



Full Length Article

Pyrolysis of hydrochar derived from biomass – Experimental investigation

Aneta Magdziarz^a, Małgorzata Wilk^{a,*}, Mariusz Wądryk^{b,c}^a AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Mickiewicza 30 Ave., 30-059 Krakow, Poland^b AGH University of Science and Technology, Faculty of Energy and Fuels, Mickiewicza 30 Ave., 30-059 Krakow, Poland^c AGH University of Science and Technology, AGH Centre of Energy, Czarnowiejska 36 Street, 30-054 Krakow, Poland

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ABSTRACT

In this study three kinds of biomass were investigated: wood biomass (pine), energy crop (*Sida hermaphrodita*) and agriculture biomass (straw) using the hydrothermal carbonization process (HTC). The HTC process was conducted in a specially designed reactor under the following conditions: 220 °C temperature and 4 h residence time. The solid (hydrochar) and liquid products of hydrothermal conversion were determined in terms of their chemical and physical properties. Furthermore, the basic parameters of the obtained hydrochars were established: ultimate and proximate analyses, higher heating value, mass and energy yield and energy densification ratio. The liquid products were analysed by measuring pH and conductivity, which confirmed their acidic and polar character, and Chemical Oxygen Demand (COD) at very high value indicating that the liquid phase contained a high concentration of organic matter and nutrients. Additionally, the TGA of hydrochar was performed in an air and inert atmosphere to simulate the combustion and pyrolysis process. Moreover, the pyrolysis process of the hydrochars was investigated using Py-GC-MS apparatus. The process was performed to analyze the composition of pyrolysis products from the hydrochars. The samples were pyrolyzed in sequence at 400, 500, and 600 °C with rapid heating and a short residence time. The pyrolysis of the hydrochars resulted in varied organic compounds dependent on the pyrolysis temperature and chemical composition of hydrochars.

1. Introduction

Pyrolysis is widely recognized as a reliable and effective process involved in the transformation of biomass and other alternative solid resources toward bioproducts that may be used in liquid and solid fuels production. Pyrolysis describes the process of a deep chemical transformation of materials conducted at elevated temperatures in the absence of O₂, mainly in an inert gas environment. It results in the production of a solid residue called biochar, a condensable organic matter called bio-oil, and gases, mainly CO, CO₂, H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₆H₆, etc. The chemical composition of the final products depends on the parameters of the process, mainly heating rate, pressure, temperature, residence time and the chemical composition of the pyrolysed material. For this reason pyrolysis can be divided into slow, fast and flash pyrolysis [1,2] while taking into account temperature, heating rates and residence time. Slow pyrolysis (conventional pyrolysis) is conducted under a long residence time and with a temperature less than 500 °C [3]. Fast pyrolysis involves high heating rates (including up to 200 °C/min) and a short residence time (c.a. 2 s). Fast pyrolysis can convert 50–75% woody biomass to py-oil [4,5]. Flash pyrolysis is characterized by much higher heating rates, e.g. 1000 °C/min and a

very short residence time (< 0.5 s) resulting in high py-oil yields up to 75–80% [6].

The possibility of converting organic matter via pyrolysis has been tested by many researchers, taking into account the various feedstock types, e.g. woody biomass [1,7–9], agricultural waste [1,10], energy crop [11], micro- and macroalgae [12,13], poultry litter [14] sewage sludge [15], etc. including also the possibility of its co-processing e.g. lignocellulosic biomass and microalgae [16], biomass [17–19], sewage sludge and biomass [20,23], and brown coal and wheat straw [21,24]. The comparative studies of biomass and organic fractions were investigated [20–22]. Thus, it has generally been proven that the process variables, i.e. temperature, heating rate, residence time, particle size and the presence and type of catalysts noticeably affect the mechanism of thermal decomposition of organic matter resulting in changes in the yields and quality of the resulting bioproducts. Moreover, the mechanism of decomposition depends crucially on the biochemical composition of biomass, especially the presence of highly stable biopolymers. Pyrolysis is a cost-effective process used in the treatment of biomass with a low moisture content. For this reason, pretreatment processes are required for high moisture content biomass in order to improve its energy quality [25,26].

* Corresponding author.

E-mail addresses: amagdzia@agh.edu.pl (A. Magdziarz), mwilk@agh.edu.pl (M. Wilk).<https://doi.org/10.1016/j.fuel.2020.117246>

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In the case of the transformation of wet biomass, the energy-consuming process of drying is necessary. The prior conversion of high moisture biomass in the near-critical water opens the way to avoiding the aforementioned issues and enables upgraded bioproducts to be obtained without an energy-consuming drying step [27,28].

In fact, hydrothermal carbonization as a pretreatment process enhances the chemical and physical properties of hydrochar compared to raw biomass, which is beneficial for further processing via pyrolysis. For instance, Garlapalli et al. [29] reported that hydrothermal carbonization before pyrolysis allowed for an improvement in char quality, e.g. by a decrease in PAH content, as well as a reduction in oxygen and ash content. Also, Yao et al. [30] observed the positive impact of hydrochar from the addition of green waste when co-processed with paper sludge. Whereas, the pyrolysis process of co-hydrothermal carbonization of sawdust and sewage sludge was also studied by Ma et al. [31] using TGA instrumental analysis, which confirmed the energy potential of hydrochar used as a solid fuel in the pyrolysis process. Moreover, the effect of different processing conditions was also investigated. For instance, Olszewski et al. [32] investigated the effect of a hydrothermal carbonization (HTC) pretreatment, where processing brewer's spent grains affected the pyrolysis behaviour of the resulting produced hydrochars using Py-GC-MS.

It was reported that differences were found that may confirm a different structure in the hydrochars compared to the precursor. Also, Guo et al. [33] presented an investigation concerning the pyrolysis and thermodynamic properties of hydrochars derived from bamboo shoot shell, taking into account various biomass to water ratios in hydrochars. In literature, different studies concerning the discussed matter could also be found, e.g. Dai et al. [34] reported comparative studies of microwave and conventional hydrothermal pretreatment of bamboo sawdust on pyrolytic decomposition. Quan et al. [35] investigated the pyrolysis of pre-treated industrial agriculture waste e.g. corn cob hydrolysis residue in order to study and promote its fuel properties. The Py-GC/MS of hydrochars analysis was also studied by Zhang et al. [36] in the case of a co-hydrothermal carbonization of mixture of the rigid polyvinyl chloride and pinewood sawdust. The results showed changes in the distribution of the pyrolysis product depending on the mixing ratio of co-HTC substrates.

The pyrolysis of organic waste, e.g. pig manure, was investigated by Gasco et al. [37] in order to compare the biochar properties with hydrochar properties obtained from the same waste. The researchers discovered that biochars had more aromatic structures and a high thermal stability compared to hydrochars characterized by aliphatic structures. Although the pyrolysis of hydrochar derived from biomass has recently been studied, the results have strongly depended on biomass origin and thus further investigation is necessary.

The main aim of this study was to investigate the energy potential of hydrochars derived from wood biomass (pine), energy crop (Virginia mallow) and agriculture biomass (straw). Therefore, the pyrolysis process of the hydrochars was studied to analyze the gaseous products as a function of pyrolysis temperature.

