



Sustainable hydrothermal co-carbonization of residues from the vegetable oil industry and sewage sludge: Hydrochar production and liquid fraction valorisation

Aleksandra Petrovič^{a,*}, Tjaša Cencič Predikaka^b, Jelena Parlov Vuković^c, Tomislav Jednačak^d, Silvo Hribernik^e, Sabina Vohl^a, Danijela Urbancl^a, Marina Tišma^f, Lidija Čuček^a

^a Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ul. 17, Maribor, Slovenia

^b IKEMA d.o.o., Institute for Chemistry, Ecology, Measurements and Analytics, Lovrenc na Dravskem polju 4, Lovrenc na Dravskem polju, Slovenia

^c Ruđer Bošković Institute, NMR Centre, Bijenička Cesta 54, Zagreb, Croatia

^d Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia

^e Faculty of Electrical Engineering and Computer Science, University of Maribor, Koroška cesta 46, Maribor, Slovenia

^f Faculty of Food Technology, Josip Juraj Strossmayer University of Osijek, F. Kuhača 18, Osijek, Croatia

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ABSTRACT

In this study, the hydrothermal co-carbonization (co-HTC) of residues from the vegetable oil industry (pumpkin oil cake – PC, hemp oil cake – HC) and sewage sludge (SS) was investigated for the first time. The co-HTC was performed at 250 °C and a treatment time of 5 h. The effects of the mass ratio of the feedstocks (1:1, 1:3 and 3:1) on the properties of the HTC products were investigated using various analytical methods (NMR, XRD, 3D-EEM, FTIR, etc.).

The co-HTC of SS with oil cakes resulted in improved fuel properties of the hydrochar and an increase in C content from 36.9 to 53.7 wt%, and an increase in the higher heating value (HHV) from 14.8 to 23.6 MJ/kg. The combination with HC gave hydrochars with a higher HHV and higher C content than the combination with PC. The hydrochar yield varied in the range of 39.4–55.3 wt%. NMR analysis revealed a higher proportion of aliphatic (~60 %) than aromatic compounds (~35 %) in the hydrochars, as well as a high content of orthophosphate and unsaturated fatty acids. The liquid fractions were rich in nutrients and organic compounds, but toxic to aquatic organisms. The hydrochars and liquid fractions performed well in the germination test with plant species.

1. Introduction

Organic residues and waste from industry are often underutilised and often disposed of as waste or incinerated, even though they can be used as secondary sources to produce valuable products. Various types of residues are generated in the vegetable oil industry, including spent bleaching earth, oil cakes, soapstocks, acid oil and others [1], which differ considerably significantly in their chemical composition and quantity. Oil cakes, or oil meals, are considered by-products that are obtained after oil extraction by pressing various nuts and oilseeds. In Europe, 73.57 Mt, i.e., 10 % of the total world production of oilseeds, are produced annually, making the EU the third largest producer in the world after the USA and Asia [2]. Oil cakes have a wide range of

applications, as they can be used as animal feed, as organic fertiliser in agriculture [3], as a substrate source for the cultivation of microorganisms and the production of enzymes [4], etc. Due to their high calorific value and high fat content, they are also an attractive source for the production of solid and liquid biofuels.

Sewage sludge (SS), which is produced during wastewater treatment, is another abundant waste suitable for energy and material recovery [5], although its high moisture content is problematic during thermal treatment and causes high operating costs. This can be avoided by using hydrothermal treatment, which converts wet materials directly into solid fuels, offering several advantages over other thermal treatment processes [6]. Hydrothermal carbonization (HTC) has proven to be a compelling method for energy recovery from biomass, as it produces

* Corresponding author.

E-mail address: aleksandra.petrovic@um.si (A. Petrovič).

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solid, carbon-rich fuels at relatively low temperatures while producing a value-added process liquid, i.e., liquid fraction (LF) [7]. Although the production of biochar is associated with high costs, the HTC method is considered cost-effective, as it requires lower costs than pyrolysis, because dewatering, i.e., pre-drying of the biomass, can be avoided [8]. In addition, other value-added products, such as catalysts, composites or supercapacitors, can be obtained from hydrochar [9]. The LF can be used for the recovery of organic or inorganic compounds, for reuse in the HTC process [10], for anaerobic digestion and photocatalytic treatment [11] and as a fertiliser [12]. Some researchers proposed treatment by membrane filtration or reverse osmosis, and combined filtration and acid leaching for P recovery [13], but the use of LF is less utilised to recover valuable chemicals such as hydroxymethylfurfural and volatile fatty acids [14].

However, the HTC treatment of SS has been investigated in several studies [5], including those that investigated the effects of HTC treatment on the subsequent pyrolysis of hydrochar [6], and those that investigated the influence of temperature on hydrochar properties [15]. So-called co-carbonization is often used to improve the hydrochar properties, whereby the mass ratio of the input materials plays a significant role in the effectiveness of the process in addition to the operating conditions [12]. Since the carbon content and calorific value of SS and its hydrochar are relatively low and they also have a high ash content, SS is often treated in combination with other energy-rich biomasses with a high volatile matter content. For example, SS has been co-carbonized successfully with algae, sawdust, food waste, agricultural waste [12], swine manure [16], lignocellulosic biomass [17] and many other feedstocks. Interestingly, there is no study on the combination of SS with oil cake, although mono-hydrothermal treatment of residues from the oil industry, such as oil palm cake, olive oil cake [18], sesame oil cake [7], jatropha oil cake [9], babassu coconut kernel cake [19] and some other oil cakes gave encouraging results. There is also no literature on HTC of pumpkin or hemp oil cakes, or their combination with SS. Valorisation of pumpkin, hemp and flax oil cake by using subcritical water extraction is otherwise well known [20].

Since positive effects of co-HTC on product properties have been observed in many studies [21], the motivation for this research is to improve SS-hydrochar properties by combining it with energy-rich oil cakes, as such a combination can bring several benefits, including improved carbon content and calorific value. Furthermore, as the vegetable oil industry generates large amounts of wastewater that reflects in the generation of SS, co-HTC of these feedstocks makes even more sense, and can help reduce processing costs through energy integration. Utilising and combining renewable feedstocks for biofuel production is in line with the EU sustainability goals, and reduces dependence on non-renewable sources while providing solutions for waste management, carbon sequestration and the mitigation of greenhouse gas emissions [22].

The aim of this study was, therefore, to carry out the co-HTC tests with SS and oil cake under constant operating conditions and three different mass ratios of the feedstocks. In order to investigate the effects of the mass ratio on the properties of the products, the feedstocks and the products were analysed for various parameters, using analytical methods such as NMR, FTIR, XRD, TGA and 3D-EEM. This study provides new insights into the production, properties and potential applications of hydrochars obtained from the co-HTC of oily waste and SS, and emphasises the importance of the mass ratio of the feedstocks for improving product properties. The work addresses the identification of synergistic effects resulting from the combination of oil cake and SS, and deepens the understanding of the co-HTC behaviour of these feedstocks. A comprehensive characterisation of the hydrochar, in particular NMR analysis with in-depth investigation of nutrient speciation (C and P) and lipid transformation (fatty acid and glyceride distribution), provides new insights into the chemical changes and nutrient transformation and dynamics that occur during co-HTC due to changes in the mass ratio of the feedstocks. The novelty of this scientific work also lies in the detailed

study of the chemical composition of the liquid fractions and their potential application beyond conventional disposal methods, as a comprehensive analysis of the liquids, covering inorganic and organic compounds, toxicity and environmental impact, has been performed rarely so far.

2. Materials and methods

2.1. Feedstocks

The experiments on co-HTC were carried out with municipal sewage sludge (SS) and two different types of oil press cake, pumpkin seed oil cake (PC) and hemp seed oil cake (HC). The reason for choosing pumpkin and hemp oil cakes as co-substrates is their high energetic potential and the fact that they are less exploited, although they are common by-products of oil production in many European countries. The oil cakes were supplied by a local oil producer, while the sewage sludge was collected at a nearby biological wastewater treatment plant. The raw materials were dried at 40 °C and ground in a laboratory mill (manufacturer IKA). The basic properties of the raw materials are shown in Fig. 1 and Table S1 in the Supplementary Material.

2.2. Hydrothermal carbonization treatment

Hydrothermal carbonization, which takes place in a liquid medium, was chosen as the most suitable method for the production of biochar and the treatment of the selected feedstocks, as it has proven to be a promising thermochemical process for the valorisation of various types of biomass and wastes [23], especially those with a high moisture content, such as SS. The co-HTC experiments with oil cakes and SS were carried out at an operating temperature of 250 °C and a residence time of 5 h, using distilled water as the process fluid. According to the literature, hydrothermal carbonization of biomass usually takes place at around 180–250 °C and 1–10 MPa [24]. The reason for choosing the temperature of 250 °C is based on the authors' preliminary studies on the HTC of oil cake, in which the best hydrochar quality was achieved at 250 °C. Temperatures below 180 °C are too low for adequate hydrolysis and carbonization of lignocellulosic biomass such as oil cake, while high temperatures reduce the hydrochar yield [25]. This is consistent with the fact that carbonization of lignocellulosic components (hemicellulose, cellulose and lignin) starts in the temperature range of 180–260 °C [26].

