Improving the recovery of phenolic compounds from spent coffee grounds by using hydrothermal delignification coupled with ultrasound assisted extraction.

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Abstract

This study focuses on the maximization of the phenolic compounds of spent coffee grounds, by coupling hydrothermal delignification with ultrasonic assisted extraction. Temperatures of 200°C, 230 °C and 260 °C were applied for hydrothermal treatment for 1h and 3h. Produced hydrochars contain high values of fuel ratio (0.35 - 0.69) compared to raw feedstock (0.20). The increment of the reaction severity decreases the energy yield from 95.23 % to 82.99 %. After the hydrothermal treatment, the total phenolic content (TPC of the process water), determined relatively to a gallic acid standard (GAE), was found to be in a similar range for all process conditions (9.52 – 8.07 mg GAE / mg of dry sample). Using methanol as a solvent into produced dry hydrochars during ultrasonic assisted extraction reveals the highest values of TPC (20.33 – 11.66 mg GAE/ mg of dry sample).

1. Introduction

Coffee is one of the most popular beverages in the world. According to the International Coffee Organization [1], the world coffee consumption has been increased from 1.14 million tons to 9.5 million tons in the last years (2010-2018). Since the world, average population is expected to grow during the next years, also coffee production and consumption is going to increase as well. This makes it necessary to find a way to valorize the residues generated by instant coffee production, called exhausted or spent coffee grounds (SCG). SCG is the main waste of the coffee industry, obtained during the processing of roasted coffee powder in hot water or steam [2]. As reported by [3], SCG represents more than 90% of initial mass (on dry basis). SCG is a wet organic material with lignocellulosic structure [4], containing a high amount of valuable compounds, such as polysaccharides, proteins, lipids, aliphatic acids, alkaloids, tannins, polyphenols [5]. SCG is a residue with a high carbon content and a high calorific value (approx. 23 MJ/kg on dry basis) [6]. Due to its properties, some researchers have investigated the exploitation of SCG as a source of sugars [7], as an activated carbon precursor [8], and for biodiesel production [9]. Recently, bioactive compounds from SCG, especially phenolic compounds (PC), have attracted enormous interest in scientific community due to their positive effects on human health related to PC antioxidant activity. Some researchers have demonstrated that PC could potentially act against cancer, cardiovascular diseases, diabetes mellitus and could have an antimicrobial, antiallergenic and anti-inflammatory effects [10].

There are various methods to extract PC from residues, such as solid-liquid extraction (Soxhlet method) and simple extraction at low temperature [11], autohydrolysis (or thermal hydrolysis) [11–14] and Ultrasound Assisted Extraction (UAE) [15]. Solid-liquid extraction is very effective, but the use of organic solvents is not an environmentally friendly technique. In contrast, autohydrolysis (or thermal hydrolysis) is an alternative technology that does not require the use

of solvents. The reaction occurs in water between 120 °C to 200 °C and the extraction time is usually 10-50 min [2, 13]. Ballesteros [2] showed that PC extraction during autohydrolysis is highly influenced by temperature. The extraction of PC at about 200 °C is more effective than the extraction at lower temperature, as a consequence of the polarity of water as a solvent is decreased, due to the low dielectric constant at increased temperature [16].

On the other hand, UAE is considered a low-cost process, versatile in terms of solvents that are used, very fast, reproducible also on an industrial scale [15]. It requires low investment compared to other novel techniques e.g. supercritical fluid extraction (SFE) or pressurized solvent extraction [17]. Due to these advantages, UAE is one of the most often used method to extract PC from by-products [18]. UAE is a technique that can be used effectively to increase the mass transfer during solid-liquid extraction processes and is successfully used to obtain high-value compounds from food or plants [18]. The high efficiency of this process is due to the acoustic cavitation effect generated by ultrasonic waves.

Acoustic cavitation is the phenomenon of creation, expansion and implosive collapse of microbubbles in ultra-sound irradiated liquid. These bubbles in the liquid can grow and violent collapse to generate temperature of 5000 K and pressure of 50 MPa [17]. This change in temperature and pressure causes a potential of damaging and rupture of cell walls of biomass, which favors the release of bioactive compounds into the solvent [15, 17]. Another effective and eco-friendly way to extract phenols from biomass could be via Hydrothermal Carbonization (HTC).