2. Materials and methods

2.1. Materials

Three kinds of biomass were investigated: wood biomass (pine), energy crop – Virginia mallow (*Sida hermaphrodita*) and agriculture biomass (straw). The pine wood was obtained from a Polish sawmill with an the average particle size of 0.5 mm, whereas Virginia mallow (called Virginia) and straw were in the form of long stem from the Polish agriculture area. The samples were cut and milled using a 1 mm particle size grinder.

2.2. Hydrothermal carbonization process

All studied samples were pretreated using the hydrothermal carbonization method. This was carried out in a stainless steel Zipperclave Stirred Reactor with a volume capacity of 1000 ml which was equipped with a MagneDrive Agitator (Parker Autoclave Engineers) under the following conditions: 220 °C temperature and 4 h residence time. A full description of the laboratory set-up is reported on pages [16,18]. The material (25 g) was dispersed in deionised water (500 ml), placed into the reactor and then sealed and heated up. When the reaction was over, the reactor was cooled down and the solution was evacuated and filtered through microfiltration paper on a Buchner apparatus using a vacuum pump. The filtered solid (hydrochar) was heated up to 105 °C then placed in a plastic container and left for further analysis. The liquid product was collected in glass bottles and kept at 4 °C. Both the solid and liquid products of the hydrothermal conversion were determined in terms of their chemical and physical properties

2.2.1. Solid material characteristics

The proximate analyses including moisture, ash and volatile matter of raw material and hydrochars were determined according to EN 15934:2012, EN 15403:2011, EN 15402:2011, respectively. The fixed carbon was calculated by difference. The ultimate analysis (carbon, hydrogen, nitrogen and sulphur content) was carried out by using an Elemental Analyser Truespec CHN and S Leco (CHNS628) according to PKN-ISO/TS 12902:2007. The higher heating values of the raw samples were determined using a KL-10 bomb calorimeter according to PN-ISO 1928:2002.

2.2.2. TGA analysis

Approximately 5 mg of biomass sample was heated in alumina crucibles (70 µL capacity) from an ambient temperature up to 700 °C. All experiments were performed under non-isothermal conditions at a constant heating rate of 10 °C/min in air atmosphere at 50 ml/min flow of gas. The thermogravimetric results were presented in the form of TG, DTG, and DSC curves, respectively, where: TG – thermogravimetry presents the weight loss of studied samples in contrast to the initial mass under an increasing temperature, DTG – differential thermogravimetry is based on the rate of weight loss, DSC – differential scanning calorimetry additionally allows for the determination of thermal effects (endothermic and exothermic).

2.2.3. Liquid products from HTC

The liquid phase filtered from the HTC solution was of a dark yellow colour. In order to clear this phase, it was distilled under low pressure resulting in 90% clear and transparent liquid, while the other 10% was dark brown. The distillate was heated in a water bath to remove water molecules. Chemical Oxygen Demand (COD) analysis was conducted according to PN-ISO 6060:2006 in order to quantify the amount of organics in the liquid phase. The COD indication method was performed by the use of potassium dichromate $\text{Cr}_2\text{O}_7^{2-}$, which is used to oxidize and transform the organic matter in the solution into carbon dioxide and water under acidic conditions. Furthermore, pH, conductivity, and oxygen demands for both HTC-water and distillate samples were conducted using a Multifunction Laboratory Meter CX-505 ELMETRON. Additionally, an acid-base titration of the distillate was carried out to determine the concentration of acetic acid. All steps were repeated at least three times and measurements taken each time.

2.3. Pyrolysis

The pyrolytic decomposition studies of the tested hydrochars were conducted using a pyrolyzer (Pyroprobe model 5200, CDS Analytical) coupled to a GC-MS (GC: model 7890B, Agilent; MS: model 5977A, Agilent). Pyrolysis tests were conducted in a sequence at 400, 500 and 600 °C. In each run samples (ca. 2.5 mg) were introduced into a quartz

tube, which subsequently was plugged with quartz wool and set in a platinum filament. Next, the sample was purged with an inert gas. The sample was pyrolysed in sequence, starting at 400 °C, and then (the same sample) was heated to 500 °C, and 600 °C. At each stage, the samples were heated rapidly to the desired temperature at a heating rate of °C s⁻¹ and held for 10 s. Between the different stages, the platinum filament with the sample inside rested at 50 °C with the inert gas flow, waiting for the GC-MS apparatus to be reset. The analytes evolved during each decomposition step were transferred for analysis to GC-MS via a transfer line (kept at 300 °C). The GC injector temperature was also kept at 300 °C, and the analysis was done in split mode (ratio 20:1). The Agilent HP-5MS capillary column of dimensions of 30 m × 0.25 mm × 0.25 µm was used for separation. The temperature programme of the GC oven was as follows: (i) 40 °C with a hold time of 7 min; (ii) heating ramp from 40 °C to 250 °C at a rate of 4 °C·min⁻¹; (iii) isothermal held at 250 °C for 30 min. The compounds and their peak areas were found by using the deconvolution algorithm. Only compounds with a height above 1.0% of the highest peak were considered. The MS spectra were interpreted based on the reference MS library (chemical base G1034C). The threshold for the match factor calculated and based on electronic library search routines was equal to 60%. Each measure was in triplicate. The relative share of selected compounds identified during analysis for a single pyrolysis step was calculated as the ratio of peak area of the particular compound to the summary peak area of all detected compounds.

3. Results

3.1. Biomass and hydrochar characteristics

The physical and chemical properties of hydrochar from wood biomass, energy crop and agriculture as well as raw materials are presented in Table 1.

The proximate analysis of the samples includes fixed carbon (FC) - the remaining solid combustible residue after heating the solid fuel and evacuation of volatile matter (VM) - its high content indicates that the solid fuel requires a long combustion time. It is significantly influenced by HTC, it increased 2.5, 3, and 1.8 times for pine, Virginia and straw,

Table 1
Biomass and hydrochar chemical and physical properties.

Parameters	pine	HTC – pine wood	Virginia	HTC – Virginia	straw	HTC – straw
Proximate analysis, wt (%)						
FC	12.11	30.46	7.90	24.75	13.75	24.88
VM	80.28	67.95	84.04	71.63	75.30	71.62
Ash	0.1	0.49	0.55	0.56	4.06	2.08
M	7.51	1.10	7.51	3.06	6.89	1.42
Fuel ratio						
FC/VM	0.15	0.45	0.09	0.34	0.15	0.35
Ultimate analysis, wt (%)						
C	48.1	66.0	48.8	58.3	48.2	57.9
H	6.57	5.91	6.37	5.67	6.53	5.03
N	0.104	0.052	0.313	0.382	0.497	0.568
S	0.01	0	0	0	0.07	0
O ^a	45.12	27.55	49.97	35.09	40.64	34.42
Energy parameters						
HHV, MJ/kg	19.20	25.86	17.53	20.95	18.18	22.40
LHV, MJ/kg	17.87	24.61	16.21	19.67	16.92	23.63
Energy densification ratio	–	1.35	–	1.20	–	1.30
Energy yield, %	–	90	–	84	–	73
Mass yield, %	–	67	–	70	–	56

FC – fixed carbon, VM – volatile matter, M – moisture, C – carbon, H – hydrogen, N – nitrogen, S – sulphur, O – oxygen, HHV – higher heating value, LHV – lower heating value