Three different mass ratios of SS were tested with PC or HC (1:1, 1:3 and 3:1). The mass ratio of solid to liquid was 1:6. The mixtures were transferred to a hydrothermal synthesis reactor (stainless steel autoclave, PPL liner with a volume of 300 mL, maximum working pressure 3 MPa), which was placed in an oven and heated at a heating rate of 4 °C/min. After 5 h of heating at the desired temperature (250 °C), the reactor was cooled to room temperature. The solid and liquid fractions were separated by vacuum filtration. The hydrochar was dried at 105 °C until a constant weight, while the process liquid, i.e., the liquid fraction, was stored in the refrigerator (4 °C). The hydrochars obtained were labelled with the abbreviation representing the name of the feedstock and the mass ratio (e.g. the mixture of pumpkin cake and SS in the same mass ratio was labelled "PC-SS 1:1").

2.3. Chemical characterization

2.3.1. Characterisation of the solid samples

Various chemical analyses were carried out to characterize the feedstock materials and the HTC products. The measurements were carried out in three repetitions, to ensure the repeatability of the results, whereby the analysis results are presented as the average value of three measurements. In addition to the determination of the higher heating value (HHV) by the combustion method, the determination of fat content by the gravimetric method [27] and the FTIR analysis by the KBr

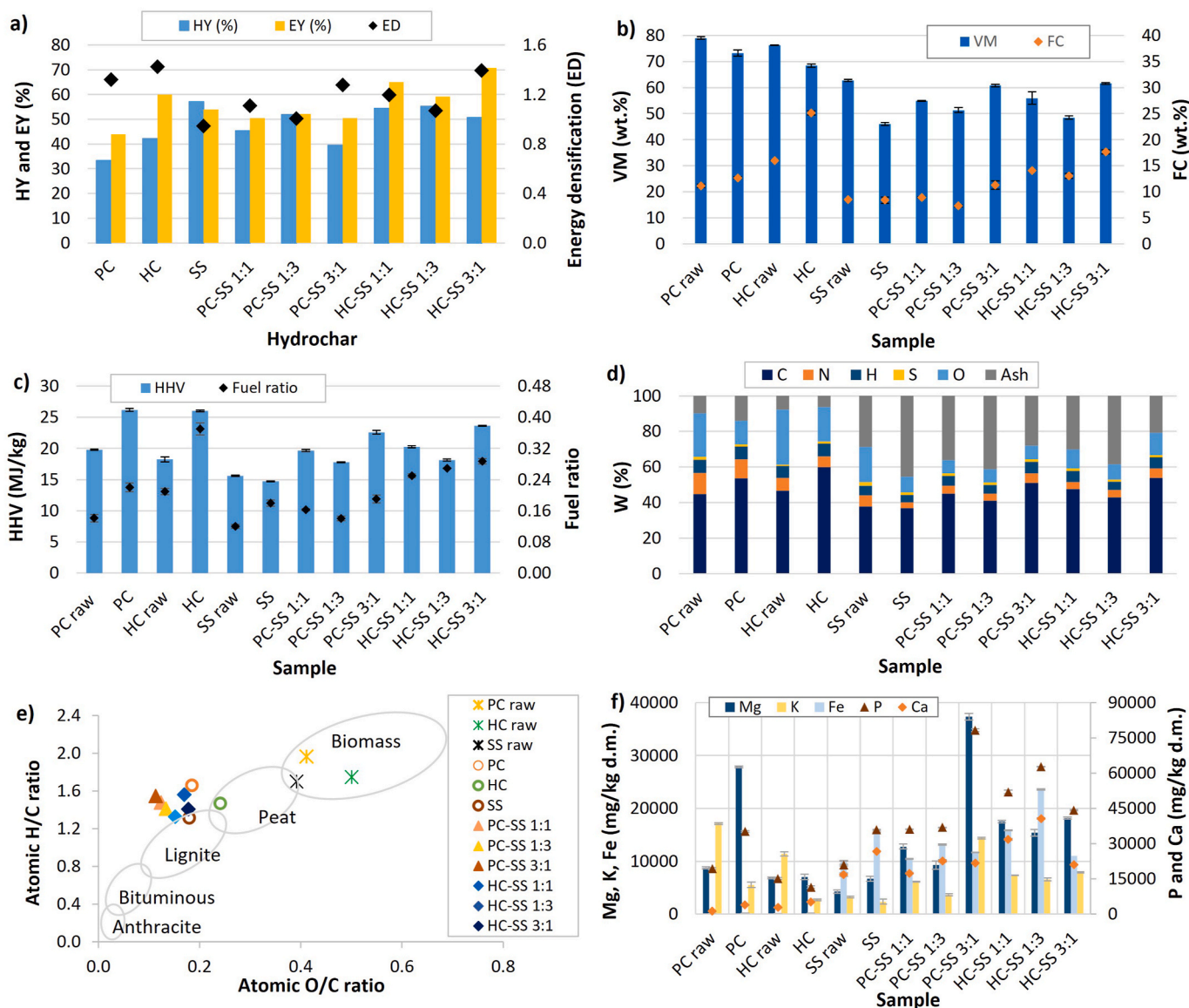


Fig. 1. The properties of hydrochars: a) Hydrochar yield, energy yield and energy densification, b) VM and FC content, c) HHV and fuel ratio, d) The content of C, H, N, S, O and ash, e) Van Krevelen diagram, and e) Nutrient content (P, K, Ca, Mg and Fe).

method, the proximate and ultimate analyses were also carried out. The hydrochar yield, energy yield, fuel ratio, energy densification and fixed carbon were calculated in addition. The equations can be found in the supplementary data (Table S2).

The ICP-OES method (inductively coupled plasma optical emission spectroscopy) was used for the determination of heavy metals and other elements in the hydrochars and LFs. The pH of the hydrochar was determined as the pH of the solution containing hydrochar/deionised water in a ratio of 1:20 (w/v %) and mixed for 1 h. The determination of PAHs (polycyclic aromatic hydrocarbons) in the hydrochar extracts after extraction with petroleum ether and acetone (volume ratio 1:1) for 5 h was carried out using the GC-MS method (gas chromatography-mass spectrometry) [28].

The XRD patterns (X-ray diffraction) of the solid samples were recorded using a D2 Phaser X-ray diffractometer (Bruker). A diffraction angle 2θ between 5° and 80° with a step size of 0.03° was measured using Cu α radiation at 30 kV and 10 mA.

2.3.2. Characterisation of the liquid samples

The LFs were characterised in terms of pH, conductivity, nitrogen

(TN) and ammonium nitrogen ($\text{NH}_4\text{-N}$) content, total phenolic compounds (TPC), volatile fatty acids (VFA), total organic carbon (TOC) and chemical oxygen demand (COD). The organic chemical compounds were identified by GC-MS (gas chromatography-mass spectrometry) using the Agilent GC-MS 6890N instrument. The toxicity of the LFs was also assessed to freshwater organisms (*Daphnia magna*) [29]. A detailed explanation of the procedures for the above methods can be found in an earlier paper by the authors [30]. In addition, the three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectra of diluted LFs were recorded using the FP 8550 spectrofluorometer (Jasco) at a scanning speed of 2000 nm/min (interval 5 nm) and an excitation/emission range of 200–450/250–600 nm.

2.3.3. NMR analysis of HTC products

The solid-state nuclear magnetic resonance (NMR) spectra of the hydrochars and raw materials were recorded using a Bruker Avance NEO 400 spectrometer with a broad band magic angle spinning (MAS) probe. The liquid ^{31}P and ^1H NMR spectra of hydrochar extracts were recorded using a Bruker Avance 600 NMR spectrometer with a 5 mm dual probe at room temperature. The detailed procedure for the NMR

measurements and the preparation of the liquid extracts is described in the Supplementary Material (Section 3.1.).

3. Results and discussion

3.1. Properties of raw materials and hydrochars

3.1.1. Physico-chemical and fuel properties

The physico-chemical properties of the raw materials and hydrochars obtained in the HTC are shown in Fig. 1 and in Tables S1 and S3. Raw oil cakes were characterised by a high content of volatile matter, carbon (C) and potassium (K), and a low content of heavy metals and ash. They were also rich in fats. The SS had a low content of carbon and volatiles and a high content of ash and heavy metals (especially Fe). All the materials were rich in phosphorus (P) and nitrogen (N). The highest P content was measured in the SS and the highest N content in the PC. The properties of both HC and PC are consistent with the data reported in the literature [3].

The results show that the mass ratio of the feedstocks influences the chemical properties of the hydrochars strongly. The addition of oil cakes to SS improved the fuel properties of the hydrochars compared to the hydrochar produced from the SS. The C and N content, as well as the volatile components, increased, while the ash content decreased. The higher C and N concentrations can be attributed to an improvement in the polymerisation and aromatisation reactions [31], which can be ascribed to a synergistic effect.

The hydrochars obtained by the co-HTC of hemp cake (HC) and SS contained higher carbon, volatile matter (VM) and fixed carbon (FC) content than hydrochar obtained from mixtures of pumpkin cake (PC) and SS. Similar results were observed for the hydrochar yield (HY), energy yield (EY) and energy densification (ED) (Fig. 1a). This can be attributed to the higher C content in the raw HC than in the PC. In

addition to the type of feedstocks and their mass ratios [32], the HY and EY are strongly dependent on the treatment temperature [33], the solids' loading and the residence time [15]. The HY of SS mixtures with oil cakes (39.43–55.25 wt%) were close to the yields reported for co-HTC of SS and lignocellulosic biomass (see Table 1) and hydrochars from oilseed cake, such as soybean cake [33]. Significantly lower values were reported for hydrochars from jatropha, pongamia pinnata and tung oil cake [34], but the treatment temperature was much higher in this study.