HTC is a promising thermochemical process to convert wet biomass into a coal-like material, called hydrochar; and a liquid, rich in organic acids (acetic, formic, levulinic or lactic acid). HTC occurs in aqueous phase in a closed reactor at long residence time (1-12 h) and temperatures

respect to autohydrolysis (180-260°C). Water has an important role during HTC. It acts both as a reaction catalyst and as a solvent. Undoubtedly, produced hydrochar is a solid fuel, hydrochar, with high carbon content and high heating value (HHV, MJ/kg). A study carried out by Kim et al., [3] shows the possibility of using SCG for the production of renewable energy in the form of hydrochar by applying HTC. The results of their study indicate that hydrochar produced from SCG is an alternative fuel.

During HTC, phenols are formed by hydrolysis from lignin and other compounds, for example Tannines. Here, the increase in concentration of phenols in liquid (in mg/l) is mainly due to the hydrolysis of lignin [19]. Moreover, some evidence in literature revealed that the hydrothermal treatment favors the extraction of valuable phenols from the parent feedstock [20]. Because of the purpose of HTC in this study is the delignification of the initial feedstock, it is called hydrothermal delignification (HDL). Nowadays, most of the studies are focusing on the application of a standard technology to extract PC. However, as far as known to the authors, no one has yet investigated and coupled two different techniques, such as HDL and UAE to extract TPC, producing a valuable biofuel in the same process. The present work addresses this gap by studying the effect of HDL with energetic purposes and as a pretreatment for the extraction of phenolic compounds followed by UAE for extraction of phenols.

2. Method

2.1. Feedstock

About 3.5 kg of SCG was provided by the canteen of the University of Hohenheim (Stuttgart, Germany). The sample was homogenized manually and stored in sealed plastic bags of 125 g. Before each HDL test, feedstock was unfrozen and the moisture content was measured. The average moisture of SCG was 61.63 wt. % ± 0.93.

2.2.Methodology

2.2.1. HDL experiments

HDL experiments were carried out in stainless steel (VA2) autoclave reactors with a total internal volume of 250 ml and experimental setup previously described by [21]. The reactor was filled with 90 g ± 0.02 of initial wet feedstock and 90 g ± 0.02 of distilled water and stirred to get a homogeneous initial slurry (0.2:0.8 ratio biomass/water). Three different temperatures (200, 230, and 260 °C) and two reaction times (1 and 3 h) were selected. Once the reaction was accomplished, the reactor was quenched in cold water for 30 min. Then, the slurry was poured into a beaker, stirred and divided in two equal parts. One fraction of slurry was filtered with a qualitative filter paper (40 µm) under vacuum to separate hydrochar and liquid. The solid was dried at 105°C until weight constancy was reached, hydrochars were labeled as HDL-X-Y (x = temperature °C, y = reaction time h); while the liquid fraction was stored in the fridge for further characterization. The second fraction of slurry was frozen at -24 °C for further experiments.

2.2.2. Ultrasonic Assisted Extraction (UAE)

The UAE were performed onto dry hydrochars and slurry fractions (Figure 1). Before each UAE the moisture of defrosted slurries was measured. Both feedstock were treated with three solvents: water, methanol (Merck, ≥99.8%) and a water methanol mixture (50:50) with a solid-liquid ratio of 1:25, g/ml. Finally, each sample was introduced in an ultrasound cleaner (VWR 142-0088, Germany) at 40 °C for 40 min. Afterwards, the samples were centrifuged (20 min, 13500 rpm, 4 °C) (Z326K, Herlme Z, Germany). Supernatant and solid residue were separated for further analyses.

2.3. Analysis

2.3.1. Fiber analysis

The modified Van Soest's method [22] was used to determine the content of cellulose, hemicellulose, lignin and water extractives of the raw SCG. The composition was determined using neutral detergent fiber (NDF) to remove extractives, acid detergent fiber (ADF) to extract hemicellulose, and acid detergent lignin (ADL) for cellulose removal. Klason lignin was determined by difference.

2.3.2. Solid hydrochar

The moisture content (MC) of feedstock and hydrochars was determined according to DIN EN 12880:2000. The volatile matter (VM) and ash content were obtained following DIN EN 15148:2009 and DIN EN 15148:2009, respectively. Fixed carbon (FC) was calculated according the Eq. 1. The elemental composition CHNS of raw feedstock, hydrochars, hydrochars after UAE and slurry residue after UAE was measured by elemental analysis (HekaTech, Euro EA). Oxygen (O) was determined by using Eq. 2. The equation of Channiwala and Parikh [23] was used to determine the Higher Heating Value (HHV (MJ/kg)) of raw material and produced hydrochars.

$$FC\ (wt.\%) = 100\% - MC\ (wt.\%) - VM\ (wt.\%) - ash\ (wt.\%); \quad (1)$$

$$O\ (wt.\%) = 100\ \% - N\ (wt.\%) - C(wt.\%) - H(wt.\%) - S(wt.\%) - Ash\ (wt.\%); \quad (2)$$