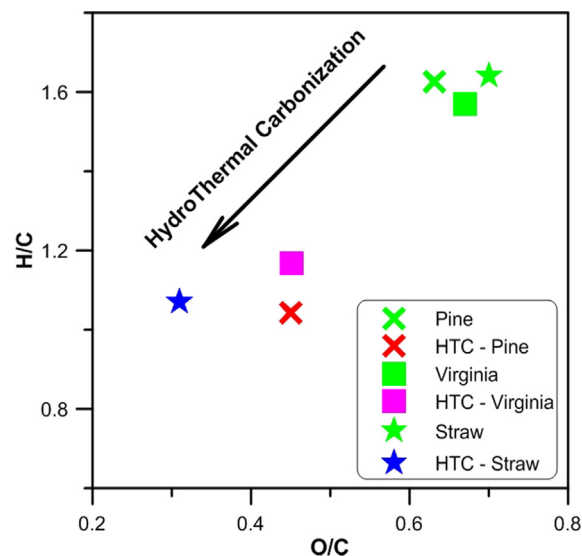


Fig. 1. Chemical properties of hydrochars versus raw biomass samples depicted on van Krevelen's diagram.

respectively. This happened due to devolatilization of volatile matter and mass conversion during hydrothermal carbonization. The fuel ratio indicated that hydrochars were mostly improved by HTC and could be used as an alternative coal fuel. Elemental composition demonstrates that C significantly increased in hydrochars by approximately 27% for pine and 16% in the case of Virginia and straw, whereas O and H decreased by 30% and 15%, respectively. Since higher and lower heating values depend on the elemental composition of the sample, especially C, S and H, they also showed an increase, 25% and 27% in the case of pine, 16% and 18% for Virginia and c.a. 19% and 28% for straw. The HHVs were found to be comparable to lignite coal. The atomic ratios are depicted in Fig. 1 as a van Krevelen diagram, which visualizes the evaluation of chemical properties of hydrochars versus raw biomass indicating that they are almost approaching lignite properties ($H/C = 0.8\text{--}1.3$ and $O/C = 0.2\text{--}0.38$). The energy densification ratio and energy yield confirmed that HTC had the most significant impact on the pine wood sample.

3.2. TGA analysis

Figs. 2–7 present the thermal behaviour of the studied hydrochars under oxidizing and inert atmosphere simulation combustion and pyrolysis processes. The decomposition of all studied biomass in an air atmosphere took place in three stages: Stage I – drying (up to 120 °C), Stage II – volatile matter release (120–400 °C), Stage III – char (120–c.a. 550 °C) (Figs. 2–4). The initial mass loss for all studied samples took place up to 120 °C. For all biomass the mass loss was very low (less than 2% based on the TG curve) confirming the hydrophobic nature of the studied hydrochars. A major mass loss took place in stage II where volatile matters were released. During this stage the structural changes start to depolymerise hemicellulose and cellulose. For all the biomass samples this stage progressed in a similar way with one DSC peak at 344, 337 and 336 °C for pine, Virginia and straw, respectively with a mass of loss more than 50% for Virginia and straw, and c.a. 45% for pine. Stage III corresponds with char oxidation. Pine and straw reacted in similar way, but within a different temperature range. For pine one exothermic DSC peak was depicted at c.a. 508 °C and mass loss was the highest, 54%, whereas straw was 467 °C and 43% mass loss. This suggests that pine contains more cellulose than Virginia and straw. In the case of Virginia, in this stage two exothermic peaks were depicted, 439 °C and 473 °C, respectively. For all biomass above 550 °C, the process was finished with a very small amount of solid residue.

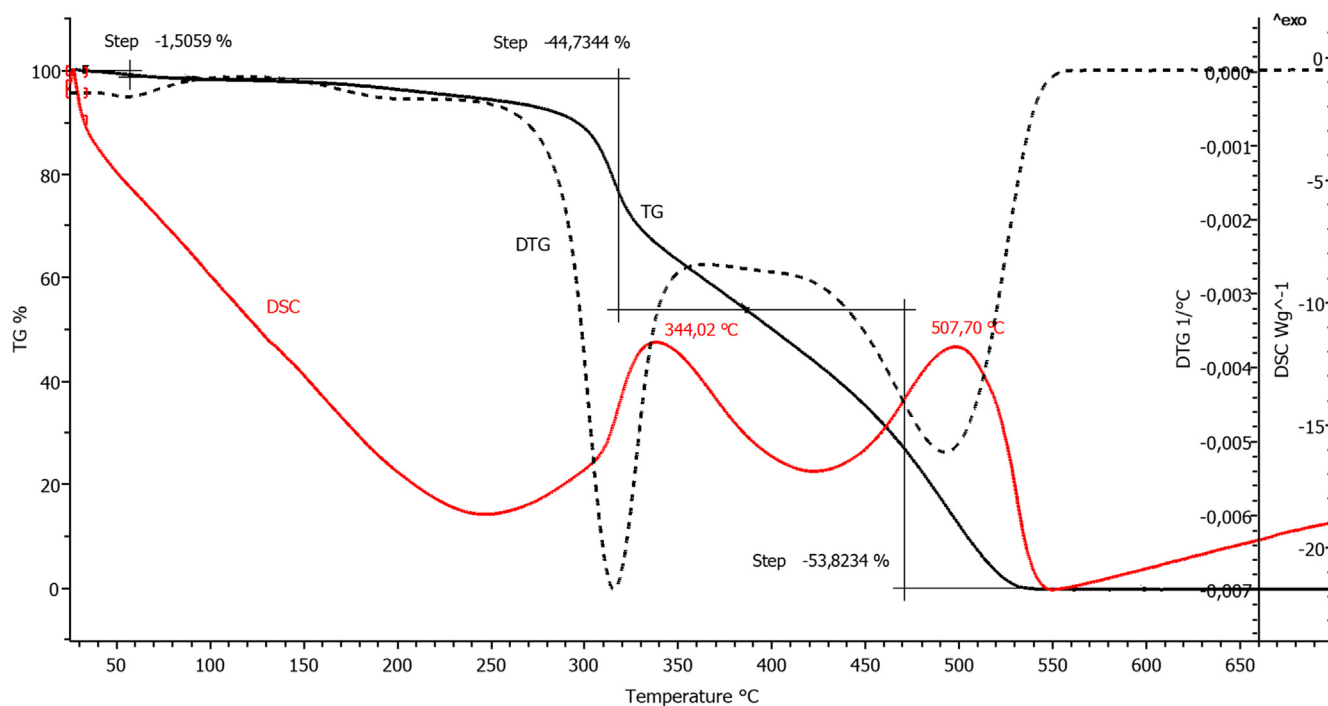


Fig. 2. TG, DTG and DSC curves for pine hydrochar at a heating rate of 10 °C/min under an air atmosphere (combustion).

In analysing the TGA results for the pyrolysis process (Figs. 5–7), it can be observed that the first stage had gone along the same pathway as during the combustion process. After the drying stage, a major mass loss occurred within a temperature range of 200 to 500 °C. This was connected with the release of volatile matter and the decomposition of hemicellulose, cellulose and lignin. Evident stages reflecting the decomposition of each structural compound were not found. In this main stage of pyrolysis, all samples decomposed with c.a. 60% mass loss (TG curves) and based on DTG curves it can be assumed that pyrolysis decomposition was almost one-stage (with a maximum DTG peak at c.a.

360 °C). However, small changes in the shape of the DTG curves were detected between 400 and 500 °C. The remaining solid residue after the pyrolysis process at 700 °C was c.a. 30 wt%.