The decrease in VM content after the HTC (Fig. 1b) proved that the devolatilisation process had taken place, and is associated with an increased ash content due to the retained minerals after devolatilisation [35]. The higher the SS content in the hydrochar, the lower the VM content and the higher the ash content. This is due to the high content of inorganic substances in the SS. Among the hydrochars obtained by mono-carbonization, the PC hydrochar had more volatile matter than the HC hydrochar, but less fixed carbon. This indicates that the volatiles in pumpkin cake are converted to gaseous and liquid products rather than solid hydrochar. This was also confirmed by the lower HY and the higher content of total organic compounds (TOC) in the LF.

In terms of fuel ratio (Fig. 1c), the combination of SS with HC resulted in higher fuel ratios (0.25–0.29) than the combination with PC (0.16–0.19). The fuel ratio refers to the ratio of fixed carbon to volatile matter, with a higher fuel ratio indicating a better fuel quality of the hydrochar, as there is more fixed carbon in relation to volatile matter, resulting in a more stable and efficient combustion [17]. The highest fuel ratios were measured at the highest oil cake content in the mixture (mass ratio 3:1), revealing the good quality of these hydrochars. In the mono-HTC, the hydrochar derived from HC had the highest fuel ratio (0.37), followed by PC (0.19) and SS (0.18).

The HTC treatment of oil cakes led to a significant improvement in the higher heating value (HHV) of thermally treated biomass, while the

Table 1

Comparison of the properties of the hydrochars obtained with the properties of hydrochar described in the literature.

Feedstocks (Mass ratio)	Temp./time	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	HY (%)	VM (% d. m.)	Ash content (% d.m.)	HHV (MJ/kg)	H/C	O/C	Ref.
SS + pumpkin cake (1:3)	250 °C, 5 h	50.99	6.58	7.72	5.33	39.43	60.82	27.87	22.59	1.55	0.11	This study
SS + hemp cake (1:3)	250 °C, 5 h	53.72	6.29	12.76	5.51	50.75	61.63	20.7	23.63	1.41	0.18	This study
SS + peanut shells (1:3)	220 °C, 12 h	50	/	/	1.8	49.1	41.9	24.9	21.72	1.13	0.28	[39]
SS + cellulose (1:1)	220 °C, 1 h	31.85	4.78	27.84	0.88	71	60.48	34.66	12.9	1.80	0.66	[17]
SS + sawdust (1:3)	220 °C, 1 h	54.05	5.72	33.39	1.66	65.61	71	4.36	/	1.27	0.46	[25]
SS	200 °C, 2 h	35.6	4.70	0.75	3.80	/	47.67	52.04	14.34	1.58	0.02	[35]
SS+10 % oak sawdust		36.90	4.24	7.75	2.15	/	40.89	46.01	15.44	1.38	0.16	
SS	230 °C, 1 h	16.55	7.82	3.39	1.51	66.4	24.64	70.52	7.36	/	/	[16]
SS + manure (3:7)		31.34	4.13	14.46	1.92	55.2	40.06	47.82	13.09	/	/	
SS + corn stalk (1:1)	250 °C, 2 h	41.01	4.07	11.16	2.51	/	43.86	40.65	16.48	1.19	0.20	[40]
Polyvinyl chloride + wheat stalk (1:9)	260 °C, 30 min	74.13	5.77	16.36	0.73	58.62	25.39	51.82	17.5	0.93	0.17	[32]
Polyvinyl chloride + corn stalk (1:9)		72.37	5.71	15.03	1.69	44.86	44.61	14	27.09	0.95	0.16	
Soybean cake	250–300 °C, 2 h	46.2–47.3	4.77–4.93	5.65–8.53	3.48–3.67	32.3–37.4	39.5–42.2	36.7–38.5	24.5–25.5	/	/	[33]
Olive pulp	250 °C, 6 h	71.5	5.9	19	1.5	34.1	48.2	2	29.5	0.95	0.16	[18]
Babassu coconut mesocarp	180 °C, 48 h	65.4	3.7	25.9	0.3	35.9	34.6	4.7	24.25	0.68	0.30	[19]
Jatropha curcusa cake	450 °C, 50 min	81.35	3.45	14.32	0.88	21	/	/	26.32	0.51	0.13	[34]
Pongamia pinnata cake		79.32	2.78	16.67	1.23	18	/	/	25.19	0.42	0.16	
Tung cake		80.98	3.11	14.94	3.11	23	/	/	24.76	0.46	0.14	

HHV value decreased in the case of SS hydrochar. Co-HTC of SS and oil cakes improved the HHV of the hydrochars compared to SS mono-carbonization and the content of oil cake in the mixture influenced the HHV strongly (Fig. 1c). PC and HC mixtures with SS resulted in comparable HHVs, with values between 17.8 and 23.6 MJ/kg. The HHVs of the hydrochars obtained are comparable to those reported for other oil cakes, and hydrochars from co-HTC of SS with peanut shells, sawdust

or corn stalks, but significantly higher than those of SS hydrochar (Table 1). This study confirms that the co-HTC of SS with oil cake can provide high quality and high calorific hydrochar.

The potential use of hydrochars as fuel and their thermal behaviour in the pyrolysis process in an N₂ atmosphere were investigated additionally by TGA analysis. The TGA curves and the discussion of their profiles, which showed encouraging results with regard to the use of

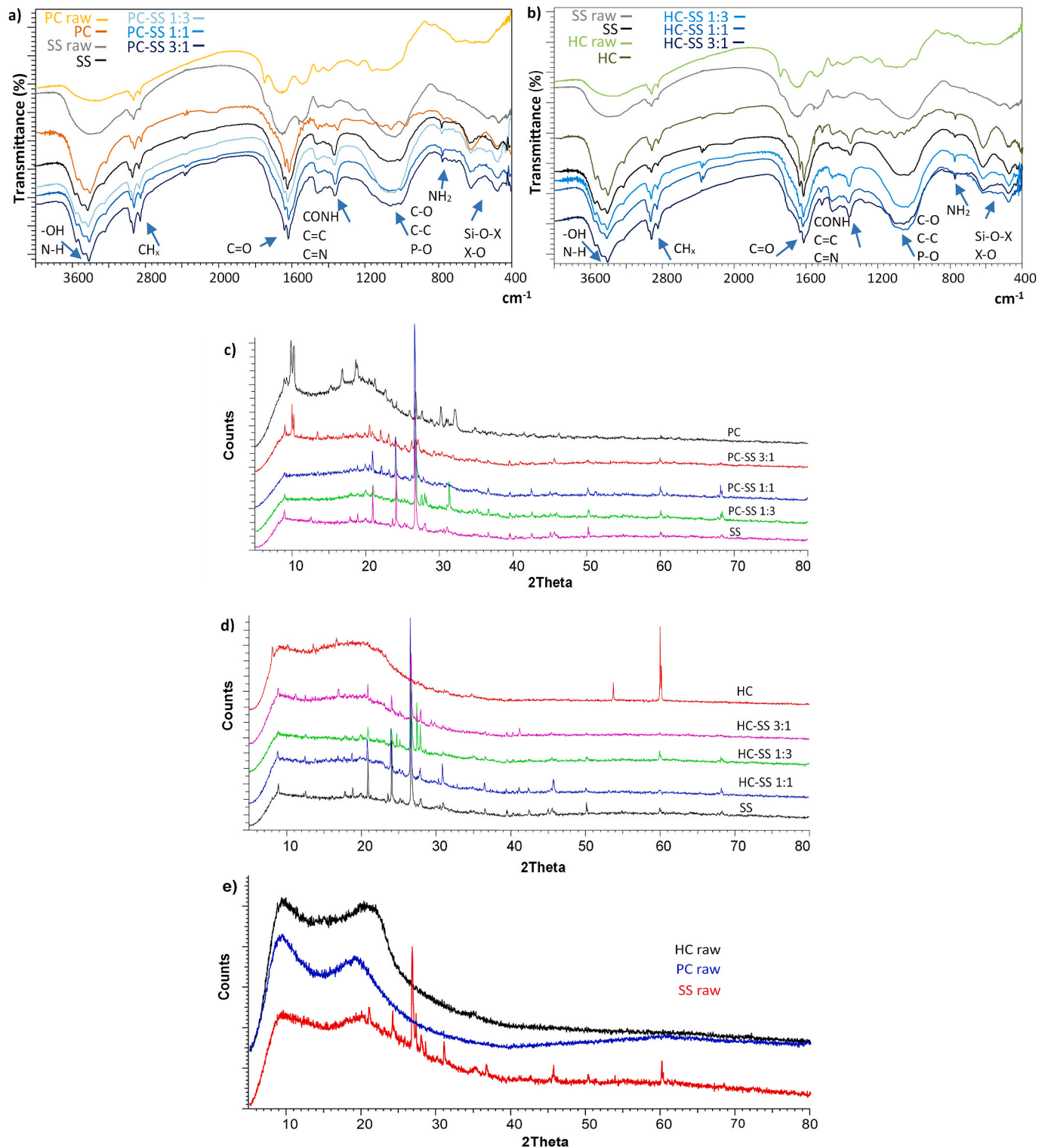


Fig. 2. a) FTIR spectra of PC-SS hydrochars b) FTIR spectra of HC-SS hydrochars, c) XRD spectra of PC-SS hydrochars, d) XRD spectra of HC-SS hydrochars, and e) XRD spectra of raw biomass.

hydrochars as solid biofuels, are presented in the Supplementary Material (Section 2, Fig. S1). HTC has also been used in other studies as an energy-efficient method for producing biochar from wet feedstocks. Although HTC produces less char than conventional pyrolysis [36], the hydrochar produced generally has a higher energy density than pyrolytic biochar, while pyrolytic biochar has a higher energy yield. In addition, a lower activation energy is required for HTC [37].