After HDL, Hydrochar mass yield (Hy) was measured as following:

$$Hy(wt.\%) = \frac{mass\ of\ dried\ hydrochars}{mass\ of\ total\ dried\ feedstock} * 100; \quad (3)$$

The energy properties (energy densification, Ed; energy yield (%), Ey; fuel ratio, FR) of hydrochar were evaluated using Eq (4)- (6):

$$Ed = \frac{HHV\ of\ dried\ hydrochars}{HHV\ of\ dried\ feedstock} * 100; \quad (4)$$

$$E\ y\ (\%) = Hydrochar\ yield * Ed; \quad (5)$$

$$FR = FC/VM; \quad (6)$$

2.3.3. Liquid phase

The TOC of PW after HDL tests was determined using a TOC Analyzer 5050A (Shimadzu Scientific Instruments, Columbia, MD, USA). DOC was measured by the filtration of initial liquid by a 0.45µm syringe filter (VWR European Cat, Leuven, Germany).

2.3.4. Total phenolic content (TPC)

Total phenolic content was determined by modified Folin–Ciocalteau method [24] 95% (vol/vol) methanol (Merck, ≥99.8%) in water solution was prepared and used as blank in the analysis. 100 µL sample, standard or blank was put into a 2-mL reaction tube. Folin reagent (VWR chemicals, quality for analysis of phenols, Germany) was 1:10 diluted with water, and 200 µL of Folin dilution was added to the reagent tube. This mixture was thoroughly mixed. Then, 800 µL 700 mM Na_2CO_3 (Merck) was transferred to each tube with a pipette followed by incubation at room temperatures for 2 h. 200 µL of reagent mixture was transferred to a clean 96-well microplate and the absorbance of each well was read at 765 nm in a microplate reader BioTek EPOCH2 (BioTek Germany, Bad Friedrichshall). Gallic acid (Alfa Aesar, 98+%, Germany) solution was used as standard in concentration ranging from 0.05 to 2.5 mM. The concentration of total phenolic compounds in PW was calculated according to gallic acid standard curve in mg GAE/g.

2.3.5. Fourier transform infrared (FTIR)

FTIR spectra of the raw SCG, hydrochar and hydrochars after HDL were acquired using Bruker ALPHA II PLATINUM-ATR, Germany. The spectra were registered in the range from 400 to 4000 cm^{-1} by averaging 24 scans.

3. Results and discussion

3.1. Feedstock characterization

The analytical determinations done to the initial raw SCG are shown in Table 1. The ultimate analysis of raw SCG is similar to the results of previous studies [25]. Pujol et al., [12] reported higher values of C and H, 58.5% and 7.4%, respectively, and lower N (1.3%). The value for ash (1.3 wt. %) is similar to the value of 0.7 (wt. %) reported by Scully et al., [26]. In the case of the SCG, the initial ash content is usually associated with the brewing process. Then, it can be reduced up to 96% of the original ash content found in roasted coffee bean [7].

3.2.Hydrochar properties

The physical-chemical properties of the hydrochars differ significantly from the raw feedstock. VM in the hydrochars decreased by 12.09 % at 200 °C and 1 h reaction time compared to the raw biomass. As the reaction temperature increased, VM decreased significantly at higher temperature (260 °C and 3 h) (Table 2). The decrease of VM is mainly due to the formation of a higher molecular weight and cross-linking [27]; [28, 29]. In contrast, FC values show an increase of 142.44 % at 260 °C and 3 h reaction time, and this agrees with other previous studies [21]. The fuel ratio (FR) of hydrochars (Table 2) reaches its maximum at 260 °C, 3 h where it is more than 3 times higher than the FR of the feedstock. Thus makes more suitable the combustion of the produced hydrochars than initial feedstock.

The initial ash content of the SCG is relatively low compared to other feedstock (Table1) [30]. Low ash content is desirable for energetic purposes, since this is what remains after combustion

[31]. In Table 2 is shown that the ash content increases with increasing temperature. The explanation of the high ash concentration in the solid is mainly due to the solid mass reduction. The soluble organic compounds formed during HDL tends to pass into the liquid phase, while the most of the inorganics precipitate into the solid phase [32][33].

