liquid phase as a result of leaching. This results in lower hydrogen to carbon (H/C) and oxygen to carbon (O/C) molar ratios leading to hydrochar with improved fuel properties. The gaseous product is usually c.a. 1 – 3% of the raw material and consists mainly of N_2 and CO_2[11,13,14]. The fuel properties of hydrochar derived from different agricultural feedstock digestate have already been studied. For instance, Cao et al. [15] investigated digestate from

the anaerobic digestion of cow manure and energy crops and assessed their effect on the HTC process. The process temperature was 210 °C and residence time in the range of 0.5 – 5 h. According to the results, when a longer residence time of the HTC process was applied, the higher heating values of hydrochars indicated a slight decrease. However, HTC affects the acquiring of more effective slagging and fouling indices of hydrochars [15]. In addition, the team of Cao et al. [16] conducted the HTC process on maize silage digestate. In this case, the conditions of the process were as follows: the temperature of the reaction was set at 180 °C, 200 °C and then 220 °C while the residence time was retained at 0.5 h. An HTC temperature of 200 °C resulted in the highest energy of hydrochar, but simultaneously caused the lowest energy content in CH_4 in the liquid phase. Hydrochar obtained at 220 °C had the highest high heating value but the lowest energy content. Both hydrochar and process water displayed the highest energy recovery at 180 °C [16]. Furthermore, Belete et al. [17] investigated anaerobically digested manure mixed with water or whey. The temperature of the HTC process was set at 180 °C, 210 °C and then 240 °C with 1 h of residence time applied. According to the research, the higher temperatures resulted in lower hydrochar yields but despite this effect, hydrochars with a higher carbon content were achieved. An increase in temperature resulted in a more carbonaceous hydrochar with raised levels of higher heating values. The highest calorific value was found for hydrochar containing whey [17]. Zhang C. et al. [18] performed the HTC process on liquid digestate and cornstalk in the temperature range of 180 – 300 °C. The interval of each process was set at 40 °C with 1 h of residence time. Increasing the temperature resulted in a lower hydrochar yield. However, a higher carbon content in hydrochars was observed [18]. Zhang D. et al. [19] also conducted the HTC process on cornstalk digestate. This time, the temperature was tested in the range of 190 – 240 °C with a residence time of 0.5 h. With an increasing temperature of HTC, the mass yields of hydrochars decreased, but the carbon content and high heating values increased. Moreover, the HTC process lowered the content of alkali and alkaline earth metals as well as hydrophilicity [19].

In this study, digestate from an agricultural biogas plant was used. The digestate was derived from straw, cattle manure and coffee grounds. It was subjected to hydrothermal carbonization and the solid product generated from this process was hydrochar. The HTC process was performed at three temperatures (190 °C, 200 °C and 210 °C) and four residence times (0.5, 1, 1.5 and 2 h) in order to evaluate the fuel properties and combustion performance of hydrochars.

2. Materials and methods

2.1. Digestate preparation

The digestate used in the research was obtained from the agricultural biogas plant BUTOR. The composition of the digestate consisted mainly of straw, cattle manure and coffee grounds. The crude digestate could not be used directly in the HTC process because the long straw stalks prevented the

mixture from being equally distributed in the reactor. Additionally, the mixer could have become blocked and damaged. Therefore, preparation of the digestate was carried out in three stages: drying, grinding and mixing with distilled water.

2.2. Hydrothermal carbonization

The HTC process was conducted in a stainless steel ZipperClave®Stirred Reactor from The Parker AutoclaveEngineers. For each experiment, the prepared feedstock consisted of 80g of digestate and 640 g of distilled water. The parameters of the HTC process were as follows:

- temperature: 190 °C, 200 °C and 210 °C.
- residence time: 0.5 h, 1 h, 1.5 h and 2 h.

Feedstock weighing 720 g was placed into the reactor and the process was conducted as follows: heating of the reactor to set the temperature and then maintaining this temperature for a specific residence time, before cooling down with water. After it reached the ambient temperature, the mixture was removed from the reactor. For each of the parameters, two reactions were performed to investigate the repeatability of the process (R1 and R2). The HTC products are: hydrochar (c.a. 8%), process water (c.a. 89%) and gaseous phase (c.a. 3 – 6%). The solid and liquid products were separated by a vacuum filtration process, whereas a small volume of gas was emitted into atmosphere. The dewatered hydrochars were dried for 24 h at 105 °C and then stored for further analysis. The feedstock was labelled as RAW DIGESTATE, whereas the hydrochars were labelled according to the HTC process performed at fix temperature and maintained residence time and run of process e.g. HTC 190/0.5 R1 is a hydrochar performed at 190 °C through 0.5 h residence time of first run of HTC.

2.3. Analytical methods for hydrochars

2.3.1. Ultimate analysis

The ultimate analysis was determined in the Elemental Analyzer LECO CHN628. The hydrochar samples were placed in the chamber of the analyzer, where they were burned in pure oxygen and at a high temperature. For coal (C), hydrogen (H) and nitrogen (N) it was 950 °C and for sulphur (S) 1350 °C. Percentage results were then obtained. Three measurements were taken for each sample of C, H, N and two measurements for S analysis. Based on the ultimate analysis the ratio of oxygen to carbon (O/C) and hydrogen to carbon (H/C) were calculated.

2.3.2. Proximate analysis

In the proximate analysis the moisture, ash and volatile matter content were measured. The moisture content was determined according to ISO 18134 – 2:2017, ash content according to ISO 18122:2022 and volatile matter according to ISO 18123:2023. The measurements were calculated using the EVAL

5E–MAC6710 thermogravimetric analyzer for the simultaneous determination of moisture, ash and volatile matter.