3.3. Liquid products from HTC

The results for the main parameters measured under the liquid phase filtrated from solutions generated during the HTC process of pine, Virginia and straw are summarized in Table 2. These are pH, conductivity, density and COD for both HTC liquid phase and their

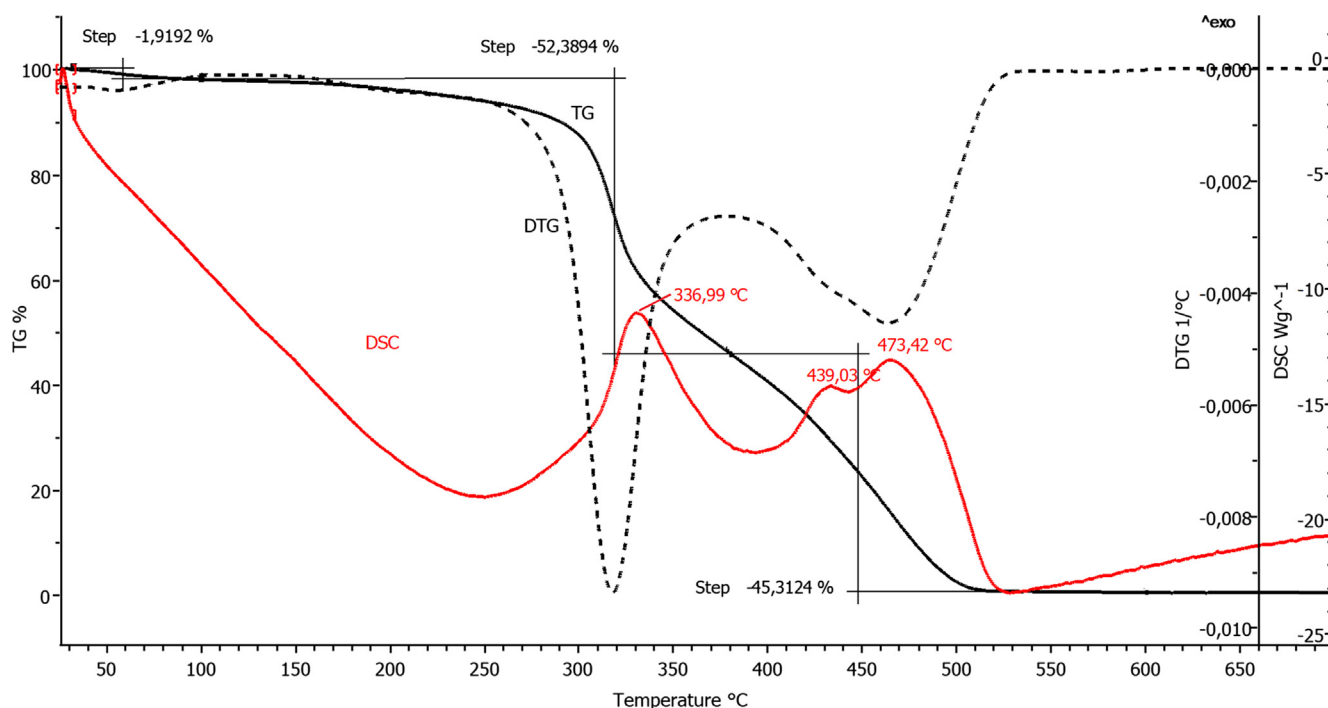


Fig. 3. TG, DTG and DSC curves for Virginia mallow hydrochar at a heating rate of 10 °C/min under an air atmosphere (combustion).

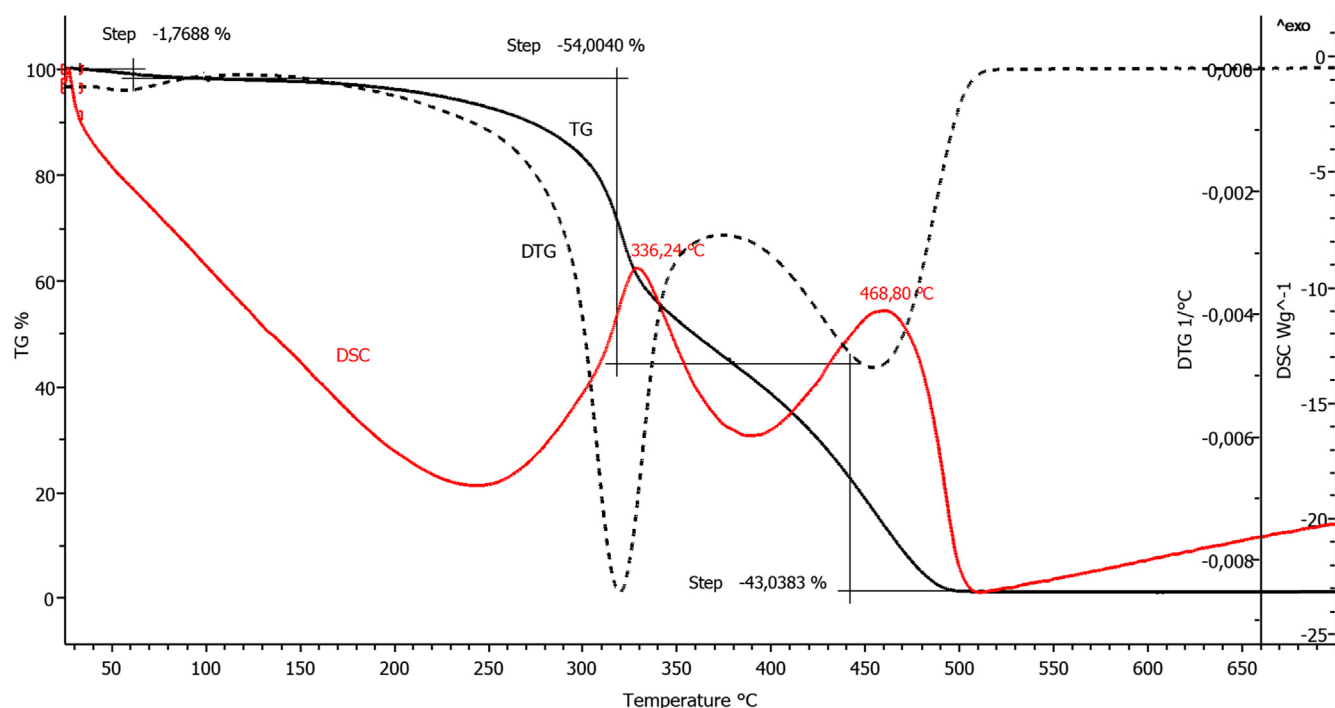


Fig. 4. TG, DTG and DSC curves for straw hydrochar at a heating rate of 10 °C/min under an air atmosphere (combustion).

distillates.

The pH of all the studied HTC liquids were acidic and those measured for distillates were lower. The conductivity of the distillates was 1.5 to c.a. 6 times lower than those measured for the HTC liquid. The highest conductivity was found for HTC straw liquid. This indicates that there were some polar compounds in the solution and suggests that most inorganic compounds did not distillate. High COD values, ranging from 18.38 to 21.35, respond to a high concentration of organic matter and nutrients. COD values of their distillates were 3 to 5 times lower. Density was almost at the same level in all HTC liquids and was slightly

lower in their distillates. The possible application of HTC liquid could be considered for biogas production, which could be used for heating the HTC reactor or in the drying process of hydrochar to remove any remaining moisture after the dewatering process.