The HHV increased from initial feedstock 21.84 MJ/kg to 33.17 MJ/kg at 260 °C at 3h (Table 3). This last value is comparable with the HHV value obtained by Vardon et al., [34] after slow pyrolysis of SCG. The hydrochar yield (wt.%) gradually decreased with the reaction temperature (Table 2) and it seems to be almost independent from the reaction time. Similar results were found in previous studies [19, 35]. Increasing the temperature from 200 to 260 °C, the Ey (%) was lowered to 82.99% and Ed increases up to 1.51 at the maximum temperature.

Table 3 shows the ultimate analysis of the initial SCG and the hydrochars obtained. The N and C content increased with the temperature, while the hydrogen content remained relatively constant among the HDL experiments. On the other hand, O content decreased with increasing temperature; the lowest value was obtained at 260 °C and 3 h and it is 47.28 % lower than the value obtained after 1 h at 200 °C.

The Van Krevelen diagram (Figure 2) shows the carbonization of hydrochars, which increases with increasing severity of the reaction for each treatment (Figure 2). In comparison with SCG, the O/C and H/C atomic ratios decreased 77.48 % and 29.58% respectively. This drop of O/C (mol/mol) and H/C (mol/mol) ratios is mainly due to dehydration and, in the case of O/C, decarboxylation occurring during the HDL process [3]. The increase of the severity produces hydrochars with properties similar to sub-bituminous coal, which can be used as a cofuel [36].

The initial pH of the SCG with water was 5.4. In the Table 4 is shown that pH of HDL liquid is even more acidic and it is affected slightly by the HDL temperature. It reaches its maximum pH,

the most basic conditions, at 260 °C (Table 4). The decrease of the pH, in matters of the initial feedstock, is due to the formation/release of organic acids such as acetic, levulinic, formic and lactic during the HDL process [28].

As expected, the TOC increased with the reaction time and decreased with temperature, however; TOC values are similar at 1 and 3 h reaction time. According to Kruse et al. [37], this is due to the start of the depolymerization reaction that occur during the hydrolysis, where organic carbon from the solid phase partially migrates to the liquid phase. Consequently, less solid remains on the final solid product, which is reflected into the Hy (Table 3). The lower TOC with the increment of the temperature proves that the organic carbon tends to migrate to the gas phase (i.e. CO_2). At 260 °C and 3 h reaction time, the lowest TOC value was obtained, which is similar to the DOC value. TOC and DOC reached similar values because of the degradation of released carbon particles from the biomass [38]. A study carried by Erdogan et al., [35] found a similar effect on the TOC and DOC.

The operating conditions during HDL have an effect on the content of different functional groups on the surface of hydrochars. Therefore, organic compounds may be adsorbed on the surface, in equilibrium with the solved species. As the temperature increases, the chemical and physical properties of water change dramatically. A crucial parameter during HDL is the dielectric constant of water. This parameter is strictly connected with the possibility for a solvent to dissolve polar or rather non-polar compounds. A high ε values is common for polar solvents, like water at standard conditions. When the temperature increases, the ε decreases. As a result, the solubility of many organic compounds is strongly improved during HDL and, consequently, the organic species are found in liquid phase. However, as demonstrated by some authors (Volpe et al. 2018; Reza et al. 2014a) phenolic compounds (PC), of interest in this paper, is found both in HDL liquid and on hydrochar.

Figure 3 shows the FT-IR spectra of the raw SCG and the hydrochars produced at different temperatures during 3 h residence time. The band between 3500 to 3000 cm^{-1} is attributed to –OH stretching vibrations (hydroxyl, phenols and carboxyl groups). In the produced hydrochars, there is a reduction of the peak with the increment of the temperature during the process, which can imply that the dehydration reaction takes place. The two peaks at 2922 cm^{-1} and 2850 cm^{-1} confirm that aromatization take place during the HDL, because these peaks represent the aliphatic -CH stretching and aromatic -C-H bending vibrations. Craig et al., [39] attributed these peaks to the aromatic character of the caffeine.

The increment of the temperature during the HDL also caused a reduction of the peaks at 1780 and 1605 cm^{-1}. According to Reza et al., [22] these peaks represent, among others, the -C=O in the carboxyl group showing the decarboxylation of the SCG with increasing temperature. Thus implies that organic carbon is released from original feedstock to form CO_2. At a wave length of 1200 and 850 cm^{-1} were higher peaks in the raw material in comparison with the produced hydrochars. It can be due to the -C-O (ester or ether) and C-H (hydroxyl) because the decomposition of the original lignin in the raw SCG during HDL (Table 1) [22]. Another possible explanation is the rupture of glycosidic units of the cellulose and hemicellulose [40].

The reduction of intensity of transmittance with the increment of the temperature during HDL in the wavelength between 800 to 500 cm^{-1} was reported on a previous study [41]. It can be suggested that this is due the aromatic character of the produced hydrochars.