2.3.3. High heating value determination

The high heating values (HHV) measurement was calculated in a LECO AC500 calorimeter using DIN51900 and ISO 1928 standards. The sample is placed in the analyzer and then burned in an aerobic environment. On the basis of this analysis, information on the energy content of the fuel is gathered. Measurements were taken for each sample of hydrochars and raw digestate then the average values were calculated.

2.3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted for samples of hydrochars in order to check how the temperature of the HTC process affects the thermal stability of the obtained hydrochars. Analysis was performed in an air atmosphere (40 mL/min) within the range, 10, 20, 30, and 40 °C /min heating rate up to 700 °C, with a Netzsch STA 449 F3 Jupiter using a standard DSC/TG sample carrier (thermocouples type S) [20].

2.3.5. Kinetic analysis

Based on the TGA results of hydrochars, a correlation between time and weight loss was obtained. This allowed to carry out calculations related to the kinetics of the combustion process of the studied materials. The main parameter that determines the kinetic of a reaction is an activation energy (E_a). In this research three calculation models were used to determine it: Friedman, Kissinger Akahira – Sunose (KAS) and Flynn – Wall – Ozawa (FWO). The α factor determines the conversion rate for the sample being tested. Measurement of temperatures corresponding to the established values of α from the tests carried out at different heating speeds from the slope of the lnβ graph compared to 1/T [21-23]**.**

Equation 1 describes the α factor which depicts the conversion rate of sample:

$$\alpha = \frac{m_{i0} - m_\alpha}{m_{i0} - m_f} \quad (1)$$

where m_{i0} was initial mass of the sample, m_a was the actual mass and m_f the mass after combustion in g.

The ratio of solid-state reaction was described by the equation 2:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (2)$$

where *t* was the time, *T* was temperature of the process, *k(T)* the constant rate, *f(α)* a kinetic model.

The rate constant *k* is related to temperature and determined in the Arrhenius equation:

$$k(T) = Aexp(-\frac{E_a}{RT}) \quad (3)$$

where R was a gas constant, A was a pre − exponential factor and E_a defines activation energy. The Friedeman method was calculated by using the equation:

$$\beta\frac{d\alpha}{dT} = A \cdot e^{\frac{-E_a}{RT}} f(\alpha) \quad (4)$$

Which after transformation gives the following equation:

$$\ln\left[\beta\frac{d\alpha}{dT}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_a,\alpha}{RT_\alpha} \quad (5)$$

In the Kissinger Akahira − Sunose method, the Coats-Redfern approximation of *p(x)* (6) was used to calculate the main equation 7:

$$p(x) = \frac{e^{-x}}{x^2} \quad (6)$$

$$\ln\left(\frac{\beta}{T^2}\right) = \ln(\frac{AR}{E_a g(\alpha)}) - \frac{E_a}{RT} \quad (7)$$

where β=dT/dt was the heating rate, and g(α) was the constant of the integral form of kinetic model at a given value of conversion.

In the Flynn − Wall-Ozawa method, Doyle's approximation was used to calculate the equation 8:

$$\ln\beta = \ln\left[\frac{E_a}{Rg(\alpha)}\right] - 1.0516 - \frac{E_a}{RT} - 5.331 \quad (8)$$

3. Results

The results of the proximate analysis are presented in Table 1. The highest moisture is obtained for raw digestate and all hydrochars have a lower moisture content confirming that the HTC process removes moisture from the material resulting in more hydrophobic properties. The ash content of all samples is in the range of 6 – 8 % and volatile matter (VM) of 65 – 72%.

Table 1

The proximate analysis of raw digestate and hydrochars.

Name of sample	Moisture %	Ash %	VM %
RAW DIGESTATE	5.75	7.86	70.30
HTC 190/0.5 R1	2.74	6.71	71.29

HTC 190/0.5 R2	3.06	7.16	71.08
HTC 190/1.0 R1	2.31	7.00	69.61
HTC 190/1.0 R2	2.79	6.71	70.14
HTC 190/1.5 R1	3.26	7.67	67.49
HTC 190/1.5 R2	6.80	6.92	66.43
HTC 190/2.0 R1	1.73	8.69	67.78
HTC 190/2.0 R2	4.75	8.97	65.14
HTC 200/0.5 R1	1.91	7.03	72.03
HTC 200/0.5 R2	2.29	7.12	71.79
HTC 200/1.0 R1	1.81	7.54	70.39
HTC 200/1.0 R2	1.84	8.52	68.46
HTC 200/1.5 R1	3.03	8.03	69.11
HTC 200/1.5 R2	1.47	7.23	70.43
HTC 200/2.0 R1	3.03	7.40	67.87
HTC 200/2.0 R2	2.22	7.44	68.36
HTC 210/0.5 R1	2.52	7.37	68.17
HTC 210/0.5 R2	1.36	7.90	68.98
HTC 210/1.0 R1	2.14	7.31	69.13
HTC 210/1.0 R2	1.29	7.62	68.74
HTC 210/1.5 R1	1.72	7.92	68.02
HTC 210/1.5 R2	1.87	8.52	65.68
HTC 210/2.0 R1	2.04	8.29	67.87
HTC 210/2.0 R2	1.92	8.76	67.44

VM – volatile matter

Table 2 summarizes the ultimate analysis. The carbon content of raw digestate has the lowest value at 47.69%. The highest carbon content, 56.41%, was found for hydrochar (R2) obtained at a temperature of 210 °C and a residence time of 2 h. Hydrogen and nitrogen contents are at similar levels for all hydrochars, approximately 6% and 3%, respectively.

Table 2

The ultimate analysis of raw digestate and hydrochars.