3.4. Pyrolysis

The qualitative analysis of products released during the thermal decomposition of the hydrochars was conducted by means of gas chromatography coupled to mass spectrometry (GC-MS). The main

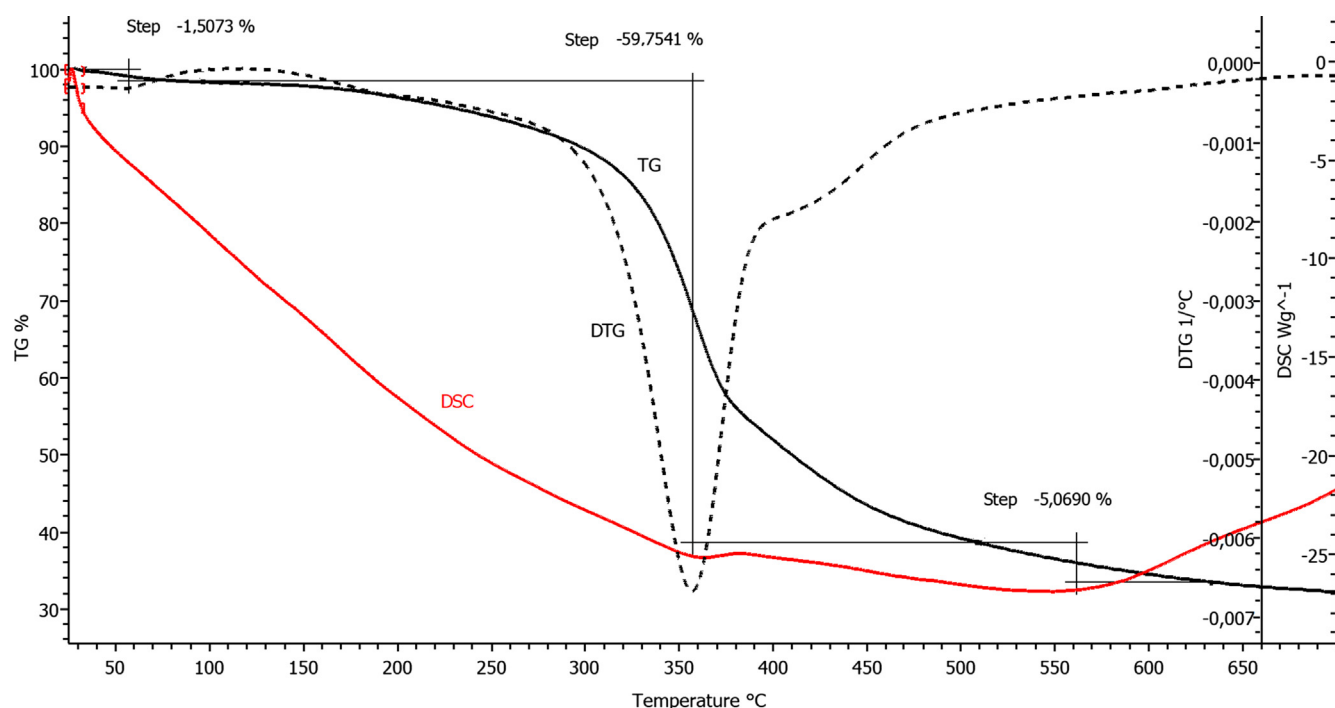


Fig. 5. TG, DTG and DSC curves for pine hydrochar at a heating rate of 10 °C/min under a nitrogen atmosphere (pyrolysis).

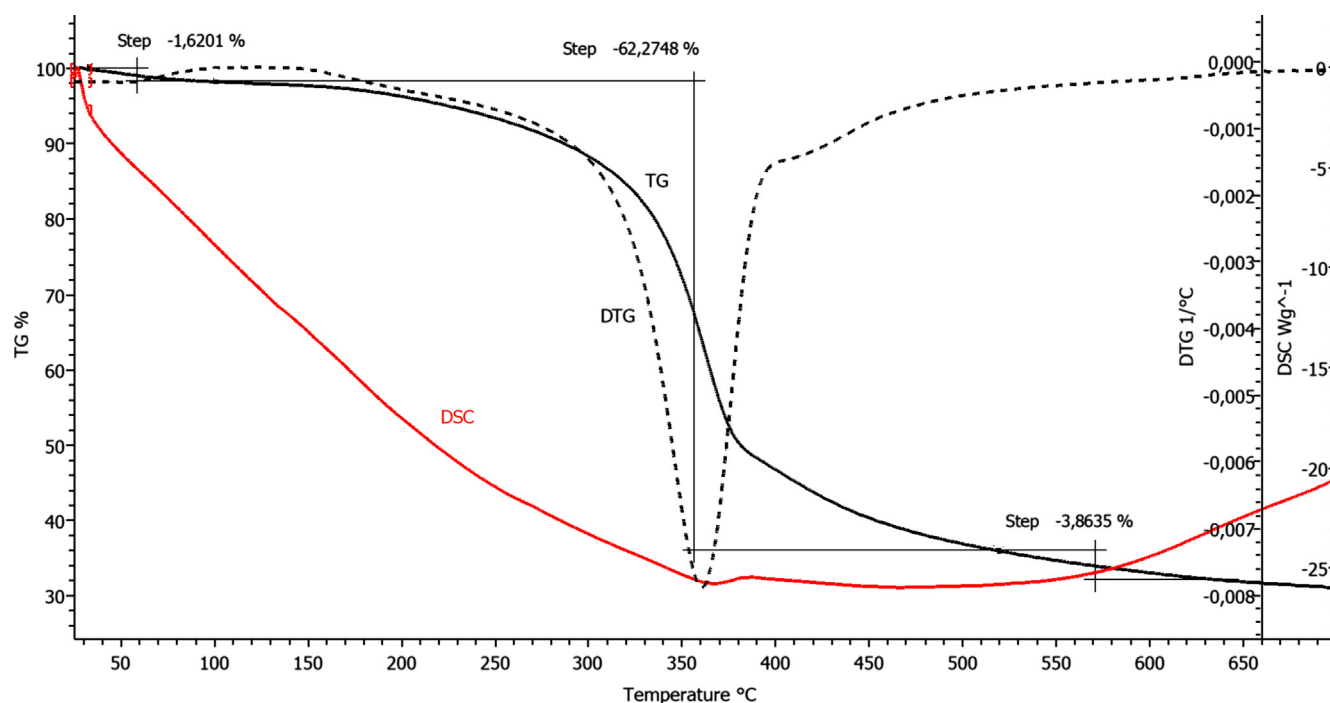


Fig. 6. TG, DTG and DSC curves for Virginia mallow hydrochar at a heating rate of 10 °C/min under a nitrogen atmosphere (pyrolysis).

compounds detected during Py-GC-MS analysis as a function of pyrolysis temperature and feedstock type are presented in Fig. 8 and Table 3.