3.3.Total phenolic content

The amount of TPC in the initial SCG is in accordance with the results reported in previous studies [42]. The difference between the results obtained in this study (17.92 mg GAE /g) and in previous studies (21.56 mg GAE /g) [43] could be due to different analysis assay used and also

the heterogeneity in between the species of coffee. It is usually higher TPC in Arabica coffee than in the blends of Arabica and Robusta beans that were used in this work. The TPC found in SCG is higher than in other agro industrial residues, such as grape pomace (14 mg GAE/g) [44]. Therefore, it is suitable and promising to use SCG for the extraction of phenolic. Products originated by the Maillard reaction, such as melanoidins, have also been determined in other studies [45]. Thus, the TPC of the process water in this study could be over-estimated by comparing it with previous results.

The hydrothermal treatment in this study is used for the delignification of the initial SCG, and it is also considered as an extraction method of phenolic compounds in previous studies (Ballesteros et al., 2017). TPC quantification was performed on the three fractions after HDL (slurry, dry solid and PW) according to Figure 1. For the slurry and solid after HDL, UAE was applied to extract phenolic compounds.

3.3.1. Total phenolic content in process water

As shown in Table 4, at the same temperatures, longer reaction time negatively influenced the amount of phenolic compounds in PW. The values of TPC decreased with the increase of the temperature and reaction time due to the promotion of the degradation (oxidation) of phenolic compounds [2]. Pérez-Martínez [46] propose that the acidic aqueous phase can promote the extraction of phenolic compounds with higher antioxidant capacity. The increase of pH of the PW with temperature and reaction time could be an additional reason of the lowered extraction of phenolic compounds at higher temperatures.

3.3.2. Total phenolic content in the slurry and hydrochar

The amount of TPC (Table 5) extracted by methanol and methanol water mixture as solvent were 4 times higher than with water as solvent. Then, the use of solvent significantly affects to extracted phenolic compounds from dried hydrochar compared to water (Table 5). Indeed, in the

case of slurry, the results are similar using different solvent. A study carried out by Ramakashmi et al., (Ramalakshmi et al. 2008) concluded that the solvent polarity has an effect on green coffee bean extracts. In general, methanol was considered as the best solvent for phenolic extraction (Adil et al. 2007). However, water was used as an environmental friendly solvent during UAE. The reason is that phenols and antioxidants have a higher solubility in organic solvents than in water [47].

The HDL conditions have an effect of TPC in hydrochar, which has the same trend as in the PW. The increase of temperature during HDL produces a decrease of TPC in the hydrochar and PW (Table 5). It may be due to the increase of temperature generates an instability or an oxidation of phenolic compounds [48, 49]. The reactivity of phenolic compounds depends on the substituents in their aromatic rings. Phenolic compounds with higher number of hydroxyl group and lower of methoxyl group will have higher stability to high temperatures [48]. Especially in water, the methoxyl groups are hydrolysed. Long reaction time during HDL leads to consecutive reactions of the phenols, thus TPC cannot be detected in the same wavelength by using Folin–Ciocalteau method. Therefore, if the extraction of a specific phenolic compound is desired, it is necessary to optimize the extraction time and temperature because some phenolic compounds degrade at 40 ^{o}C, such as caffeic, p-coumaric, ferulic and p-hydroxy-benzoic acid [48]. The temperature has a direct influence on the rate and intensity of cavitation because they are dependent on the vapor pressure of the solvent. The increase in solvent viscosity and surface tension generates a disturbance in the cavitation effect [49].

On the other hand, it was expected that an increment of the severity also produces a decrement of the TPC yield. In Table 5 can be seen that at same temperature the yield to TPC (mg GAE/g) is similar. Compared to the influence of the reaction temperature the influence of the reaction time is negligible [50].

However, TPC in the slurry after HDL have similar values independently of the solvent used for the extraction. The lower TPC values in the dry hydrochar compared with the slurry may result from drying and further processing. Another reason is that the water in the slurry (~85 wt.% dry basis) modifies the S-L ratio. This effect is in accordance with previous studies (mention Liu et al. 2013 here), showing that the extraction yield of phenolic compounds increases proportionally with the increase in the S-L ratio. According to the authors, this is attributed to the principle of mass transfer from the hydrochar to the solvent. The differences between the concentration inside and outside the cells results in an increase in transport force and diffusion rate [51]. This variation of the S-L ratio may lead to a dilution of the used solvent, decreasing the extraction efficiency [52].