Name of sample	C %	H %	N %	S %	O %	O/C	H/C
RAW DIGESTATE	47.69	5.77	3.13	0.01	29.79	0.47	1.45
HTC 190/0.5 R1	52.83	6.00	3.11	0.05	28.55	0.41	1.36
HTC 190/0.5 R2	52.36	5.99	3.17	0.11	28.16	0.40	1.37
HTC 190/1.0 R1	52.68	6.02	3.31	0.02	28.66	0.41	1.37
HTC 190/1.0 R2	54.00	6.06	3.24	0.02	27.18	0.38	1.35
HTC 190/1.5 R1	53.40	5.95	3.14	0.03	26.55	0.37	1.34
HTC 190/1.5 R2	51.08	6.33	3.03	0.03	25.81	0.38	1.49
HTC 190/2.0 R1	53.70	5.78	3.14	0.04	26.93	0.38	1.29
HTC 190/2.0 R2	52.14	6.05	3.08	0.04	24.97	0.36	1.39
HTC 200/0.5 R1	54.67	6.05	3.18	0.01	27.15	0.37	1.33
HTC 200/0.5 R2	54.20	6.02	3.23	0.01	27.13	0.38	1.33
HTC 200/1.0 R1	55.14	5.99	3.27	0.01	26.24	0.36	1.30
HTC 200/1.0 R2	54.61	5.91	3.13	0.01	25.98	0.36	1.30
HTC 200/1.5 R1	54.29	6.03	3.23	0.01	25.39	0.35	1.33
HTC 200/1.5 R2	55.57	5.97	3.21	0.01	26.54	0.36	1.29
HTC 200/2.0 R1	54.18	5.99	3.03	0.02	26.35	0.36	1.33
HTC 200/2.0 R2	55.57	6.00	3.16	0.02	25.59	0.35	1.30
HTC 210/0.5 R1	54.51	6.01	3.17	0.02	26.40	0.36	1.32
HTC 210/0.5 R2	54.95	5.96	3.25	0.02	26.56	0.36	1.30

HTC 210/1.0 R1	54.93	5.93	3.18	0.02	26.49	0.36	1.30
HTC 210/1.0 R2	55.65	6.03	3.10	0.01	26.30	0.35	1.30
HTC 210/1.5 R1	56.26	6.02	3.16	0.01	24.91	0.33	1.28
HTC 210/1.5 R2	55.69	6.02	3.19	0.02	24.70	0.33	1.30
HTC 210/2.0 R1	55.85	6.04	3.11	0.02	24.65	0.33	1.30
HTC 210/2.0 R2	56.41	6.00	3.20	0.02	23.69	0.32	1.28

C- carbon, H – hydrogen, N – nitrogen, S – sulphur, O – oxygen

Fig. 2 presents the HHV values of hydrochars and raw digestate. The results are in line with the carbon content determined by ultimate analysis. All hydrochars have higher values than the raw digestate, and the highest values are produced by hydrochars at 210 °C.

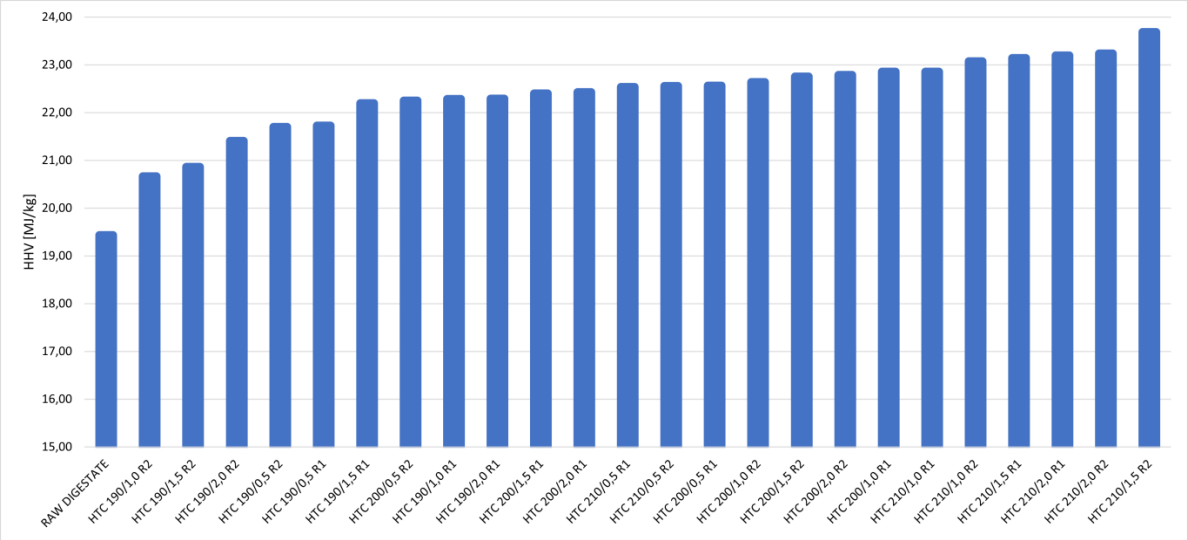

Fig. 2. HHV of raw digestate and hydrochars.

The molar ratios of H/C and O/C are depicted in a Van Krevelen diagram and this presents in which region, dedicated to different fuels, the hydrochars (average for R1 and R2) and raw digestate are situated (Fig. 3). Therefore, in such a way, changes in the chemical composition under the hydrothermal carbonization process might be observed by comparing the initial and hydrothermally carbonized feedstock. Hydrochars obtained at 200 °C and 210 °C are found in the same region as lignite and peat, and hydrochars obtained at 190 °C are depicted in the biomass region.