Generally, it was found that the pyrolysis decomposition of the hydrochars resulted in a heterogeneous mixture of compounds with different functional groups. It was found that the feedstock type does not significantly influence the qualitative composition of gaseous products from decomposition of hydrochar. The main types of compounds identified were aromatic, cyclic and aliphatic hydrocarbons, phenol and its derivatives, furan derivatives as well as other oxygen compounds

(e.g. acids, ketones, aldehydes). Carbon oxides were also detected indicating that the deoxygenation of the raw structure occurs via both decarboxylation and decarbonylation processes. It is also worth mentioning that the carbon monoxide share rises gradually with an increase in the processing temperature for all tested samples, indicating the increasing importance of decarbonylation pathways. The transformation of polysaccharides occurring in the hydrochars resulted in the formation of furan derivatives, cyclic ketones and aldehydes. The structural composition of the hydrochars was partially formed from carbohydrates derivatives. The presence of light oxygen compounds, e.g. acetic acid,

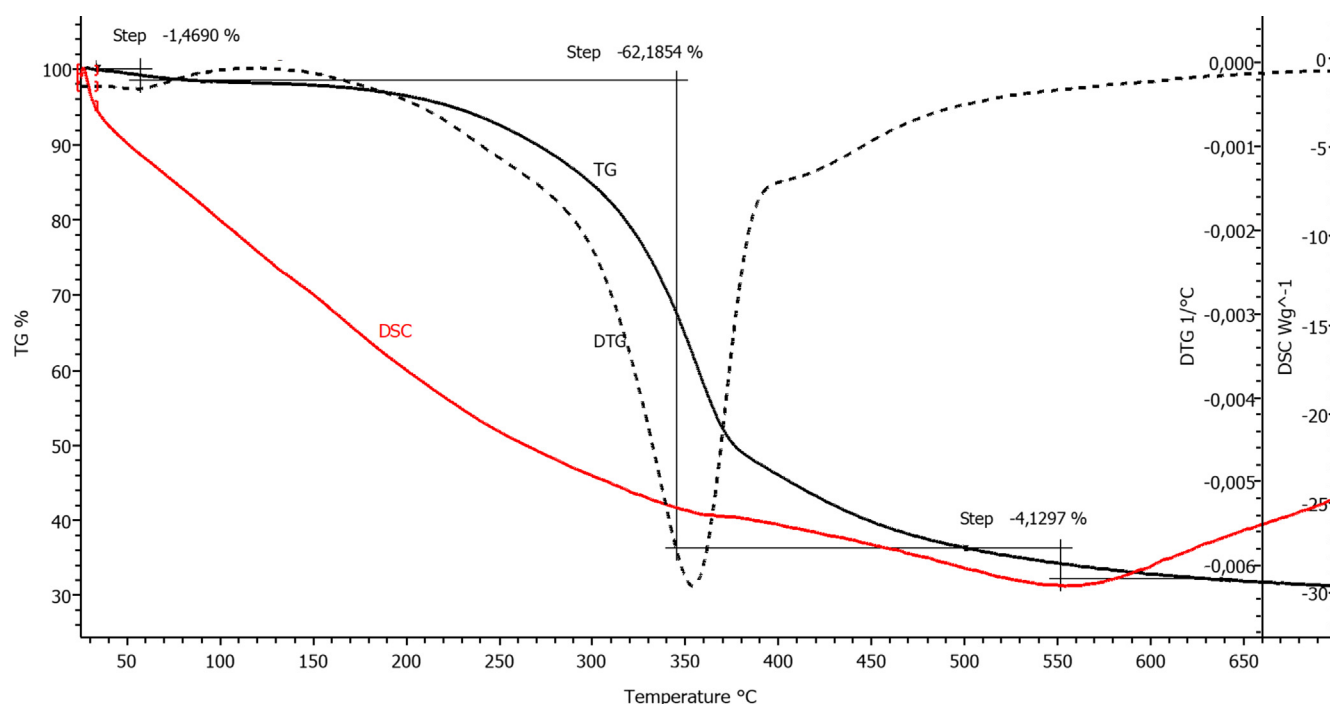


Fig. 7. TG, DTG and DSC curves for straw hydrochar at a heating rate of 10 °C/min under a nitrogen atmosphere (pyrolysis).

Table 2
Liquid phase characteristics.

Parameters	HTC – Pine wood	HTC – Virginia	HTC – Straw
pH	3.04	3.33	3.88
pH _{distillate}	2.82	2.61	3.04
Conductivity, mS	1.77	2.41	4.14
Conductivity _{distillate} , mS	1.19	0.96	0.71
COD, gO ₂ L ⁻³	21.35	19.36	18.38
COD _{distillate} , gO ₂ L ⁻³	4.26	6.88	5.38
Density, kg/m ³	1.0050	1.0047	1.0048
Density _{distillate} , kg/m ³	1.0008	1.0012	1.0003

COD – Chemical oxygen demand.

acetaldehyde, and acetone, could also be the result of the decomposition of polysaccharides. A phenol derivatives compound group was detected as 2-methoxyphenol, 2,6-dimethoxyphenol, 4-methoxy-3-methylphenol and was probably formed from lignin. Lignin is the most thermally stable polymer present in lignocellulosic biomass thus its decomposition during hydrothermal pretreatment did not take place within the HTC temperature range. Additionally, it was found that furans were formed mainly at 400 °C and gradually decreased at higher processing temperature.

Concluding, an increase in pyrolysis temperature led to the gradual

decomposition of complex molecules mainly to stable aromatics. The increase of pyrolysis temperature caused the detachment of methoxy groups from lignin derivatives (e.g. methoxyphenols). It is also worth emphasizing that an increase in the amount of phenol at higher temperatures could also be the result of cellulose degradation. Moreover, the formation of more intensive aromatic hydrocarbons at higher temperatures could be connected with the conversion of furan-rings to benzene-rings.

4. Conclusions

Hydrothermal carbonization of pine, Virginia, and straw conducted at 220 °C through 4 h resulted in enhanced chemical and physical properties of raw materials. The improvement in energy properties was attributed to higher fixed carbon, lower volatile matter, and higher energy densification caused by dehydration and decarboxylation reactions. Thermogravimetric analysis was used to analyse the hydrochars combustion and pyrolysis behaviours. To confirm the potential of the hydrochars as solid fuel, the pyrolysis process was investigated in detail. Pyrolysis of the hydrochars resulted in the mixture of various compounds among which were identified hydrocarbons, oxygen compounds, and including: phenols, furans, acids, ketones and aldehydes. To summarise, hydrothermal carbonization should be promoted as a

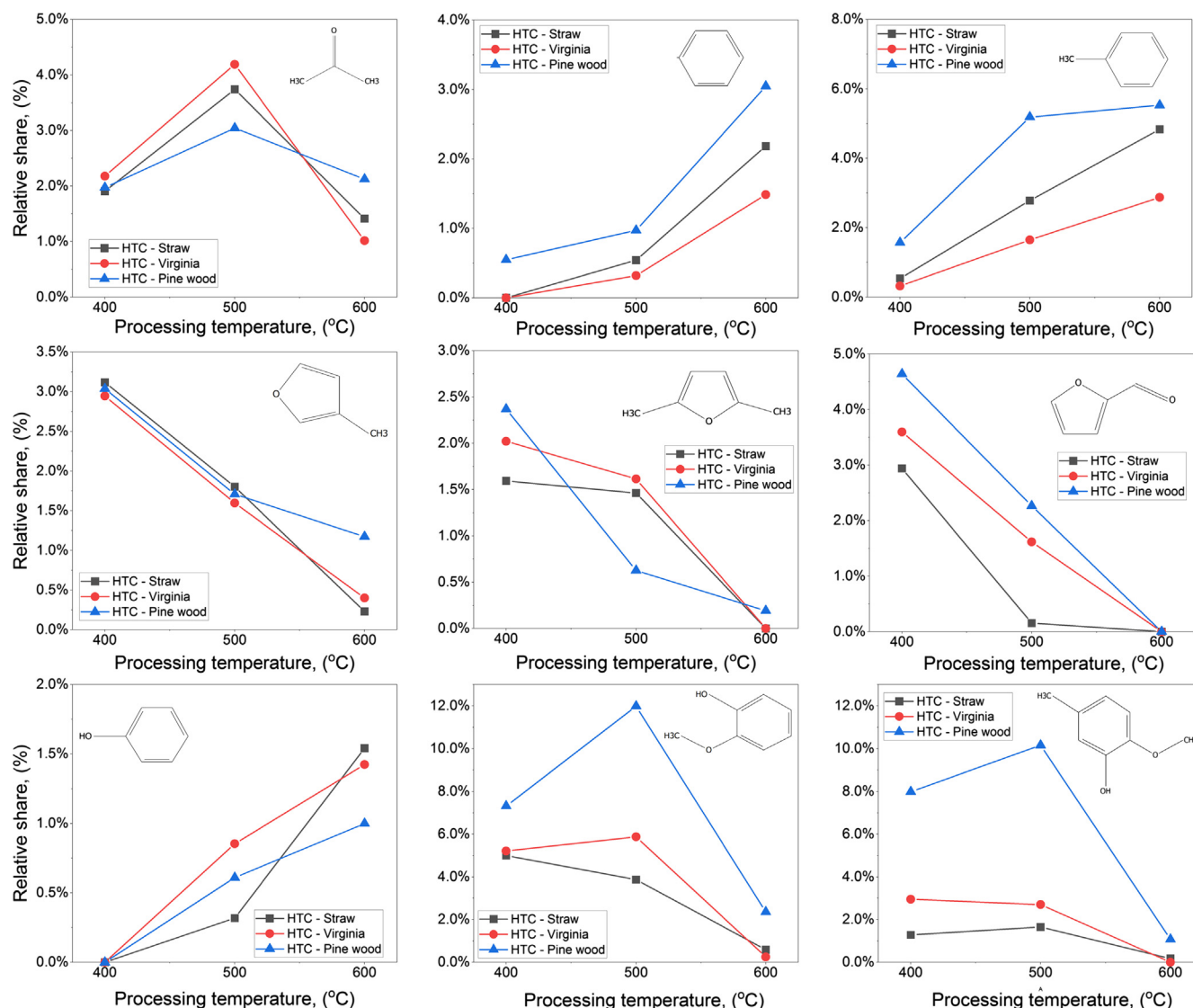


Fig. 8. The peak area for selected compounds as a function of pyrolysis temperature (Py-GC-MS results).

Table 3
Compounds identified during pyrolysis of hydrochars.

RT	Compound name	Straw HTC			Virginia HTC			Pine HTC		
		400	500	600	400	500	600	400	500	600
2.739	Carbon monoxide	+	+	+	+	+	+	+	+	+
3.077	Carbon dioxide	+	+	+	+	+	+	+	+	+
2.691	Ethane	-	+	+	-	+	+	-	+	+
3.168	Ethylene//Propene	-	+	+	+	+	-	-	+	+
3.217	Acetic acid, hydrazide	+	+	-	+	+	-	-	+	+
3.347	Acetaldehyde, hydroxy-	+	-	-	+	-	-	+	-	-
3.590	Acetone	+	-	+	+	+	+	+	+	+
3.720	1,4-Pentadiene//3-Methyl-3-buten-1-ol, acetate	+	-	-	-	-	-	-	+	-
3.880	1,3-Cyclopentadiene	-	+	-	-	+	-	-	-	-
3.983	Cyclopropylacetylene	+	-	-	-	+	-	-	+	+
4.333	Methyl vinyl ketone in. 2-Butanone	-	+	-	-	+	-	-	+	-
4.323	1-[(1-Oxo-2-propenyl)oxy]-2,5-pyrrolidinedione	-	-	-	-	-	-	-	+	-
4.423	Acetic acid ethenyl ester	+	-	-	+	-	-	-	-	-
4.592	Furan, 3-methyl-	+	+	+	+	+	+	+	+	+
5.128	Acetic acid	+	+	-	-	+	-	-	+	+
5.225	1,4-Cyclohexadiene	+	+	+	+	+	-	-	+	+
5.542	2-Butenal	+	+	-	+	+	-	+	+	+
5.663	Benzene	-	+	+	-	+	+	+	+	+
5.879	3-Buten-2-one, 3-methyl- lub 4-Penten-2-one	+	+	-	+	+	-	+	+	-
6.222 6.153	2-Propanone, 1-hydroxy-	+	-	-	+	-	-	+	+	-
6.265	Cyclopentane, 1,2-dimethyl-	-	+	-	-	+	-	-	+	-
6.607	Heptane//3-Pentanone, 2-methyl-	-	+	-	-	+	-	-	+	+
6.610	Propanoic acid, ethenyl ester	-	-	-	-	-	-	+	-	-
7.012	Furan, 2,5-dimethyl-	+	+	-	+	+	-	+	+	+
7.650	2-Vinylfuran	+	+	-	+	+	-	-	-	-
8.275	1-Methylcyclohexa-1,3-diene	-	+	-	-	+	-	-	+	+
8.343	1,2,3,6-Tetrahydrobenzylalcohol, acetate	+	-	-	+	+	-	-	-	-
9.379	Toluene	+	+	+	+	+	+	+	+	+
9.949	1-Hydroxy-2-butanone	-	-	-	-	-	-	+	-	-
9.946	1-(1'-pyrrolidinyl)-2-butanone	-	-	-	-	-	-	+	-	-
10.102	Propenoic acid, propyl ester	-	-	-	+	-	-	-	-	-
10.406	1-Hexene, 3,4-dimethyl-	-	+	-	-	+	-	-	+	+
10.838	Octane	-	+	-	-	+	-	-	-	-
10.941	Propanoic acid, 2-oxo-, methyl ester	+	+	-	+	-	-	+	+	+
11.059	Furan, 2-ethyl-5-methyl-	+	+	-	+	+	-	+	+	+
11.565	Carbonocyanidic acid, ethyl ester	+	+	-	+	+	-	+	+	-
11.661	Furan, 2,3,5-trimethyl-	-	-	-	-	-	-	-	+	+
12.415	p-Cresol	+	+	-	+	+	-	+	+	+
12.676	3-Cyclopentene-1-acetaldehyde, 2-oxo-	-	+	-	-	-	-	-	-	-
12.721	Propanoic acid, 2-methyl-, anhydride	+	+	-	-	-	-	-	-	-
13.007	Furfural	+	+	-	+	+	-	+	+	-
13.880	Ethylbenzene	-	+	-	-	+	-	-	+	+
14.282	o-Xylene//m-Xylene	+	+	+	-	+	+	-	+	+
14.556	3H-Pyrazole, 3,4-diamino-	+	-	-	-	-	-	-	-	-
14.519	1,2-Cyclopentanedione	+	-	-	+	-	-	+	-	-
14.543	2-Propanone, 1-(acetyloxy)-	+	-	-	+	+	-	+	+	-
15.163	1H-Imidazole-4-methanol lub 1H-Pyrrole-2-ethanamine, 1-methyl-	+	-	-	-	-	-	-	-	-
15.294	butanedioic acid, phenyl	-	+	+	-	-	-	-	-	-
15.360	Styrene	+	+	-	+	+	+	+	+	+
15.391	p-Xylene//m-Xylene	-	-	-	-	-	-	-	+	+
15.694	Nonane	-	+	-	-	-	-	-	-	-
16.361	2-Cyclopenten-1-one, 2-methyl-	+	+	-	+	+	-	+	+	+
16.610	1-Pentanone, 1-(2-furanyl)-	+	+	-	+	+	-	+	-	-
17.441	2,5-Hexanedione//Lauric acid, 3,5-dimethylphenyl ester	-	-	-	-	-	-	+	-	-
18.088	Proline, 2-methyl-5-oxo-, methyl ester	-	-	-	+	-	-	-	-	-
18.275	Aletamine	-	-	-	-	-	-	+	-	-
18.660	Benzene, 1-ethyl-4-methyl-	-	+	-	-	-	-	-	+	-
18.701	Acetophenone	-	+	-	-	-	-	-	+	-
19.103	2-Furancarboxaldehyde, 5-methyl-	+	+	-	+	+	-	+	+	+
19.247	Cyclohexane, butylidene-	-	-	-	-	-	-	-	+	-
19.889	4(1H)-Pyrimidinone, 2-methyl-//1H-Imidazole, 1-acetyl-	-	-	-	+	-	-	-	-	-
19.901	Cyclodecane//1-Decene	-	+	-	-	-	-	-	-	-
20.023	4(1H)-Pyrimidinone, 6-methyl-//4'-Methyl-a-pyrrolidinopropiophenone	-	-	-	+	-	-	+	-	-
20.040	Benzene, 1,2,4-trimethyl-	-	+	-	-	+	-	-	+	-
20.476	Benzene, propoxy-	-	-	-	+	-	-	-	-	-
20.383	1-Pentanone, 1-(2-furanyl)-//1-(3H-Imidazol-4-yl)-ethanone	-	-	-	-	-	-	-	+	-
20.580	Phenol	-	+	+	-	+	+	-	+	+
21.277	o-Cymene//p-Cymene	-	-	-	-	-	-	-	+	-
21.242	Benzene, 1-methoxy-4-methyl-	-	+	-	-	+	-	-	+	+
21.608	Limonene	+	+	-	-	-	-	-	-	-
22.322	Benzene, 1-propynyl-	-	-	-	-	+	-	-	+	-
22.273	Indene	-	+	-	-	+	-	-	+	-

(continued on next page)

Table 3 (continued)

RT	Compound name	Straw HTC			Virginia HTC			Pine HTC		
		400	500	600	400	500	600	400	500	600
22.338	2-Ethyl-5-propylcyclopentanone	-	-	-	-	-	-	+	-	-
22.438	3-Methyl-3-cyclohexen-1-one//2,4-Hexadiene, 2,5-dimethyl-	+	-	-	-	-	-	-	-	-
22.615	2-Pyrrolidinecarboxylic acid, 1,2-dimethyl-5-oxo-, methyl ester//4,4-Dimethyl-2-cyclopenten-1-one	+	-	-	-	-	-	-	-	-
22.758	Piperidine, 2-propyl-, (S)-	-	-	-	+	-	-	-	-	-
23.303	p-Cresol	-	-	-	-	+	+	-	+	+
24.097	1-Undecene	-	+	-	-	-	-	-	-	-
24.418	Undecane	-	+	-	-	-	-	-	-	-
24.137	Benzene, 4-ethenyl-1,2-dimethyl-	-	-	-	-	-	-	+	-	-
24.483	Phenol, 2-methoxy-	+	+	+	+	+	+	+	+	+
24.971	Benzofuran, 2-methyl-	-	+	+	-	+	+	-	-	+
26.537	Naphthalene, 1,2-dihydro-	-	+	+	-	-	-	-	-	-
26.760	Benzene, (1-methyl-2-propynyl)-	-	+	-	-	-	-	-	-	-
26.758	2-Methylindene//Benzene, (1-methyl-2-propynyl)-	-	-	-	-	+	-	-	+	-
27.176	Phenol, 3,4-dimethyl-	-	+	-	-	-	-	-	-	-
27.328	Phenol, 4-ethyl-	-	-	+	-	-	-	-	-	-
27.717	Phenol, 4-methoxy-3-methyl-	-	+	-	-	+	-	+	+	-
27.897	Naphthalene	-	-	+	-	+	+	-	+	+
27.954	Azulene	-	-	-	-	-	+	-	-	-
27.921	1-Dodecene	-	+	-	-	-	-	-	-	-
28.222	Dodecane	-	+	-	-	-	-	-	-	-
28.303	2-Methoxy-5-methylphenol	+	+	+	+	+	-	+	+	+
28.708	1H-Benzimidazole, 5,6-dimethyl-	-	+	-	-	+	-	-	+	-
28.984	Benzofuran, 4,7-dimethyl-	-	+	-	-	-	-	-	+	+
29.483	6-Methoxy-2,6-dihydropyran-3-one	-	-	-	-	-	+	-	-	-
31.149	1,4-Benzenediol, 2-methoxy-	-	-	-	-	-	+	-	-	-
31.209	Phenol, 4-ethyl-2-methoxy-	+	+	+	+	+	+	+	+	+
31.352	3,4-Dimethoxytoluene//2-Propanone, 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-	-	-	-	-	-	-	+	-	-
31.732	Tridecane	-	+	-	-	-	-	-	-	-
32.426	2-Methoxy-4-vinylphenol//4-Hydroxy-2-methylacetophenone	+	+	+	-	+	+	-	+	-
33.661	Phenol, 2,6-dimethoxy-	+	+	+	-	+	+	-	-	-
33.817	Eugenol	-	-	-	-	-	-	-	+	-
34.142	Phenol, 2-methoxy-4-propyl-	-	-	-	-	-	-	-	+	+
35.310	Vanillin	+	-	-	-	-	-	-	-	-
36.722	3,5-Dimethoxy-4-hydroxytoluene	-	-	+	-	+	+	-	-	-
36.801	Phenol, 2-methoxy-4-(1-propenyl)-	-	-	-	-	+	+	-	+	+
38.102	Benzo[b]thiophene, 3,5-dimethyl-	-	-	-	-	-	+	-	-	-
50.587	n-Hexadecanoic acid	+	+	-	+	+	+	+	+	-
54.580	9,12-Octadecadienoic acid (Z,Z)-	+	-	-	-	-	-	+	-	-
62.131	Tetracosane	-	-	-	-	-	-	+	-	-
67.773	Propenoic acid, 2-cyano-3-(1-methyl-5-phenylthio-2-pyrrolyl)-, methyl ester	-	-	-	-	-	-	+	-	-
68.263	Hexacosane	-	-	-	-	-	-	+	-	-
72.350	eicosane// <u>octacosane</u>	+	-	-	+	-	-	+	-	-
74.116	Squalene	+	-	-	+	-	-	+	-	-

good pretreatment method for high moisture content biomass in energy application.

CRedit authorship contribution statement

Aneta Magdziarz: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Writing - original draft. **Małgorzata Wilk:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Writing - original draft, Writing - review & editing, Supervision. **Mariusz Wądrzyk:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Writing - original draft, Visualization.

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.

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