3.3.3. FTIR analysis of UAE SCG

Figure 4 represents the Fourier transform infrared (FTIR) of the hydrochars produced at 200, 230, and 260 °C and 3h after UAE treatment. Differences in the peak intensity of diagrams (Figure 4) with different solvents and increment of temperature are caused by different solubility of HDL products in the solvents. In general, the use of methanol as a solvent during the UAE caused a reduction of the peak intensities of the produced hydrochars, which is confirmed by the high extraction effect on phenols and other components (Table 4 and Table 5). However, in the hydrochars produced at 200 °C (Figure 4), the use of water: methanol (50:50) mixture produces a similar effect than only methanol as a solvent, which seemed to cause a reduction of the peak intensity of the functional groups. This could be due to the degradation of the carbohydrates that has not occurred completely, so non-degraded lignin is accessible by solvents. At 230 °C the degradation of the cellulose is completed. However, the lignin is partially degraded and the released phenols have similar miscibility into water and methanol. Therefore, the peaks of the hydrochars after UAE release equal transmittance intensity. Figure 4 shows that at 260 °C, the

decrease of the peaks associated to dehydration, aliphatic C-H (3500 – 3000 cm^{-1}) and decarboxylation reactions (1780 and 1605 cm^{-1}) have a similar intensity after UAE. On the other hand, the peaks of the aromatic functional groups found at a wavelength between 1600 to 1400 cm^{-1} were also reduced after extraction compared to the original hydrochar and hydrochar after UAE. These peaks are associated to the aromaticity were reduced if only methanol is used as solvent, due to the high solubility of phenolics. The peak of the wave length between 1000 to 850 cm^{-1} are associated to the methoxy groups and ether bonds, respectively. During HDL, these bonds are hydrolyzed. Plus, the peaks were also reduced by the UAE due to its support of the extraction of compounds containing those groups.

4. Conclusions

This study shows the potential of the SCG as source of renewable energy by using HDL because of the high HHV (28.54 - 33.17 MJ/kg) and low ash content (1.93 - 2.38 wt. %). UAE and methanol as solvent combined produced the highest extraction of TPC, therefore showing the possibility of a renewable source of TPC for industrial applications (e.g. pharmaceutical). The study of the functional groups on the surface by FT-IR reveals that they were influenced by the UAE treatment used for the extraction of phenols.

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Figure captions

Fig 1. Scheme of experimental design. (PW: Process water; UAE: Ultrasound Assisted Extraction)

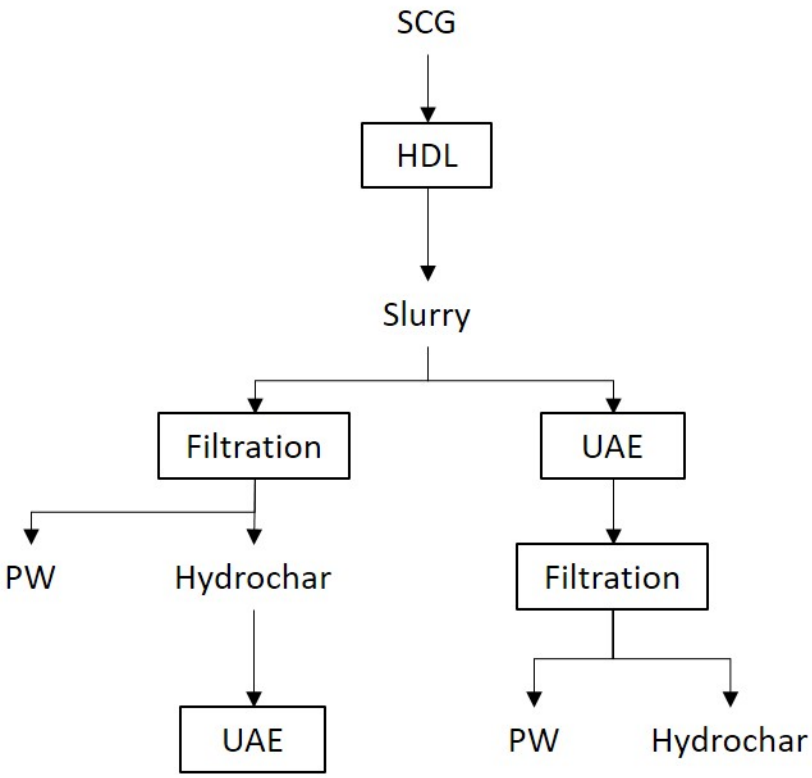

Fig 2. Van Krevelen diagram of produced hydrochar and raw material.