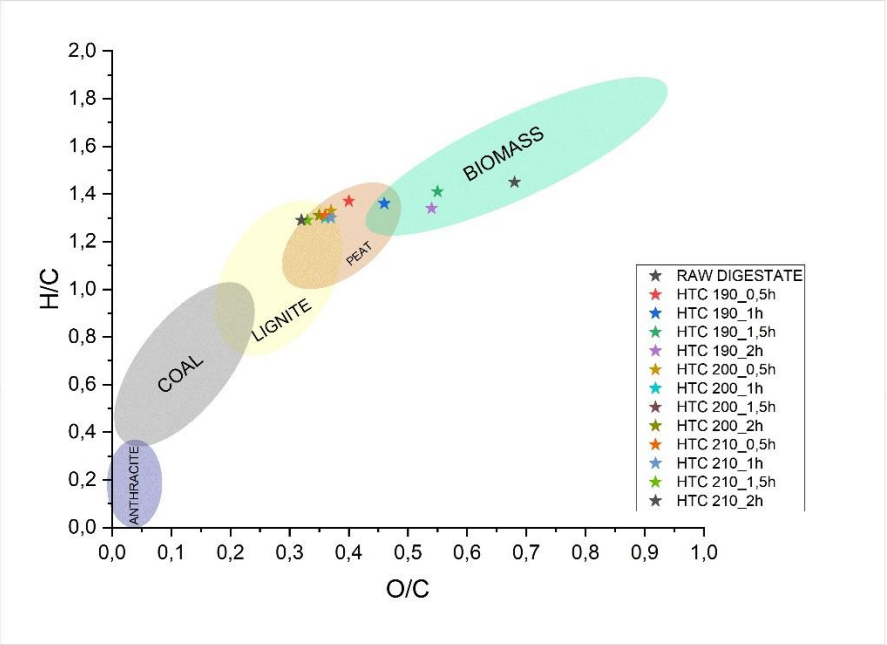

Fig. 3. Van Krevelen diagram.

TGA analysis of raw digestate and hydrochars generated at temperatures of 190, 200 and 210 °C and residence times of 0.5, 1, 1.5 and 2 h is presented in the form of TG/DTG curves in Fig. 4 – 7. This technique simulates the combustion process. Based on the TGA results the behaviour of the combustion process can be discussed. In general, the combustion process of all cases can be divided into three zones: moisture release, the main combustion process with volatile matter release and char combustion, and final combustion. A small peak of DTG observed for raw digestate up to 140 °C confirms that the initial material has a higher content of moisture compared to hydrochars. This specific behaviour proves that HTC process changes the hydrophilic properties of digestate to the hydrophobic properties of hydrochar. The main combustion process for all samples occurred at temperatures up to 540 °C, where volatile matter was released and char was combusted, and was identified by two stages found in the temperature regions, c.a. 240 – 340 °C and 380 – 540 °C, respectively. For raw digestate, the lower mass loss rate was registered in the first stage of combustion in the temperature range of 230 – 340 °C, with DTG maximum at 304 °C. This effect is a result of the presence of hemicellulose and protein, which degrade in different temperature ranges. On the other hand, the DTG curves of hydrochars derived at different conditions exhibited significantly higher mass loss rate in narrower temperature range of 260 – 330 °C, with DTG maximum registered at 310 – 319 °C. This effect results from the more homogeneous structure of carbonaceous hydrochar and a limited presence of volatile matter that combusts in a narrower temperature range. In the second stage of combustion, the maximum DTG peak for raw digestate was registered at 492°C, whereas for hydrochar in the range 425 – 452°C. These effects were

observed probably due to lignin presence in raw digestate, which requires higher temperatures for decomposition. In contrast, in the case of hydrochars the lignin structures are already partially decomposed due to depolymerization reaction occurred during HTC process. In addition, the higher content of aromatic compounds might be combusted in a lower temperatures range [24-26]. The combustion was finally concluded at 540 °C. Moreover, the profiles for 200 and 210 °C performed at all applied residence times, in particular at 1.5 and 2h, were very similar to each other, whereas at 190 °C, especially at the second peak of DTG, it occurred slightly earlier in comparison to 200 and 210 °C. This behaviour indicates that the material was not behaving in a similar way, which probably indicates that the carbonization process at 190 °C was not sufficient. Final residues after the combustion process for all tested samples were less than 10%, which are consistent with the results of proximate analyses concerning ash contents (Table 1). Concluding, the combustion process of raw digestate differed from hydrochars, which had a more unified character and shape of combustion profiles at all temperatures. The longer the time of HTC at each temperature, the more uniform profiles were observed (Fig. S1 – S3). In general, the hydrochar combusted later and in a shorter period of time than raw digestate, but probably in a more stable manner.