The properties of the hydrochar are improved by the synergistic effects that occur when oil cakes and SS are combined, which is due to an improved Maillard reaction [25], in which insoluble solids are formed from the sugars and proteins of the feedstocks (SS and oil cakes), which increase the organic and carbon retention in the hydrochar. The improvements are reflected in higher carbon content, higher calorific value, higher hydrochar yield, higher energy density, lower ash content, resulting in improved biochar-like properties, higher thermal stability and higher carbon sequestration potential, improved nutrient content, resulting in more balanced nutrient profiles (including nitrogen, phosphorus and potassium), the formation of stable carbon structures, greater porosity, surface area and reactivity, resulting in increased adsorption capacity and better catalytic properties.

The additional interactions between the specific components of the feedstocks also result from the different reactivities and thermal stabilities of the materials [38]. Furthermore, the inorganic salts and minerals in SS can have a catalytic effect on the carbonization process. The above-mentioned synergistic effects have also been observed in the co-HTC of SS with agricultural waste [39], or in the co-HTC of lignite and industrial biowaste [38].

Elemental analysis (Fig. 1d) revealed the highest C content in the HC hydrochar (59.81 wt%), followed by PC (53.68 wt%) and SS hydrochar, which had the lowest C content (36.89 wt%). The PC hydrochar contained a considerable amount of N (10.53 wt%), which was lower in the other hydrochar types. The content of sulphur (S) in the hydrochars was less than 1.6 wt%. Similar to this study, an increase in C content was observed when the SS was mixed with lignocellulosic materials such as corn stalks [40] or manure [16].

The H/C atomic ratio (Fig. 1e) of the hydrochars decreased compared to the raw samples, and lower ratios were observed for hydrochars from the co-HTC process than for hydrochars from the mono-carbonization process. The same applies to the O/C atomic ratios. Lower H/C and O/C ratios indicate a higher carbon content, and are typically associated with better fuel quality, as they indicate more carbon available for combustion [32]. The lowest H/C ratios for the mixtures of oil cakes and SS were observed at a mixing ratio of 1:3. The H/C and O/C ratios of the hydrochars from the co-HTC of SS and oil cakes are comparable to those of hydrochars from a mixture of SS with cellulose [17] or sawdust [25]. In contrast, slightly lower values were found for mono-HTC from olive pulp and other oil cakes (Table 1).

The presence of the above-mentioned elements and their characteristic bonds such as C–C, C–H_x, N–H, C–N, C=O etc. on the surface of the hydrochars was confirmed by FTIR analysis (Fig. 2a and b). The FTIR spectra of the hydrochars showed peaks for aromatic (C=C) and aliphatic (C–H_x) bonds, as well as for C=O and C–N groups, which became stronger and sharper after HTC treatment, indicating that aromatic compounds were formed during the carbonization [33]. The differences were also observed in the peaks of the hydroxyl groups (OH). The changes in the mass ratio of the feedstocks had relatively little effect on the FTIR spectra, as the spectra of the hydrochars were quite similar. Changes in the peaks for the phosphate (P–O) and silicate groups (Si–O), as well as metal oxides (X–O), can also be observed in the spectra of SS and its hydrochars. The PC, HC and their hydrochars showed FTIR profiles similar to other lignocellulosic materials.

3.1.2. Results of solid-state ¹³C NMR spectroscopy

Despite the complexity of the lignocellulosic biomass [41] and the fact that the spectra were not separated, the ¹³C CP MAS NMR spectra showed considerable differences in their composition. Extensive studies

of lignocellulosic samples by solid-state NMR spectroscopy in recent decades have revealed the main characteristic functional groups of lignocellulosic compounds and the spectral regions in which their protons and carbons resonate [42]. The aromatic lignocellulosic carbons exhibit ¹³C NMR signals in the spectral range between 110 and 165 ppm, while the signals of the saturated carbons are found in the range of 0–110 ppm [43] (see Table 2, Fig. 3a and Fig. S2).

The analysed samples contained a higher proportion of aliphatic and a lower proportion of aromatic compounds. The highest amounts of carbons of the NCH and OCH₃ groups were present in the raw PC, HC and SS samples, while the hydrochars contained a significantly lower proportion of NCH and OCH₃ carbons.

The most exposed peaks, observed between 165 and 190 ppm, were assigned to the carbon atoms of the carboxyl and -N–C=O groups of lignin, hemicellulose, polypeptides, proteins, and amino and carboxylic acids. The results show that the mono-carbonization of the PC, HC and SS samples led to a significant intensity of reduction of the corresponding carbon atoms. In addition, a higher content of aromatic C and C–O groups was observed after the HTC reaction. A high treatment temperature during HTC resulted in a lower content of cellulose carbons resonating in the spectral range 57–108 ppm [44]. The spectra were not resolved sufficiently; therefore, it was not possible to distinguish the signal at 55 ppm, which was assigned to the methoxy carbons of lignin. The integrated peak areas of the aliphatic carbons in the mixed samples showed a lower amount of all functional groups, with the exception of the O–C–O group in the PC-SS 1:3 sample and the O-alkyl-C group in the HC-SS 1:3 sample. The assignment and chemical composition of the analysed samples are consistent with the previously published data on similar raw materials and their hydrochars [45].

3.1.3. The content of nutrients

The content of minerals, i.e. macro- and micronutrients, in hydrochar determines its potential for agricultural utilisation. As shown in Fig. 1f, the hydrochars were rich in the macronutrients P, Ca, Mg and K. The P content increased after HTC treatment in the PC hydrochar (from 19,451 up to 35,199 mg/kg) and the SS hydrochar (from 20,898 up to 35,884 mg/kg), and decreased in the HC hydrochar (from 15,231 to 11,487 mg/kg). The combination of SS and PC led to a significant increase in P content when PC predominated in the hydrochar (3:1 ratio), while, for the 1:1 and 1:3 ratios, values were measured comparable to SS-hydrochar. On the other hand, the combination of HC and SS showed the highest P content when SS was predominant (ratio 1:3), although the other two ratios also resulted in higher P contents. This is due to the differences in chemical composition. High N, P and mineral contents are also characteristic of other oil cakes and their chars [2,33].

A detailed investigation of P speciation was performed by NMR analysis. The ³¹P NMR spectra of the oil cakes and their hydrochars analysed after NaOH-EDTA extraction are shown in Fig. 3b and Fig. S3, and the characteristic spectral regions, the corresponding phosphate groups and their proportions determined by previously described methods [45,46], are listed in Table 3. Most of the samples consist predominantly of orthophosphate, whereby the ratio of the feedstocks has no significant influence on the orthophosphate distribution. The hydrolysis, decarboxylation and polymerisation reactions that occur during HTC treatment are responsible for the hydrolysis of polyphosphate to inorganic orthophosphate, which predominates after HTC treatment [47]. Nobre et al. [31] reported that P can also react with the metal cations and precipitate on the surface of the hydrochar as P salts. Since the raw SS contained high levels of Ca and Fe, this could also occur in the present study. However, based on the integrated phosphorus peak intensities in the spectra, some differences in the orthophosphate distribution can be recognised, which can be attributed to the different origin and thermal treatment of the samples. Significant differences between the composition of the PC, HC and SS raw samples were found in the spectral range of the monoesters. In addition, due to the HTC treatment of the raw samples, the highest pyrophosphate content was

Table 2
¹³C CP MAS NMR assignments and percentages of functional groups of the analysed samples.

Sample	Alkyl-C (0–45 ppm)/% ^a	NCH/OCH ₃ (45–65 ppm)/ % ^a	O-Alkyl C (65–90 ppm)/% ^a	O–C–O (90–110 ppm)/% ^a	Aromatic-C (110–145 ppm)/ % ^a	Aromatic C–O (145–165 ppm)/ % ^a	COO/N–C=O (165–190 ppm)/ % ^a	Total Al–C (0–110 ppm)/ % ^a	Total Ar–C (110–165 ppm)/ % ^a
PC raw	34.45	21.77	19.04	2.34	4.14	0.90	17.36	77.60	5.04
SS raw	36.03	18.80	18.34	3.32	8.60	0.67	14.24	76.49	9.27
HC raw	14.71	17.83	42.33	10.25	7.38	1.21	6.29	85.12	8.59
PC	55.04	6.02	6.02	1.27	25.81	2.44	3.40	68.35	28.25
SS	40.66	4.82	2.42	3.30	39.40	5.72	3.68	51.20	45.12
HC	43.03	8.31	5.93	3.71	33.35	5.10	0.57	60.98	38.43
PC-SS 1:1	48.36	5.71	5.05	2.24	31.07	4.07	3.50	61.36	35.14
PC-SS 1:3	45.55	5.31	3.46	2.77	34.77	4.70	3.44	57.09	39.47
PC-SS 3:1	51.56	5.92	6.46	1.94	28.09	2.94	3.09	65.88	31.03
HC-SS 1:1	48.45	7.57	1.02	4.33	33.09	4.09	1.45	61.37	37.18
HC-SS 1:3	42.35	6.37	8.78	4.02	31.73	4.47	2.28	61.52	36.20
HC-SS 3:1	47.40	6.98	5.24	3.72	32.09	3.61	0.96	63.34	35.70

^a Calculated from the integrated proton peak intensities.

found in the HC hydrochar, while no pyrophosphate was present at all in the SS hydrochar. Interesting results were observed in the phosphate distribution in the hydrochars obtained from co-HTC, which generally had a significantly lower pyrophosphate content than PC and HC hydrochar. In the mixtures, the highest pyrophosphate proton content was found in the HC-SS 3:1 sample, while no pyrophosphate was found in the HC-SS 1:1 and HC-SS 1:3 samples.

3.1.4. Structure determination by XRD analysis

The changes in the chemical structure, i.e., the crystallinity of the materials due to HTC and the effects of the mass ratio of the feedstocks on the crystallinity are shown in the XRD spectra of the raw materials and hydrochars in Fig. 2c–e.

The raw PC and HC showed two broad peaks typical of lignocellulosic material [48], the first at 9°, corresponding to crystallographic cellulose [34], and the second at 20°, corresponding to sp³ hybridised carbon of amorphous components such as lignin [49]. A broad diffraction peak indicates low crystallinity, and is assigned to the starch and cellulose structures of the oil cakes [9]. For the raw SS these two peaks were less pronounced, while the peaks observed at 25°, 27°, 31°, 33°, 46° and 60°, corresponding to phosphates and silicates, were more intense.

HTC treatment of oil cake leads to the destruction of the amorphous and crystalline structures of hemicellulose and lignin contents [50], followed by the decomposition of the microcrystalline structure. Therefore, the above peaks become lower, and, at the same time, new sharp peaks appear [7], such as in the spectra of the PC hydrochar, indicating the increased crystallinity after HTC treatment. In the PC hydrochar, the peaks of K and Mg phosphate were more intense in the 2θ range between 25° and 35°, while, in the HC hydrochar, two additional sharp peaks were observed, one at 54° and another at 61°, reflecting Ca and Mg phosphates (Ca, Mg)₃(PO₄)₂.

The SS hydrochar showed three strong and sharp peaks at 21°, 24°, and 27°, as well as several other small peaks above 30° specific to ash minerals. The peak at 27° reflects the graphite structure [50]. The diffraction peaks at 21° and 24° represent the crystalline phase of silica, i.e. quartz, while the other, small peaks represent the potassium, magnesium and calcium phosphates and silicates (SiO₂, MgSiO₃), metal silicates and metal oxides (Fe₂O₃) deposited on the surface of the hydrochar during HTC [51].

The PC and HC hydrochars were more amorphous than the SS hydrochar, while mixtures showed characteristics of both materials, reflecting the coexistence of crystalline and amorphous phases in the

hydrochars. The higher the proportion of oil cake in the hydrochar, the more the spectra resembled the spectra of hydrochar made from pure oil cake. The spectra of the hydrochars from the HC differed from those of the PC mixtures in a similar way to those of the hydrochars from pure oil cakes.

3.1.5. Heavy metal content

A high Fe content was found in the hydrochars from SS (Fig. 1f). The high Fe content in the SS is a consequence of the addition of coagulants (FeCl₃) during wastewater treatment. Considerable amounts of Zn, Cu, Cr and Ni were also found in the SS samples, while the Cd content was low (Table S3). The PC and HC hydrochars contained low concentrations of heavy metals (except Zn), but were rich in Mg and Ca. In contrast, a considerable amount of Pb was detected in the SS-derived hydrochars. The quality of the hydrochar is related closely to the heavy metal content. The heavy metal values of the obtained hydrochars exceeded the limits of the EBC Standard for biochar for agricultural purposes, but the obtained hydrochar could be used as a raw material in industry, as there are no limits for such use [52]. The problem of high heavy metal content in SS hydrochars is well known, and has been identified in many previous studies [16], although researchers are still looking for an efficient solution. For example, a leaching process can be applied to reduce the heavy metal content in sewage sludge before HTC treatment. However, the co-HTC of oil cake with SS at the highest mass ratio (3:1) reduced the content of heavy metals compared to that in the SS-hydrochar, but the levels did not fall below the EBC limits in most cases. The content of heavy metals in the hydrochars obtained from the mono-carbonization of oil cakes (with the exception of PC hydrochar in the case of Zn) was below the limits.

3.1.6. Organic compounds

The organic compounds identified by the GC-MS analysis in the liquid extracts of the hydrochar include various fatty acids (hexadecanoic, octadecanoic, octadecadienoic, octadecenoic i.e., oleic acid) and their esters, derived mainly from the degradation of lipids and proteins of the oil cake and SS (Table S4). Amides (9-octadecanamide, oleic diethanolamide), ketones (2-pentadecanone, cyclopentadecanone, 2-hexadecanone), alkenes (hexadecene, heptadecene, eicosene...), aldehydes (octadecadienal) and cycloalkanes (cyclohexadecane, cyclopentadecane, cycloheptadecane) were identified in addition. Alkenes, aldehydes, ketones and organic acids are products of the degradation of cellulose and hemicellulose [53]. Interestingly, hexadecenoic acid (methyl ester) was only found in the HC samples and SS, but not in the

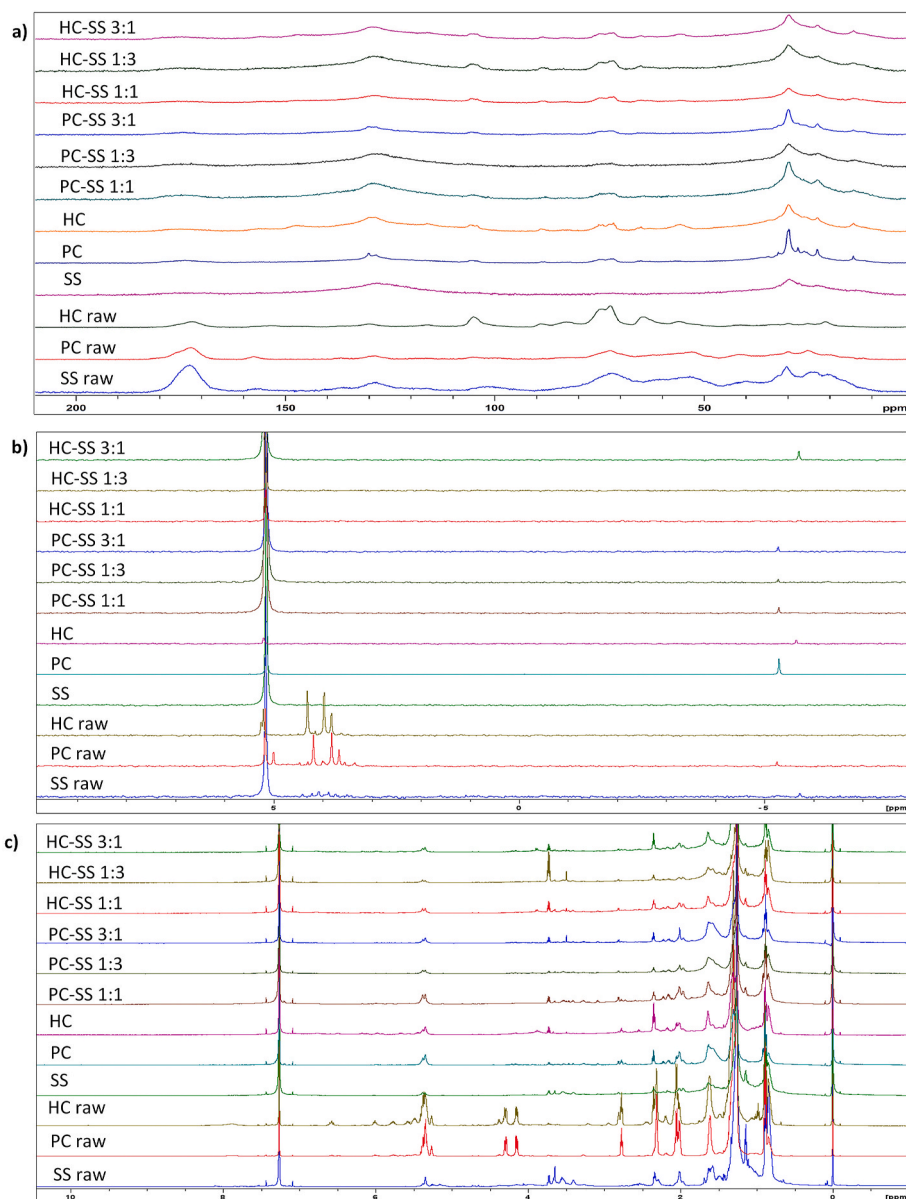


Fig. 3. a) ^{13}C NMR spectra b) ^{31}P NMR spectra, and c) ^1H NMR spectra of raw samples and hydrochars (in D_2O for ^{31}P and ^{13}C NMR spectra, and in CDCl_3 for ^1H NMR spectra).

PC samples, while eicosene was only present in the SS, PC and their mixtures. 2-methoxy-4-propyl phenol and 4-ethyl-2-methoxy-phenol, the representatives of phenols, as well as pyridines, piperidines, and pyrrolidines, the representatives of heterocyclic organic compounds with nitrogen atom in the ring, were detected mainly in the PC and HC samples and their mixtures with SS. The presence of aromatic heterocyclic N-containing organic compounds results from the decomposition of proteins and lignin, via reactions of hydrolysis, decarboxylation, deamination, condensation, polymerisation and aromatisation [54]. Similar compounds to those found in this study have been identified in biocrude produced from algae using HTC [55].

In addition to the organic compounds, the content of polycyclic aromatic hydrocarbons (PAHs), pollutants that can arise during HTC and are known to be toxic or carcinogenic pollutants, was determined in the hydrochars (Table S3). With the exception of the PC and PC-SS 3:1 samples the PAHs concentrations were relatively low, and also below the limits of the EBC Standard (6 mg/kg d.m.). The PC hydrochar contained 2.1 mg/kg PAHs, HC 0.05 mg/kg and SS 0.64 mg/kg. The values for the mixtures were between these values, whereby a higher PAHs content

was only found in the PC mixtures. In general, two- and three-ring PAHs dominated, while four- and five-ring PAHs were found in the mixtures with a higher oil cake content. PAHs can form mainly at higher temperatures when condensation and decarboxylation reactions take place and free radicals are formed, which promote the formation of PAHs and lead to the formation of aliphatic and aromatic compounds, i.e., amorphous hydrochar [56].

The gravimetrically determined fat content in the hydrochars obtained from the mono-carbonization was higher than in the corresponding raw samples (Table S3). Hydrochars from the PC mixtures had a higher fat content (6–17 wt%) than that of the HC mixtures (4–6 wt%). After extraction with a water-methanol-chloroform mixture, the fatty acids and glycerides in the hydrochars were also quantified by NMR analysis according to previously established equations [42]. The proton NMR data revealed several differences in the composition of the raw samples and their hydrochars (Table 4, Fig. 3c and Figs. S4 and S5). The raw PC and HC contained a high proportion of triglycerides (~90 %) and a low proportion of diglycerides and fatty acids (Table S5). All the samples contained a lower amount of linolenic acid than linoleic acid. In

Table 3
³¹P NMR assignments and percentages of phosphates in the analysed samples.

Sample	Orthophosphate (~5.20 ppm)/% ^a	Monoester (3.15–5.10 ppm)/ % ^a	Pyrophosphate (~5.60 ppm)/% ^a
SS raw	87.57	11.08	1.37
PC raw	25.09	72.76	2.15
HC raw	20.05	79.95	–
SS	100	–	–
PC	80.12	–	19.88
HC	64.35	–	35.65
PC-SS	99.45	–	0.55
1:1			
PC-SS	99.63	–	0.37
1:3			
PC-SS	98.85	–	1.15
3:1			
HC-SS	100	–	–
1:1			
HC-SS	100	–	–
1:3			
HC-SS	98.04	–	1.86
3:1			

^a Calculated from integrated proton peak intensities.

Table 4
Percentages of fatty acids and acyl groups found in the lipids extracted from raw oil cakes, SS and hydrochars.

Sample	L _n ^a (%)	L ^a (%)	U ^a (%)	M _U ^a (%)	S + M ^a (%)
SS raw	4.78	35.28	41.08	1.02	58.92
PC raw	4.77	31.14	36.29	0.38	63.71
HC raw	8.58	28.25	40.48	3.65	59.52
SS	5.98	29.17	37.57	2.42	62.43
PC	6.24	20.57	30.01	3.20	69.99
HC	10.52	27.53	43.03	4.93	56.97
PC-SS 1:1	6.84	18.86	35.60	9.90	64.40
PC-SS 1:3	13.47	15.77	32.16	2.92	67.84
PC-SS 3:1	10.76	12.91	29.78	6.09	70.22
HC-SS 1:1	8.67	18.04	28.74	2.03	71.26
HC-SS 1:3	8.13	16.13	36.63	12.37	67.37
HC-SS 3:1	7.65	10.75	33.84	15.44	66.16

^a L_n (linolenic acid), L (linoleic acid), U (unsaturated), M_U (monounsaturated) and saturated + modified (S + M) acyl group.

general, the hydrochars contained a higher proportion of mono-unsaturated fatty acids and a lower proportion of linoleic acid. Mono-carbonization resulted in a higher content of unsaturated fatty acids in the HC and SS samples, while the PC samples showed a slightly different behaviour during the mono-carbonization process. A similar distribution of fatty acid species is characteristic for the lipid extracts of soya bean and canola oil cakes [42].

3.2. Chemical composition of the liquid fractions

3.2.1. Inorganic compounds and minerals

The chemical composition of the liquid fractions (LFs) from the HTC experiments is shown in Fig. 4 and Table S6. After HTC most of the nitrogen was found in the LF. High levels of total nitrogen (TN) and ammonium nitrogen (NH₄-N) were found in the LFs, especially in those of PC, followed by HC, with the highest values measured in the PC and PC-SS 3:1 sample (Fig. 4a). This is consistent with the N content in the raw materials, as the raw PC had the highest N content. The distribution of N in the HTC products depends mainly on the treatment temperature and the hydrolysis reaction, while the reaction time plays a minor role [57]. During hydrolysis, ammonia-N and organic-N are released from biomass proteins and (aromatic) N compounds are formed [58]. Thus, N can be present in the LFs in both forms, with organic-N dominating at lower processing temperatures and ammonium-N dominating at higher temperatures [59].

In terms of P content, the LFs of the oil cakes were rich in P, while the samples obtained from co-HTC with SS contained less P (Fig. 5b). It appears that co-HTC with SS retains P in the hydrochars, as the hydrochars obtained from co-HTC have higher P content than hydrochars from mono-carbonization. Significant P contents in the LFs are a consequence of the presence of orthophosphate and polyphosphates in the raw samples [47]. Significantly lower P and N contents were found in the process water from olive pomace [60], while SS [61] and the mixtures of SS with municipal organic waste yielded comparable values [58].

The content of the macronutrients Ca, Mg and K varied, depending on feedstocks and their mass ratios (Fig. 4c), with the highest concentrations observed for K (727–2856 mg/L). The LF obtained from HC contained more Mg and Ca than the LF obtained from PC, while the latter contained more K. The same applies to the LFs obtained from the co-HTC experiments. The LF from SS contained relatively low amounts of K and Mg. Considerable amounts of Fe were found in all samples with SS as a feedstock, while the content of other heavy metals was low (Table S6). These LFs also contained higher concentrations of Cr than the other samples. The content of Cd and Pb in the samples was negligible. The trace elements Cu and Zn were also detected, which are important micronutrients for plant growth.

The pH of the LFs (Table S6) was basic, with the exception of two LFs obtained from HC (sample HC and HC-SS 3:1), as the values ranged between 7.09 and 7.52. The basic pH indicates the presence of alkaline compounds in the LFs and the release of ammonia-N during HTC treatment, while the acidic pH reflects the presence and higher content of organic acids [58]. This is consistent with the results of other chemical analyses, as the two previously mentioned samples had the lowest content of NH₄-N and the highest content of volatile fatty acids (see Fig. 1d). Alkaline pH values in the treatment of SS by HTC have also been observed in other studies [57]. Conductivity, reflecting the presence of salts and minerals in the LFs, ranged from 13.57 to 30.63 mS/cm, with the highest values measured in the PC samples (Table S6).

Due to their high nutrient and organic matter content, the LFs and hydrochars from this study have the potential to be used in agriculture as soil conditioners. The performance of the HTC products in germination tests with cress seeds is shown in the Supplementary Material (Section 4.2., Fig. S6). Both the LFs and the hydrochars delivered encouraging results. The LFs have also been shown to be successful in soil remediation in previous studies [62]. In addition, the recovery of nutrients from LFs by processes such as chemical treatment (struvite precipitation) and membrane separation is a current research focus of many studies [10].

3.2.2. Organic compounds

Oil cakes contain between 10 and 25 wt% lignin, 15–40 wt% cellulose and 20–60 wt% hemicellulose [2], suggesting that they can be a good source for the extraction of valuable organic compounds, especially aromatic phenols, esters and ethers, if a suitable thermochemical technology is used for their extraction or conversion [63]. High values of chemical oxygen demand (COD) and total organic carbon (TOC) were detected in the LFs (Fig. 4e), indicating a high organic matter content in the samples. Different organic compounds and Maillard products, such as organic acids, alkenes, aldehydes, furans, pyrroles, pyrazines, pyridines and phenols, can be identified in the LFs as products or intermediates of HTC reactions [57], with sugars, alcohols, aromatics and organic acids being detected the most frequently [64]. The TOC content varied between 14,889 and 42,199 mg/L, with the highest values found in the LFs of PC, followed by HC and SS LFs. The TOC values of the LFs (with the exception of the PC sample) were in the range of the LF reported for SS (4000–28,000 mg/L) [65]. The COD values showed the same trend as the TOC values. In general, the COD values of the LFs of HTC-treated biomass varied in a wide range, from 20 to 100 g/L [66]. For the samples obtained from the co-HTC of HC and SS, the values ranged from 50,954 to 53,214 mg/L, while, for the combination of PC and SS, they ranged from 60,466 to 81,187 mg/L. These values were in

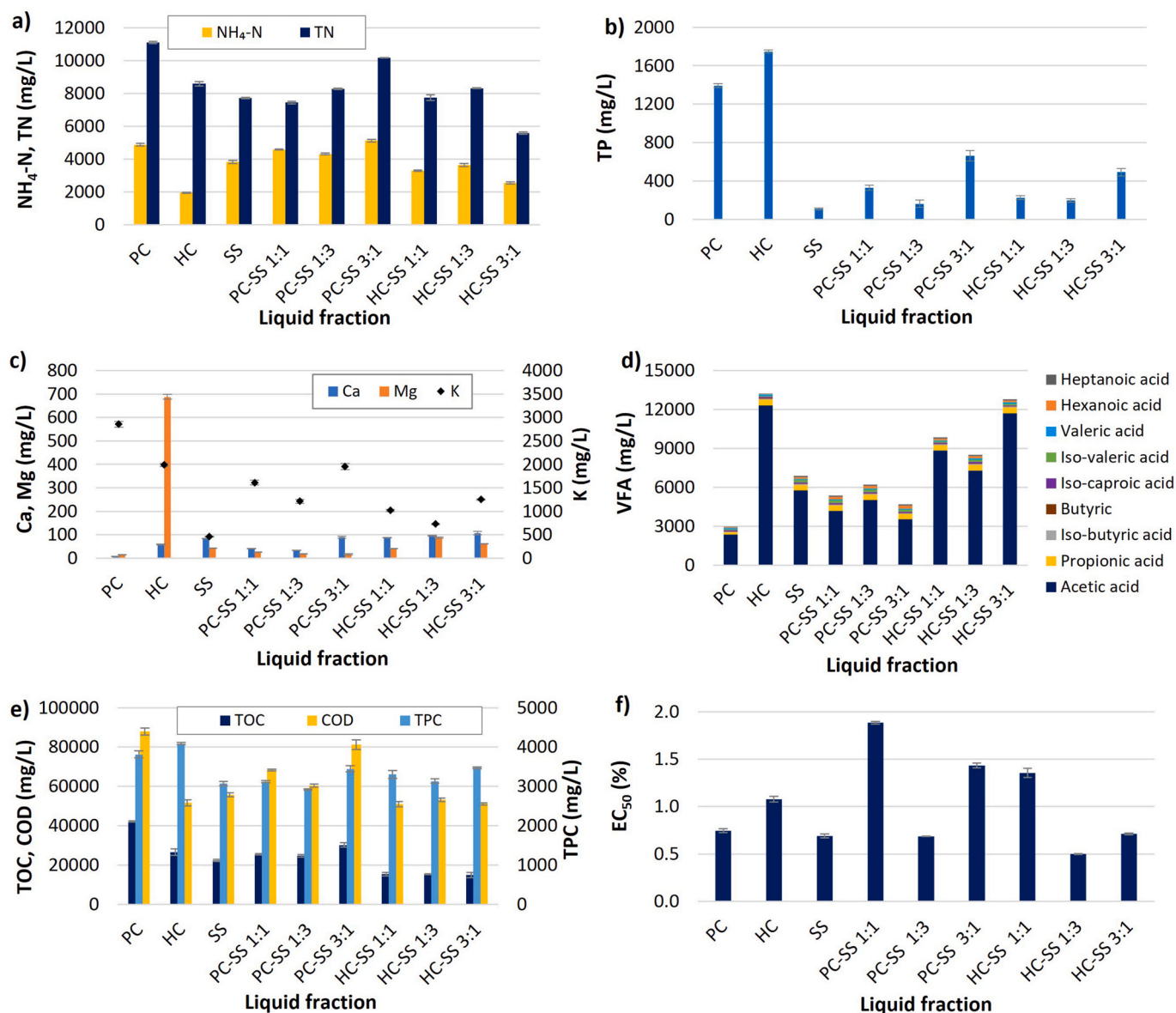


Fig. 4. The content of: a) NH₄-N and TN, b) TP, c) Ca, Mg and K, d) VFAs, and e) TOC, COD and TPC in the LFs. The results of the toxicity test with the microorganism *Daphnia magna* are shown in graph f.

the same range reported for the LFs of SS treated at a slightly lower temperature and shorter residence time [67].

The GC-MS identification revealed that most LFs contained volatile fatty acids (acetic acid, propionic acid), 2-butanone and various pyrimidine, pyrazine and pyrrolidine compounds (Table S7). The LFs of the oil cakes had a similar composition, while the LFs of the SS were different. The proportion of oil cake in the mixture influenced the organic components in the LFs. The LFs obtained from the combination of PC and SS were rich in 2-butanone, 2-methyl-pyrimidine, 2,6-dimethyl-pyrazine and 1-acetylpyrrolidine in addition to volatile fatty acids (VFA). The combination of SS and HC yielded LFs rich in volatile fatty acids, 2-methoxyphenol (guaiacol), 2-methyl-2-cyclopenten-1-one, 1-acetyl pyrrolidine, N-acetylenediamine, ethyl- and 2,6-dimethyl pyrazine, 2-methyl pyrimidine, 2 aziridinyethyl amine and others. Such compounds have been detected in the LFs of SS [58], digested SS [57] and cow manure [64], as well as in waste-derived fuels [31].

The detailed analysis of the volatile fatty acids revealed that the LFs obtained from HC and its combination with SS contained a higher proportion of VFAs (Fig. 4d) than the PC liquids. Almost double the amount

of volatile fatty acids was measured in the HC-SS 3:1 sample (12,811 mg/L) than in the PC-SS 3:1 sample (4686 mg/L). The proportion of acetic acid was the highest, followed by propionic, iso-valeric, hexanoic, heptanoic and iso-caproic acid. High concentrations of acetic acid, one of the main products of hydrolysis, were also found in the LFs derived from lignocellulosic biomass [68], with a distribution of VFA species comparable to that in the present study [69]. In addition to the above-mentioned acids, other VFAs, such as lactic and formic acids, can be formed during HTC under alkaline conditions by the reaction of reverse aldol condensation [70].

The total phenolic compounds (TPC) in the LFs determined by the Folin-Ciocalteu method varied between 2916 mg/L and 4080 mg/L (Fig. 4e), with the HC liquids showing slightly higher values. The co-HTC of oil cakes with SS led to a decrease in TPC content compared to mono-carbonization. The values were almost in the same range as the values of the LF of HTC-treated olive pomace [71], which proved to be a promising source for the extraction of phenolic compounds. Few data are available on the use of other oil cakes for this purpose, although it is known that oil cakes are rich in phenolic compounds [72]. Phenolic

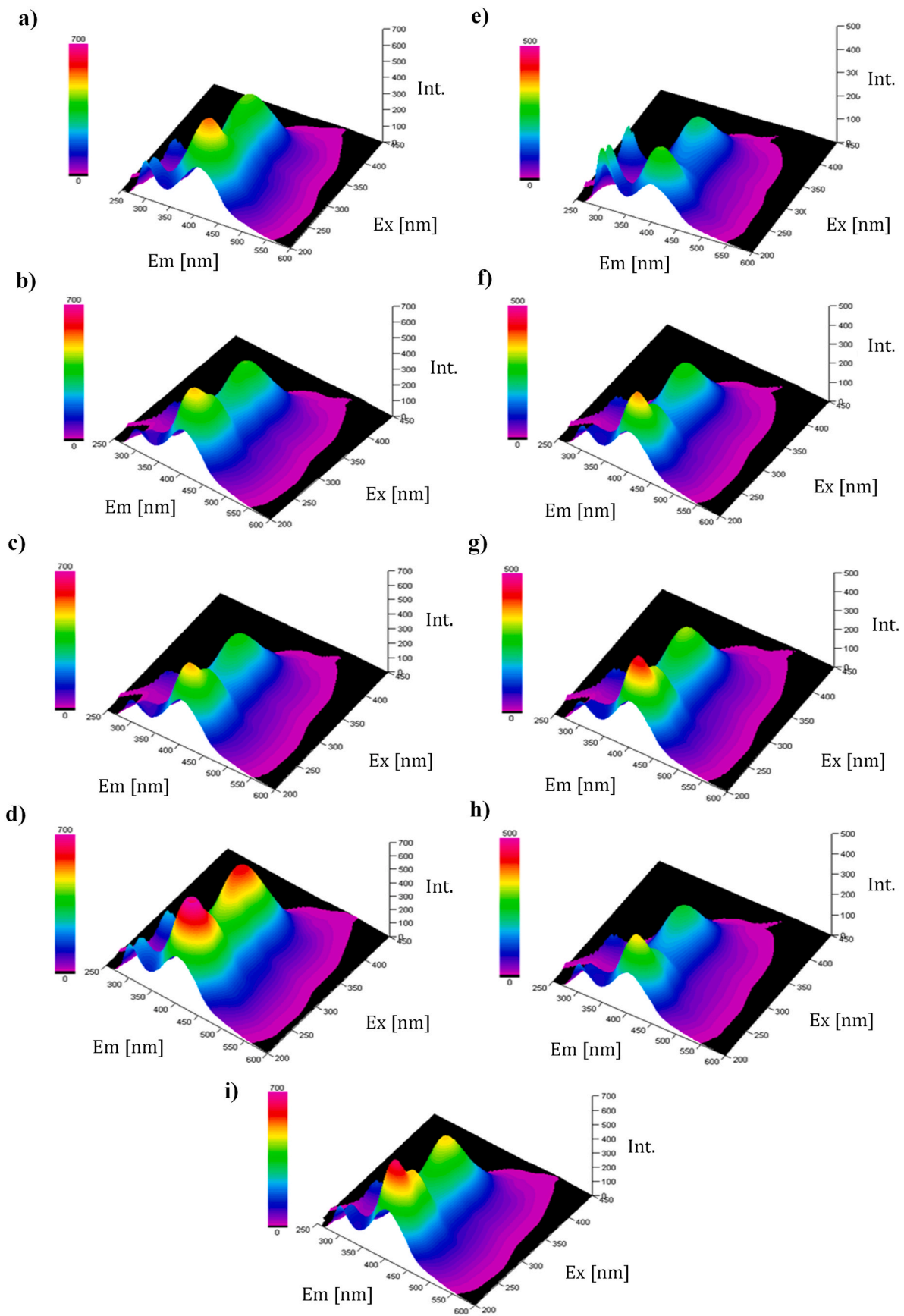


Fig. 5. The 3D-EEM spectra of liquid fractions: a) PC, b) PC-SS 1:1, c) PC-SS 1:3, d) PC-SS 3:1, e) HC, f) HC-SS 1:1, g) HC-SS 1:3, h) HC-SS 3:1, and i) SS.

compounds that can be present in the LFs of HTC-treated biomass include phenol, catechol, guaiacol and syringol [73], which are formed during the hydrolysis and dealkylation of lignin [64], with guaiacol, together with catechol, being the most abundant aromatic compounds in the LFs. The higher content of phenols in HC liquids suggests that HC contains a higher lignin content than PC. Phenolic compounds are used widely in industry, medicine and flavour chemistry, and are, therefore, in great demand.

The presence of the aforementioned organic compounds in the LFs can be explained by the reaction pathways that characterize the transformation of biomass in aqueous media close to the supercritical state [74]. Since the raw materials used in this study were composed of lignocellulosic and non-lignocellulosic components (proteins, fats and minerals), the HTC reaction pathways are complex. The degradation of proteins leads to the formation of protein-derived intermediates, e.g. Maillard reaction products, which lead to the accumulation of N-containing compounds, mainly amino acids and organic acids, amines, nitriles, hydrazines and ammonium nitrogen [51]. Lignin depolymerises to aromatic oligomers, which are further hydrolysed to phenols and methoxylated benzenes, which polymerise to aromatic compounds [53]. Hemicellulose and cellulose hydrolyse to oligosaccharides and monosaccharides (glucose), which isomerise to form fructose, which then dehydrates to furfural derivatives (furfural and hydroxymethylfurfural-HMF), which polymerise to char [23]. In addition, various organic acids can be formed from monosaccharides. Lipids are hydrolysed to volatile fatty acids, aldehydes and unsaturated intermediates, which are decarboxylated to form alkanes and alkenes [75]. Inorganic substances form ash, inorganic salts, alkali metals and alkaline earth metals. The protein-like and microbial substances are converted into humic-like compounds, i.e., heterocyclic amines, by Maillard and Mannich reactions between the proteins, carbohydrates and lignin-derived phenols [10]. The occurrence of the Maillard reaction between amino acids and reducing sugars also influences the colour, odour and viscosity of the LF [35].

The 3D-EEM spectra (Fig. 5) showed a strong influence of the mass ratio of the feedstocks on the organic composition of the LFs, especially humic-like substances and aromatic proteins. All the samples were rich in fulvic acid-like components, represented by peaks in the excitation/emission (Ex/Em) range of 200–250/380–600 nm, and in the humic acid-like components in the Ex/Em range of 250–450/380–600 nm. Lower intensities were found for type I aromatic proteins (Ex/Em range 200–250/250–330 nm), type II aromatic proteins (Ex/Em range 200–250/330–380 nm) and soluble microbial products (SMP) originating from the SS (Ex/Em range 250–450/250–380). This indicates that most of the proteins were converted to fulvic acid and humic acid-like compounds by Maillard and Mannich reactions. The LFs of PC and its combinations with SS showed peaks with higher intensity (especially those of fulvic substances and humic-like substances) than those of HC and its mixtures with SS. The higher the PC content, the higher the intensities of fulvic substances and humic-like substances, while a high SS content resulted in a lower content of aromatic proteins and SMP. The most intense peaks for aromatic proteins (of both types) were observed in the LFs from the mono-carbonization of oil cakes.

The above observations were consistent with the results of the GC-MS, TOC and COD analyses. The content of humic-like substances in the liquids is also related to the pH conditions during the HTC. Acidic conditions promote the decomposition and dissolution of organic biomass and the formation of humic acid precursors (saccharides, furans, organic acids and phenols), while alkaline conditions promote the production of humic acids from the above-mentioned precursors [70]. This also applies to the present study. Humic and fulvic substances were otherwise also found in the LFs of sugarcane waste biomass [76] and in SS combinations with wheat straw and rice husks [12]. Since humic acids play an important role in soil remediation, the LFs could serve as a valuable source for their recovery, especially those obtained from PC and their mixtures.

3.2.3. The toxicity of the liquid fractions

The use of LF from HTC is often neglected in practice, as LF has a complex chemical composition, and can be harmful to the environment due to its high content of organic substances and nutrients, as well as its unfavourable pH value [14].

Therefore, the LFs were tested for their toxicity to freshwater microorganisms (*Daphnia magna* species) by determining the concentration of the LF that causes toxic effects in 50 % of the test population of *Daphnia magna* microorganisms after 24 h of exposure (EC₅₀). The LFs obtained were highly toxic, as they influenced microorganisms even at very low concentrations (Fig. 4f). The lower the EC₅₀ value, the higher the inhibitory effect. For example, the LF of the samples PC, SS and PC-SS 1:3 was already toxic at concentrations below 1 %. The HC-SS 1:3 and HC-SS 3:1 samples exhibited similar toxicity, while all the other LFs had EC₅₀ values between 1 and 2 %. Interestingly, co-HTC did not reduce the toxicity of the LFs.

The EC₅₀ values are comparable to the values for LFs from the co-HTC of SS with cheese whey in a previous study [77]. The toxic effects of LFs were also observed in other studies. For example, in one of the studies, a strong inhibitory effect of LFs was observed on anaerobic microorganisms due to the high NH₃-N content [78]. Similarly, undiluted LF from HTC treated microalgae was toxic to marine bacteria (EC₅₀ = 1.8 %), while a 20 % dilution was suitable for the growth of microalgae [79]. On the other hand, the process water of vinasse and sugarcane bagasse was not toxic to marine microorganisms [80]. High toxicity of LF to *Artemia salina* and *Paramecium caudatum* was also reported, with dilution ratios ensuring the death of no more than 50 % of the organisms, ranging from 45 to 142 [66]. In addition to microorganisms, the LF from SS was also toxic to the freshwater vascular plant *Lemna minor* [67]. The toxic effects observed in these studies were attributed to various reasons, such as high levels of dissolved organic compounds [81], including various hydrocarbons, furfural and HMF in the LFs [82], high salinity and high levels of heavy metals [66].

4. Conclusions

The co-HTC of oil cakes with SS proved to be successful, as the fuel properties of the hydrochars were improved significantly and synergistic effects were observed between the raw materials.

The higher the oil cake content, the better the chemical properties of the hydrochar (including higher C content, energy yield, calorific value and lower ash content), which is a consequence of the better fuel properties of oil cakes than those of SS. Co-HTC with HC resulted in better quality fuels than co-HTC with PC. The hydrochars were rich in aliphatic compounds, unsaturated fatty acids and nutrients, with P mainly in the form of orthophosphate. They contained relatively high amounts of heavy metals, especially Fe, which originated from the SS, while the PAH content was low.

The LFs had a high content of organic components such as TPC, VFA (especially acetic acid) and humic-like substances, as well as a relatively low P and high N content. The LFs were toxic to the freshwater microorganisms even at very high dilutions, but other chemical properties and the germination test indicated that they could be used as N fertilisers in agriculture (like the hydrochars). The toxicity of the LFs raises concerns about its impact on the environment, indicating the need for further research to minimise potential harm. Further studies should also discuss the scalability and economic feasibility of hydrothermal co-carbonization of SS and oil cake for large-scale application, as well as the impact on sustainability, energy efficiency and carbon footprint, as these are crucial aspects for practical implementation.

CRedit authorship contribution statement

Aleksandra Petrović: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Tjaša Cencić Predikaka:** Resources, Methodology, Data curation. **Jelena**

Parlov Vuković: Writing – original draft, Visualization, Methodology, Formal analysis, Data curation. **Tomislav Jednačak:** Resources, Methodology, Formal analysis. **Silvo Hribernik:** Methodology, Investigation, Formal analysis. **Sabina Vohl:** Methodology, Investigation, Formal analysis. **Danijela Urbanc:** Writing – review & editing, Supervision, Resources. **Marina Tišma:** Writing – review & editing, Supervision, Resources. **Lidija Čuček:** Writing – review & editing, Validation, Supervision, Funding acquisition.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.energy.2024.132760>.

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