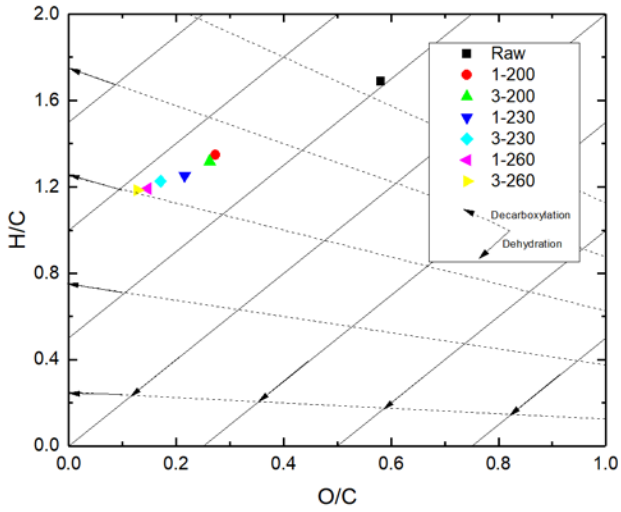

Fig 3. FTIR of raw spent coffee grounds and corresponding hydrochars produced at 200, 230 and 260 °C during 3h.

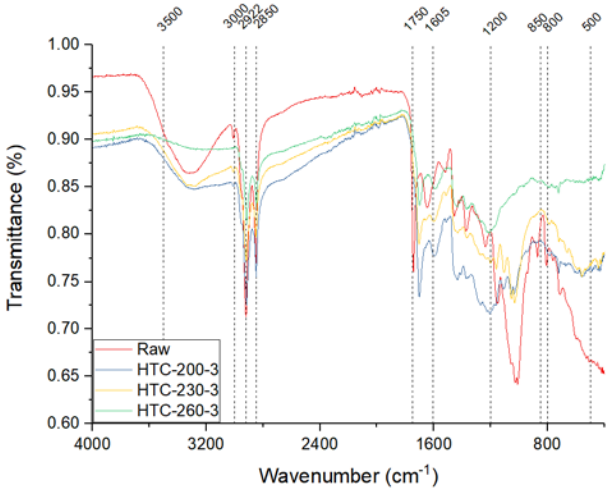

Fig 4. FTIR of produced hydrochars at 200, 230 and 260°C during 3 h and after UAE.

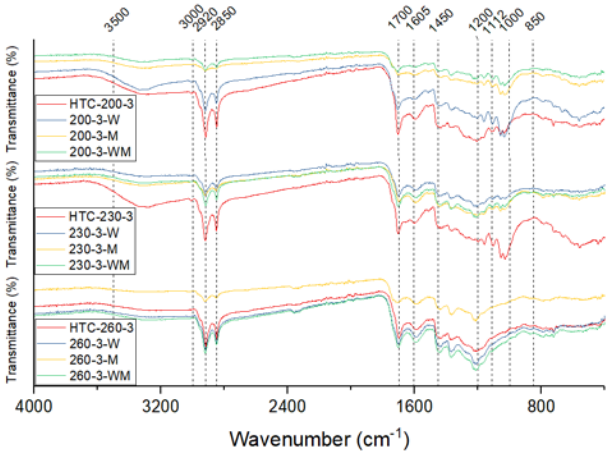

Table 1. Properties of initial SCG

Proximate analysis (wt. % dry basis)	
VM	82.45
Ash	1.30
FC	16.42
Ultimate analysis (wt. % dry basis)	
N	2.28
C	50.36
H	7.09
S	0.00
O	38.97
Fiber analysis (wt. % dry basis)	
Cellulose	19.56
Lignin	21.98
Hemicellulose	32.41
Extractives	26.05

Table 2. Physical properties of the raw material and the obtained hydrochars.

	Proximate Analysis (wt. % dry basis)						
Sample	VM	Ash	FC	Hy (%)	Ed	Ey (%)	FR
Raw	82.45	1.30	16.42	-	-	-	0.20
HDL-200-1	72.48	1.93	25.59	73.33	1.30	95.23	0.35
HDL-200-3	67.68	2.02	30.29	73.76	1.30	96.25	0.41
HDL-230-1	67.53	2.07	30.40	62.80	1.37	86.10	0.49
HDL-230-3	64.48	2.19	33.33	62.73	1.44	90.33	0.52
HDL-260-1	60.34	2.30	37.36	57.03	1.48	84.19	0.62
HDL-260-3	57.81	2.38	39.81	54.92	1.51	82.99	0.69

Table 3. Ultimate analysis, O/C and H/C atomic ratios and higher heating value (HHV) of raw material and obtained hydrochars

	Ultimate Analysis (% wt. dry basis)					Atomic ratio		HHV
Sample	N	C	H	S	O	O/C	H/C	(MJ/kg)
Raw	2.28	50.36	7.09	0.00	38.98	0.58	1.69	21.84
HDL-200-1	2.84	64.50	7.25	0.00	23.48	0.27	1.35	28.54
HDL-200-3	2.84	65.06	7.15	0.00	22.73	0.26	1.32	28.70
HDL-230-1	3.04	68.30	7.14	0.00	19.65	0.22	1.25	30.13
HDL-230-3	3.27	71.10	7.27	0.00	16.17	0.17	1.23	31.62
HDL-260-1	3.30	72.91	7.24	0.00	14.26	0.15	1.19	32.41
HDL-260-3	3.36	74.28	7.34	0.00	12.64	0.13	1.19	33.17

Table 4. TOC, DOC, pH and TPC (mg GAE /g) in the process water.

Sample	TOC (g L^{-1})	DOC (g L^{-1})	pH	Pressure (bar)	TPC (mg GAE /g)
Raw	-	-	5.4	-	17.92
HDL-200-1	16.00	12.62	3.66	29.7	9.52
HDL-200-3	17.50	11.08	3.82	33.75	8.27
HDL-230-1	13.40	11.36	3.91	54.5	9.35
HDL-230-3	16.76	10.01	3.98	61.25	8.47
HDL-260-1	12.75	11.24	4.18	89.15	8.74
HDL-260-3	12.26	11.04	4.29	93.25	8.07

Table 5. TPC into the hydrochars and slurry after UAE treatment.

	Slurry (mg GAE/ g dry sample)			Hydrochar (mg GAE/ g dry sample)		
Sample	Water	Methanol	Water:Methanol	Water	Methanol	Water:Methanol
HDL-200-1	27.29	31.36	32.33	5.09	20.33	19.60
HDL-200-3	24.56	34.40	30.47	4.77	20.99	21.56
HDL-230-1	24.32	22.72	34.87	3.40	16.79	15.76
HDL-230-3	24.96	27.04	25.05	3.49	17.42	15.33
HDL-260-1	30.11	31.54	31.29	1.92	12.79	9.75
HDL-260-3	27.50	32.02	29.13	1.98	11.60	9.17

Supplementary information for

Improving the recovery of phenolic compounds from spent coffee grounds by using hydrothermal delignification coupled with ultrasound assisted extraction.

Table A1. Ultimate composition (wt. %) of the hydrochars and slurry after ultrasound assisted extraction

Dry solid hydrochar												
	water				methanol				water: methanol			
Sample	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	N (wt.%)	C (wt.%)	H(wt.%)	S (wt.%)	N(wt.%)	C(wt.%)	H(wt.%)	S(wt.%)
HDL-1-200	2.62	66.80	7.38	0.00	2.98	64.23	6.62	0.00	2.57	66.53	7.43	0.00
HDL-3-200	2.72	67.35	7.21	0.00	3.26	64.72	6.16	0.00	2.64	66.12	7.17	0.00
HDL-1-230	2.92	69.35	7.18	0.00	3.46	67.31	6.04	0.00	2.85	69.57	7.16	0.00
HDL-3-230	3.14	72.15	7.27	0.00	3.71	70.14	5.95	0.00	3.24	74.71	7.51	0.00
HDL-1-260	3.24	73.53	7.06	0.00	3.75	72.48	6.11	0.00	3.24	73.68	7.15	0.00
HDL-3-260	3.26	74.65	7.24	0.00	3.77	74.07	6.25	0.00	3.47	62.89	6.61	0.00
Slurry												
	water				methanol				water: methanol			
Sample	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)	N (wt.%)	C (wt.%)	H (wt.%)	S(wt.%)
HDL-1-200	1.36	66.01	7.35	0.00	3.32	60.60	5.75	0.00	2.80	65.06	7.19	0.00
HDL-3-200	2.74	66.58	7.03	0.00	3.27	59.16	5.49	0.00	2.95	67.03	7.02	0.00
HDL-1-230	3.08	71.04	7.24	0.00	3.43	60.14	5.36	0.00	3.05	69.89	6.91	0.00
HDL-3-230	3.29	72.72	7.08	0.00	4.05	68.95	5.59	0.00	3.47	72.34	6.81	0.00
HDL-1-260	3.35	75.05	7.20	0.00	4.17	72.09	5.51	0.00	3.43	75.04	7.13	0.00
HDL-3-260	3.49	76.16	7.05	0.00	4.46	70.78	5.68	0.00	3.57	76.64	7.18	0.00