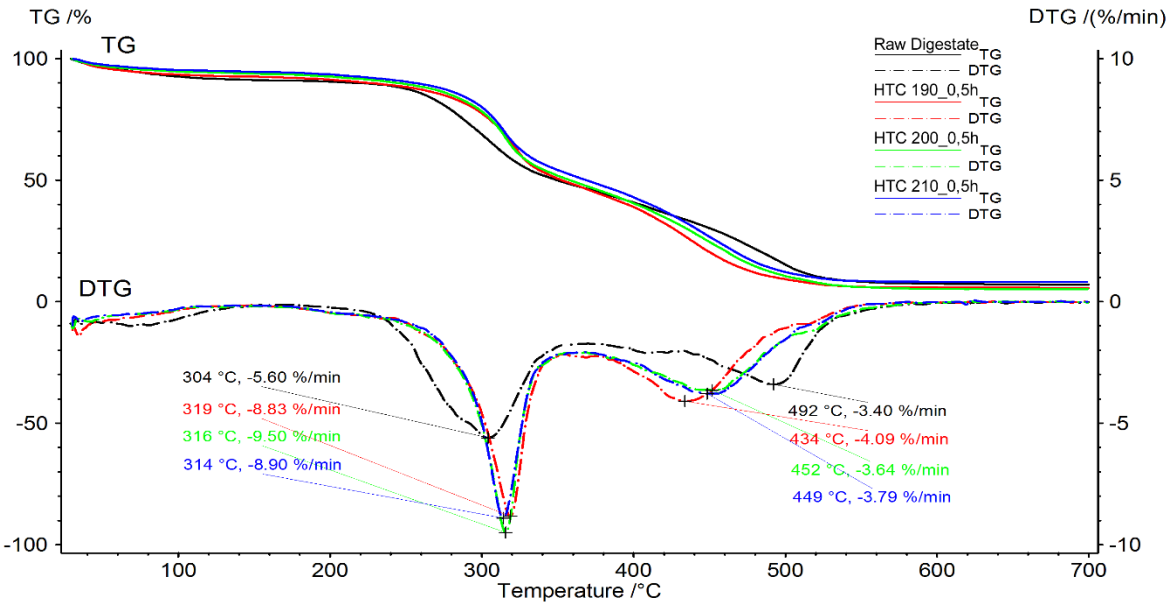

Fig. 4. TG and DTG curves for raw digestate and hydrochar performed at 190, 200 and 210 °C and 0.5 h of residence time.

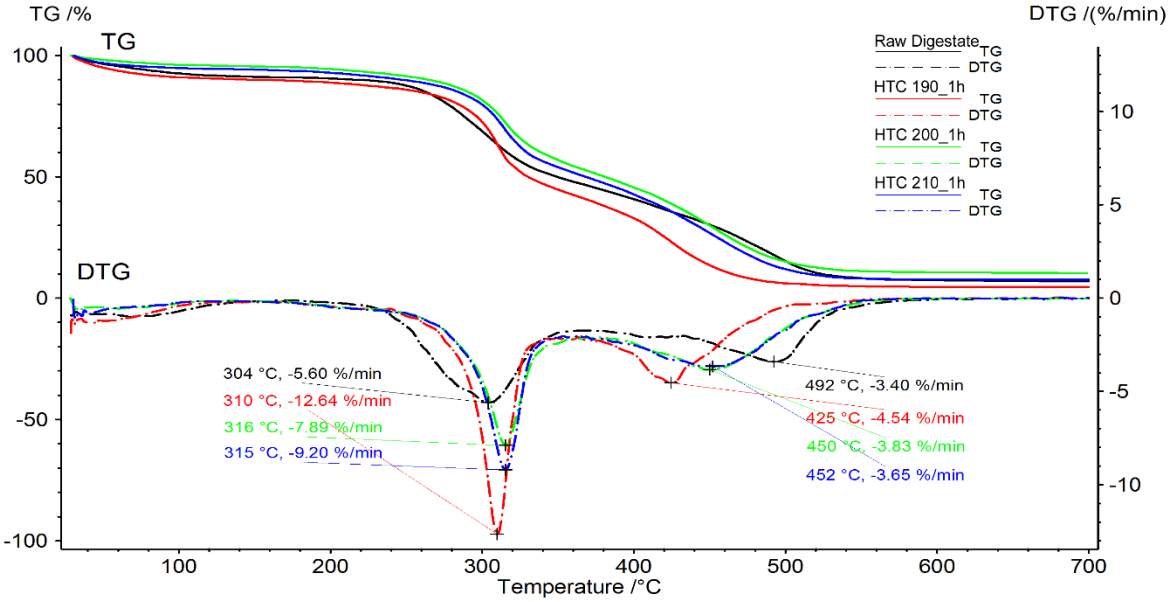

Fig. 5. TG and DTG curves for raw digestate and hydrochar performed at 190, 200 and 210 °C and 1 h of residence time.

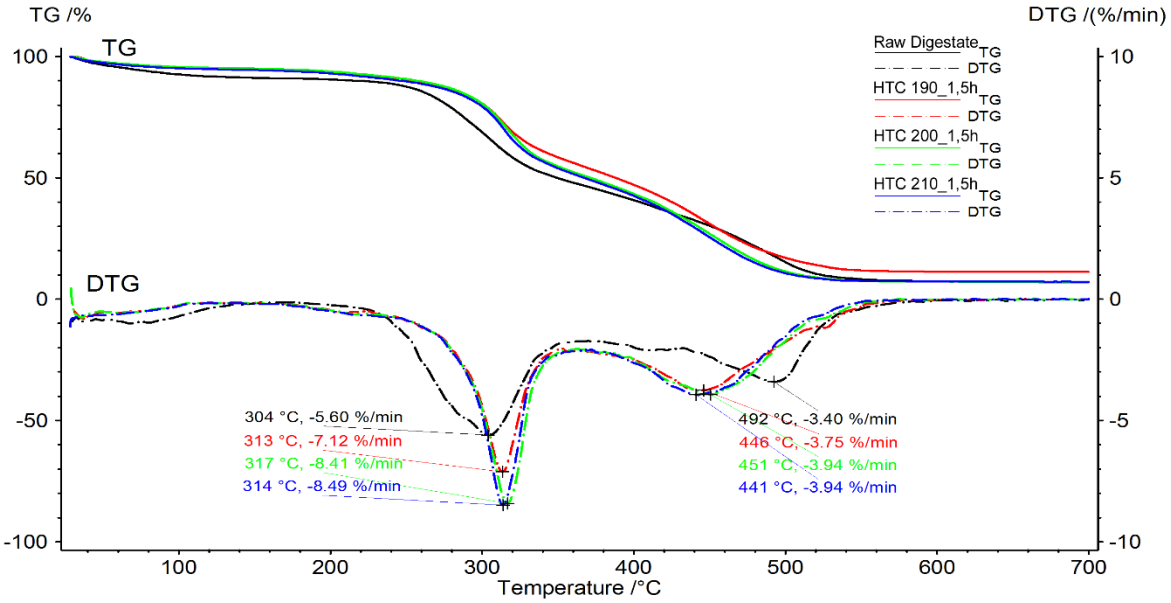

Fig. 6. TG and DTG curves for raw digestate and hydrochar performed at 190, 200 and 210 °C and 1.5 h of residence time.

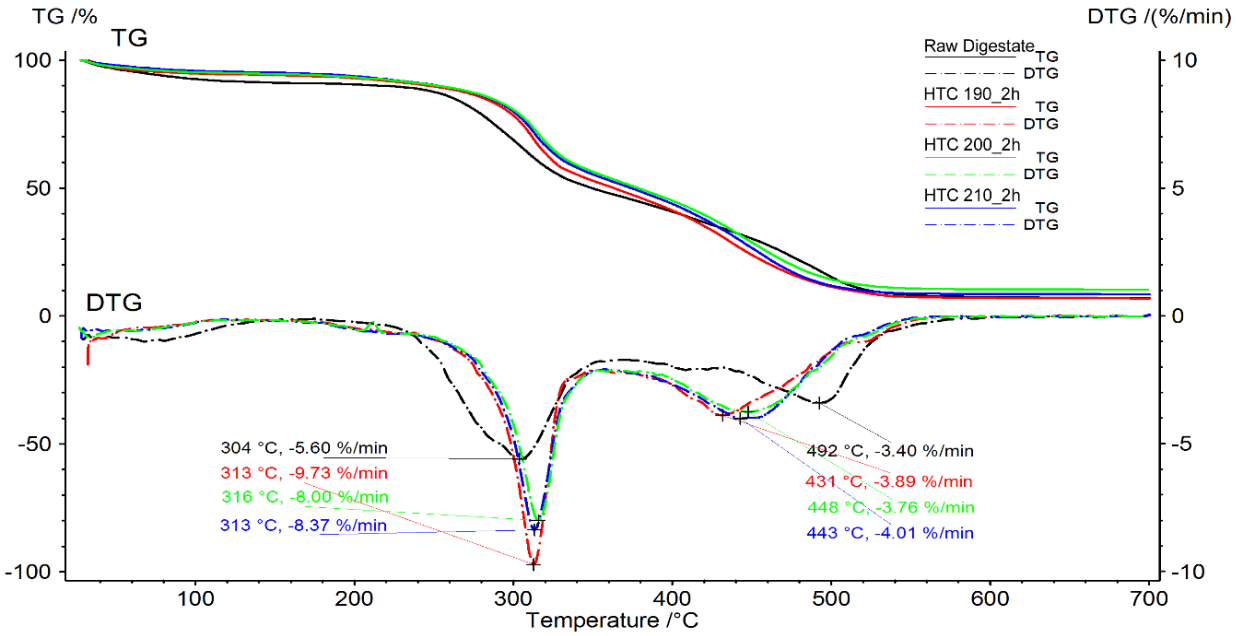

Fig. 7. TG and DTG curves for raw digestate and hydrochar performed at 190, 200 and 210 °C and 2 h of residence time.

Fig. 8 – 11 presents a comparisons between TG and DTG curves for different heating rates, namely 10, 20, 30, and 40 °C/min, registered for raw digestate (Fig. 8) and hydrochars derived at 190, 200 and 210 during 2h of residence time. An increase in the mass loss rate was observed with the increase in the heating rate. This effect is visible both the first, more intense stage of combustion, and the second, less intense stage. The increased mass loss rate is partly due to the overlap of thermal effects from the decomposition of the sample compounds with the increase in the heating rate. At the same time, the increase in heating rate leads to a shift of these effects to higher temperatures.

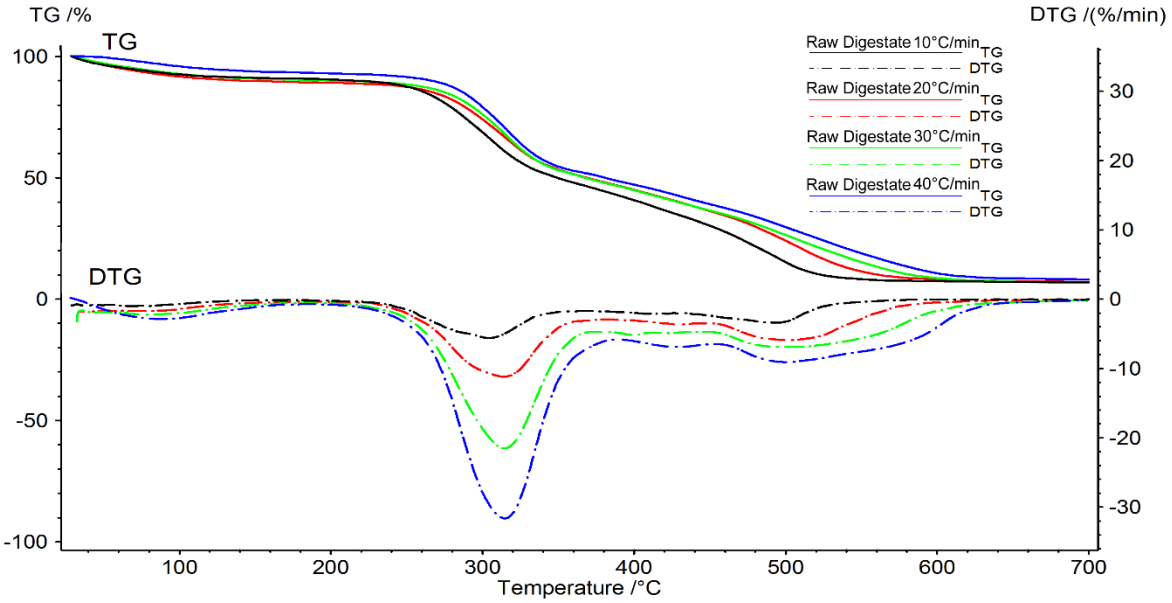

Fig. 8. TG and DTG curves for raw digestate within 10, 20, 30, and 40 °C/min heating rate up to 700 °C.

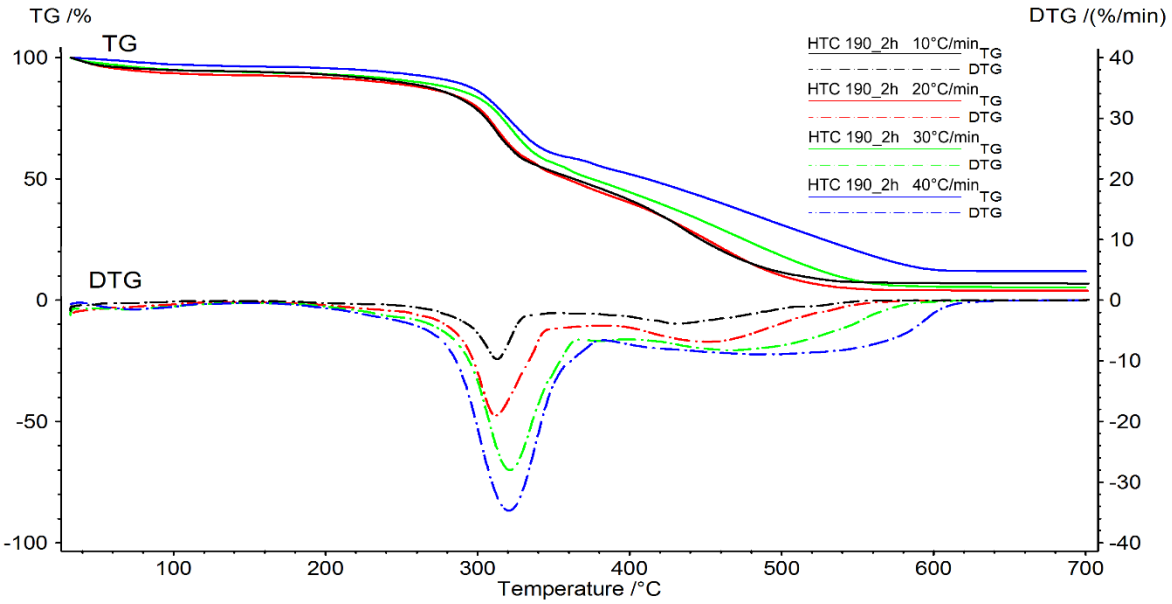

Fig. 9. TG and DTG curves for the hydrochars derived at 190 C within 10, 20, 30, and 40 °C/min heating rate up to 700 °C.

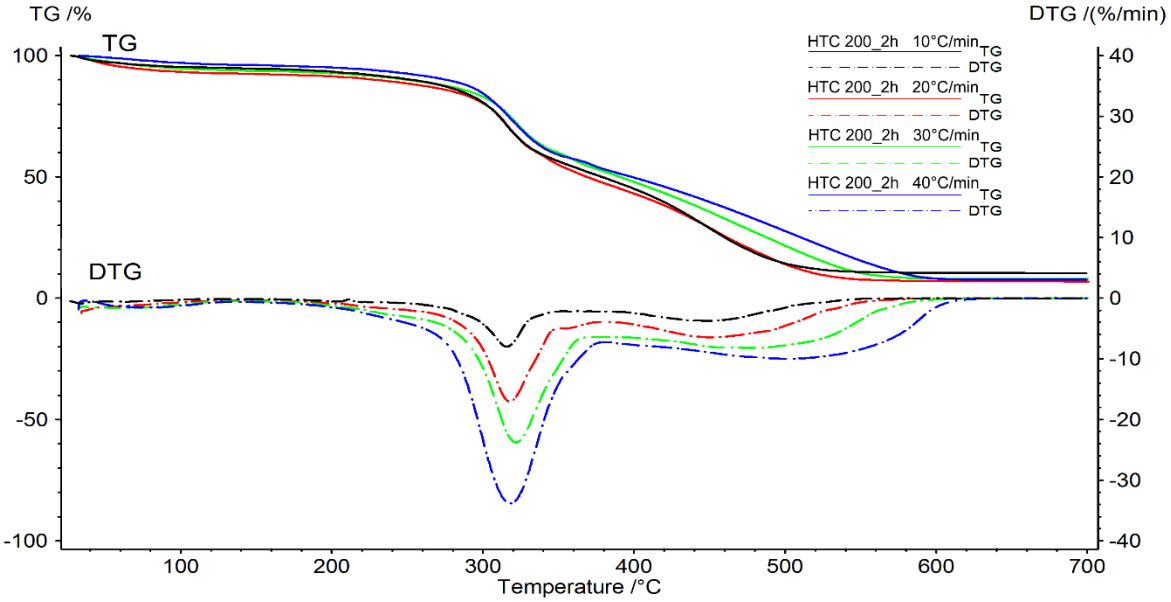

Fig. 10. TG and DTG curves for the hydrochars derived at 200 C within 10, 20, 30, and 40 °C/min heating rate up to 700 °C.

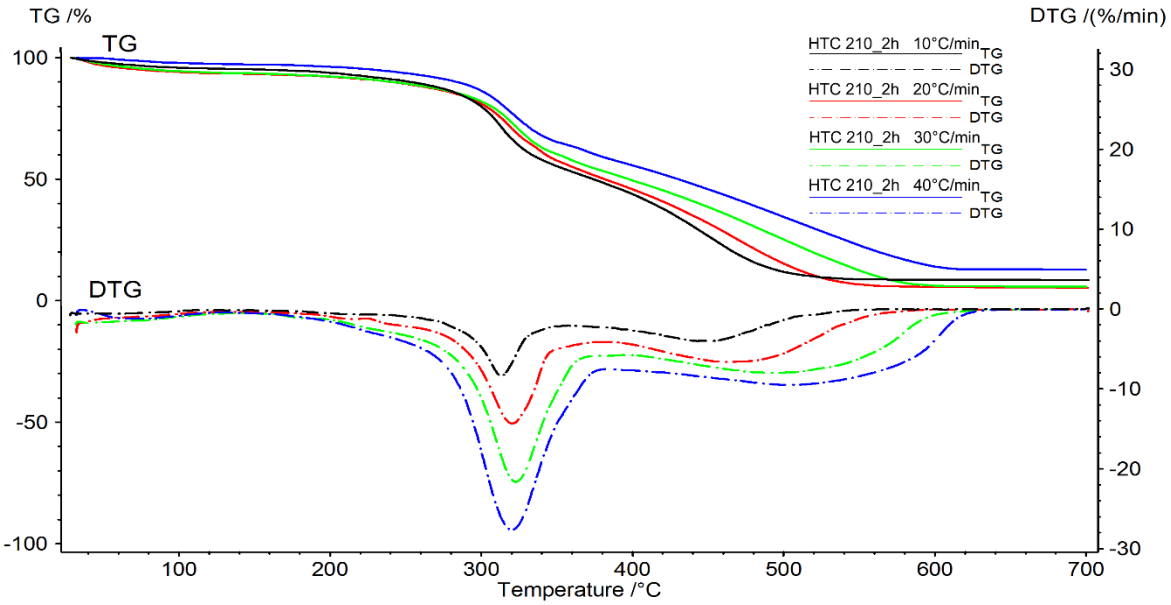

Fig. 11. TG and DTG curves for the hydrochars derived at 210 °C within 10, 20, 30, and 40 °C/min heating rate up to 700 °C.

The activation energy depends on the change in mass, where its loss is observed with the change in temperature in the TGA analysis. Kinetic analysis allow for a more accurate estimation of the fuel properties of materials to be used in the energy sector. In kinetic analysis three methods were used: Friedeman, Kissinger Akahira – Sunose (KAS) and Flynn – Wall – Ozawa (FWO) [27]. The results are

shown in Table 3. The activation energy was determined by measuring temperatures corresponding to the determined values at different heating rates in the TGA analysis of 10, 20, 30 and 40 °C/min., Similar values of activation energy for hydrochars produced in 190 °C and 2h and raw digestate were obtained for each of the methods. For hydrochars produced in 200 and 210 °C the results for the KAS and FWO methods were consistent, and for the Friedeman can be seen the difference. This may be due to the discrepancy of the equations used for the calculations. On the basis of the calculations performed, it can be concluded that the lowest activation energy for all methods is characterized by raw digestate. In general, the activation energy for hydrochars were higher than for raw digestate and increased with longer residence time which probably resulted from the release of unstable volatile matter and the generated aromatic compounds from undergoing aromatization reaction during hydrothermal carbonization process. These trend is line with the results presented by Chen et al. [28] who suggested that it can provided hydrochar with higher thermal stability. For hydrochars produced in the HTC process at 200 °C and 210 °C, the activation energy reaches values within 200 kJ/mol For the Friedman method, the highest value of activation energy is characterized by hydrochar produced in 210 °C and 2 h, for the KAS and OFW methods, the highest values are for hydrochars produced in 210 °C and 1 h [28]. Lang et al. [29] performed the HTC process of the cattle manure in 180, 200 and 220 °C and residence time 10 h. TGA analysis was then performed to estimate kinetic behaviour and KAS and FWO models were used to calculate the activation energy. For 220 °C the highest value of activation energy was obtained, where for both methods it reached the value within 175 kJ/mol. This is caused by degradation of easily reactive hemicellulose and the content of lignin with thermal stability. For hydrochar produced at 180°C and 200°C, slightly lower values were obtained than for cattle manure. According to the research, it was due the fact that during the HTC process the specific surface area of hydrochar is increased. As a result, this affects the reaction on the surface during the combustion process [29]. On the other hand, Zhang et al. [30] obtained hydrochars from the HTC process at 200 °C and a residence time 2 h. The raw material in the process was rice straw. The TGA results were used to calculate the activation energy by the KAS method. For raw rice straw, the average value was 222 kJ/mol. However, value for hydrochar produced from rice straw after the HTC process was within 233 kJ/mol. The increase in the value of activation energy is associated with the content of hemicellulose. During the HTC process, a lot of interrelated reactions take place and bonds with weak thermal stability in hemicellulose are broken. The observed increase of cellulose content has also an impact on the obtained results. [30].

Table 3

Activation energy results for raw digestate and hydrochars.

Method	RAW DIGESTATE kJ/mol	HTC 190/1.0 kJ/mol	HTC 190/2.0 kJ/mol	HTC 200/1.0 kJ/mol	HTC 200/2.0 kJ/mol	HTC 210/1.0 kJ/mol	HTC 210/2.0 kJ/mol
Friedman	156	177	180	175	161	174	187
KAS	159	168	181	172	200	201	175
FWO	152	169	181	203	200	220	176

4. Conclusions

The HTC process was conducted using agricultural digestate. As a result, solid, liquid and gaseous products were obtained. The solid product was hydrochar, which was then analyzed to determine its fuel properties. The fuel properties of hydrochars primarily depend on the temperature and residence time of the HTC process. The results of the ultimate analysis confirm that the hydrothermal carbonization process of agricultural digestate increases the carbon content in hydrochars. Furthermore, hydrochars produced at 210 °C have a higher carbon content and higher HHV values than hydrochars produced at 190 °C and 200 °C. On the basis of the conducted research, it can be concluded that as the temperature of the HTC process increases, hydrochars with better fuel properties are obtained. Moreover, based on the TGA results, hydrochars combusted later and shorter and had higher thermal stability suggested by estimated activation energy than raw digestate and had similar combustion profiles, in particular, hydrochar performed at 200 and 210 °C for 1.5 and 2 h.

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Data Availability

Data is available on request

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Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: