

Influence of Process Water Reuse on the Hydrothermal Carbonization of Paper

Barbara Weiner,^{*,†} Juergen Poerschmann,[†] Harald Wedwitschka,[‡] Robert Koehler,[†] and Frank-Dieter Kopinke[†]

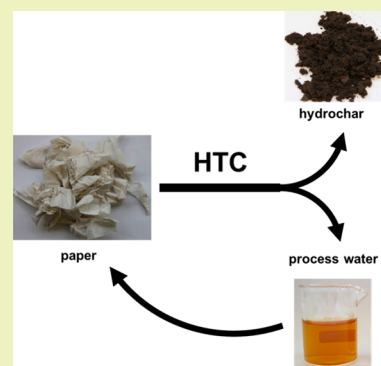
[†]Department of Environmental Engineering, Helmholtz-Center for Environmental Research—UFZ, Permoserstrasse 15, D-04318 Leipzig, Germany

[‡]Department of Biochemical Conversion, DBFZ—Deutsches Biomasseforschungszentrum, Torgauer Straße 116, D-04347 Leipzig, Germany

S Supporting Information

ABSTRACT: Process water reuse was exercised in the hydrothermal carbonization (HTC) of paper at 200 °C for 16 h, four times. Results showed that hydrochar mass yields increased significantly in the first recirculation step but only slightly in further steps. At the same time, solid carbon content did not increase, and a constant organic carbon distribution between the three product streams, hydrochar, process water (PW), and gas phase, was observed over all recycling steps. Dissolved organic carbon content (DOC) and chemical oxygen demand (COD) of the PWs increased, as well as total acids content, among those specifically lactic, acetic, formic, and propionic acid. Surprisingly, the aerobic biodegradability of the PWs decreased as indicated by lower biochemical to chemical oxygen demand (BOD/COD) ratios in reused process waters. Subsequent methanogenesis of the PW revealed that a high amount of biogas was produced; however, no increase was seen with each recirculation step.

KEYWORDS: Hydrothermal carbonization, Process water, Recirculation, Dissolved organic carbon, Biogas



INTRODUCTION

During hydrothermal carbonization (HTC) biomass is heated under subcritical conditions in an aqueous solution for several hours in a closed system. Typical process conditions are temperatures of 180–250 °C, elevated pressures of 1.5–4.0 MPa, reaction times of 2–24 h, and dry substance contents of 5–20 wt %.¹ As products, a solid carbonaceous material, the hydrochar, is obtained, but a significant amount of the organic carbon is dissolved in the process water (PW). Only minor amounts of gas are formed. Yields of hydrochars and carbon distribution depend on feedstock and process conditions.² The chemical processes during HTC are complex.³ Initially hydrolysis takes place. For example hydrolysis of cellulose leads to glucose formation.⁴ Further dehydration and decarboxylation lead to formation of organic acids, highly reactive intermediates, such as 5-hydroxymethyl furfural (HMF) from carbohydrate degradation, and phenols as fragments of lignin.⁵ By ongoing polymerization, the intermediates react to form water-soluble polymeric substances and insoluble solids, i.e. hydrochars. Therefore, the PW can contain reactive organic materials when carbonization conditions are relatively mild (low temperature and/or short reaction time), while others, such as short chain organic acids, can be regarded as stable final products in PWs.⁶

Many feedstock materials have been employed for HTC, among those cellulose, lignin,⁷ and lignocellulosic materials,⁸ but also waste biomass, such as municipal solid waste,⁹

distiller's grains,¹⁰ and maize silage.¹¹ Hydrochars obtained by HTC have higher carbon contents than their feedstocks. Thus, the heating value of hydrochars is significantly increased due to carbonization. Therefore, hydrochars can be used not only as fuel to replace oil-derived energy sources¹² but also find application as biochars for soil amendment and sustainable carbon materials.^{1,13}

Because of its high dissolved organic carbon (DOC) content and high chemical oxygen demand (COD), the PW needs to be treated in a wastewater treatment plant prior to discharge. This can be costly as large amounts of liquids are recovered during HTC. Therefore, minimizing the amounts of PW is a key for an economically feasible HTC process.

In HTC on a pilot plant scale, PW recirculation is an established approach, however, detailed chemical analysis of the influences of PW recycling on hydrochar and PW composition are still missing.¹⁴ Recirculation gives an energetic advantage to the HTC process by reducing heating costs when mixing hot PW with the feedstock, because the heat of reaction of HTC was measured to be comparatively low despite the principally exothermic nature of the process.¹⁵ Moreover, the amount of PW that needs to be treated is significantly reduced. Stemann et al. have recently demonstrated the impact of PW recirculation

Received: June 3, 2014

Revised: July 15, 2014

Published: August 13, 2014

on the HTC of poplar wood.¹⁶ They showed that hydrochars had increased carbon contents but lower mass yields due to additional dehydration reactions during the carbonization. Furthermore, a plateau in DOC concentration was reached after around ten steps. However, as wood contained 25% residual water, only 75% of PW were used in each subsequent step, thus a dilution effect took place. Blöhse reported an energetic advantage as well as an increase of solid carbon mass yield by recirculation of PW in a 200 L quasi-continuous reactor.¹⁷ Furthermore, it was shown that in a 25 L batch reactor PW of sugar beet pulp was recirculated for 12 times leading to an increase in DOC content in each HTC-step with a positive influence on methane production from recirculated PW in subsequent anaerobic digestion.¹⁸ Up to now, the data concerning the impacts of PW reuse are confusing and partly contradictory. Thus, additional research is needed to clarify organic carbon, mass and energy balances, along with analytical studies of the process water composition on the molecular level to identify its toxicity, biodegradability and potential to produce biogas by anaerobic digestion.

Herein, the effects of process water reuse during HTC of paper were investigated. Tissue paper was chosen as a model substance for cellulosic biomass containing >95% of cellulose.¹⁹ It remains to be clarified, if hydrochar carbon and mass yields increase due to additional carbonization of dissolved organic matter from the PW and if a plateau in the DOC formation can be observed. Moreover, the remaining PWs of each step were analyzed for their potential to form methane by anaerobic digestion. Next to the determination of bulk parameters in liquid and solid phase, also the change in organic acid components upon PW reuse was analyzed.

METHODS

Experimental Section. Commercial unbleached tissue paper (80.0 g) was cut into small stripes and immersed in 10 mM aqueous H₂SO₄ solution (800 g) in step 1 to obtain a solid to liquid ratio of 1:10. The mixture was poured into a glass insert and placed in a 1.8 L autoclave (b.coal 2.0 institute, Artec Biotechnologie, Bad Königshofen, Germany), which was tightly closed and heated to 200 °C for 16 h. After cooling to room temperature, the mixture was filtered under vacuum through slow filter paper (Schleicher & Schuell 589/3, 2 μm, Germany). The solids were washed three times with distilled water (total 750 mL) in order to completely remove the PW for carbon balance analysis of the liquid and solid phase. The solids were dried at 105 °C for 16 h. For recirculating steps 2–5, process water of the previous step was used as liquid phase and mixed with freshly cut tissue paper in such a way that a constant solid to liquid ratio of 1:10 was maintained. Additional information on the recirculation procedure can be found in the Supporting Information (Table S1). Experiments were performed in triplicate (step 1) or duplicate (steps 2–4). Values are reported as averages over these experiments. Error bars in the figures correspond to estimated standard deviations among individual experiments. For step 5, error bars correspond to standard deviations representing instrumental errors (triplicate measurement of the same solution).

Process Water Analysis. Process water and wash water were filtered through 0.45 μm syringe filters (regenerated cellulose; Lab Logistics Group, U.S.) prior to DOC analysis. DOC was analyzed using a total organic carbon analyzer TOC 600 (Shimadzu, Germany). The DOC content of the wash waters was added to the organic carbon content of the liquid phase in order to establish the carbon balance. The COD was determined using test kits (LCK014, Hach Lange, Germany). Titrations of acids were performed with 0.1 M aqueous NaOH-solution using an automated titrator (TitroLine, Schott-Geräte GmbH, Germany). The total amounts of acids were calculated by the amount of NaOH used to reach the equivalence point. The pH was

measured with a pH meter (MP 225, Mettler Toledo, Gießen, Germany) and the conductivity on a multimeter (MultiLine P4, WTW, Weilheim, Germany). Ion chromatography was performed on a Dionex ion chromatograph (DX500) equipped with an anion suppressor (ASRS300), conductivity detector (CD20) and two IonPac AS18 Anion-Exchange columns (4 × 250 mm) in series using a flow rate of 0.8 mL/min and gradient elution with the following program: 2 mM KOH from 0–10 min, increase to 20 mM KOH over 5 min, followed by an increase to 40 mM KOH over 15 min and held for 10 min. Prior to analysis, the samples were filtered through 0.2 μm syringe filters (PTFE; VWR international, U.S.) and Dionex OnGuard II RP cartridges for removal of hydrophobic substances and diluted 2000 fold. The biochemical oxygen demand (BOD) was measured respirometrically with a BOD-analyzer OxiTop OC110 (WTW, Weilheim, Germany) for 20 days.

Hydrochar Analysis. Elemental analysis (C, H, N) of hydrochars was performed on an automatic analyzer (CHN 932, LECO Instrumente, Germany). Oxygen content was calculated from the difference between the sum of the carbon and hydrogen content to 100%. The paper did not contain significant contents of nitrogen and ash. High heating values (HHVs) were calculated according to the work of Channiwala and Parikh.²⁰ The equation, HHV improvement, and energy yield calculations can be found in the Supporting Information (Table S1). For FTIR spectra, hydrochars were prepared as KBr discs and spectra were recorded on a PerkinElmer FTIR 2000 spectrometer (PerkinElmer, Massachusetts, U.S.).

Biochemical Methane Potential Test. The biochemical methane potential test was carried out according to the guideline VDI 4630 (fermentation of organic materials, characterization of the substrate, sampling, collection of material data, fermentation tests).²¹ The potential methane production was obtained from the incubation of triplicate anaerobic batch cultures containing both the substrate and a methanogenic inoculum at a predetermined substrate/inoculum ratio. Incubation took place in glass culture bottles at mesophilic conditions (38 °C) over 32 days. The biogas volume was measured using the Eudiometer technology.²¹ The methane content was determined with the Geotech GA2000 Landfill Gas Analyzer (Warwickshire, UK). The test was stopped when the daily biogas production did not exceed 1% of the total accumulated biogas (see Standard DIN 38414-58). The methanogenic inoculum was a mixture of sewage sludge from a wastewater treatment plant and of digested effluent from an agricultural biogas plant. To monitor the inoculum performance, each test run included triplicate control cultures containing inoculum and microcrystalline cellulose. The required inoculum performance was achieved when the inoculum converted at least 70% of the reference cellulose to biogas during the incubation period as defined by the American Society for Testing and Material.²²

RESULTS AND DISCUSSION

Carbon Balance. After HTC, 70% of the carbon from the initial feedstock was found in the hydrochar and 20% was transferred into the PW as DOC (Figure 1). Upon reuse of PW, the carbon distribution between the two process streams remained constant when the combined carbon input of paper and DOC from the reused PW was considered. Carbon recoveries were 85–95% in all recirculation steps. However, the solid carbon fraction increased in hydrochars from 69% in step 1 to 81% in step 2, when only solid carbon input was taken into account (Figure 2a). Upon further recycling steps, only a slight increase was observed. These findings were in accordance with an increase in mass yields of hydrochars (Figure 2b). However, solid mass yields increased with a slightly larger factor than the solid carbon fraction, thus the carbon content of the hydrochars decreased from 55% in step 1 to 49% in further steps (Table 1).

Hydrochar Characterization. The solid mass yield of the hydrochars as referred to the input of solid paper material increased significantly from step 1 (57%) to step 2 (73%) and

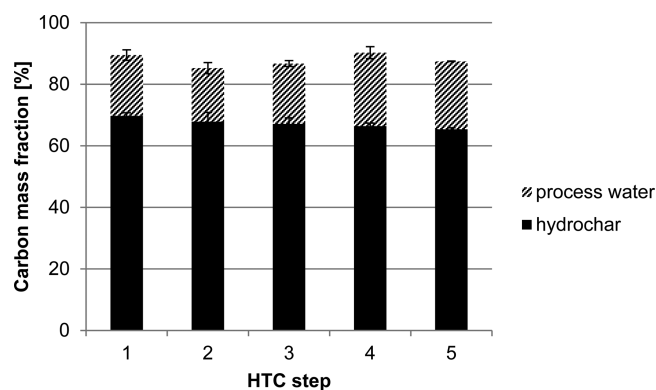


Figure 1. Carbon distribution between solid and liquid phase from step 1 to 5 as percent of total carbon input (= paper C + DOC of PW from previous step). HTC conditions: 16 h at 200 °C, tissue paper as substrate, solid:liquid = 1:10. Error bars correspond to standard deviations among individual experiments.

then only slightly up to step 5 (76%) (Figure 2b). This finding suggests that dissolved organic molecules from the PW underwent carbonization to form additional solid material, and thus increased the yield in hydrochars. A detailed discussion is given below.

Elemental analysis revealed that upon HTC the H/C ratio of hydrochars vs paper input decreased (Table 1). This was most pronounced in step 1, namely the ratio decreased from 1.56 to 1.25. The molar ratios of the feedstock and all hydrochars were depicted in form of a van Krevelen diagram (Figure 3). It can be seen that upon HTC the H/C and O/C ratios decline because of the increase of the C-fraction. This is due to dehydration and decarboxylation reactions during the HTC process. Comparing H/C to O/C decline for step 1 and steps 2–5, it can be concluded that less dehydration reactions occur when PW is reused. At the same time, the oxygen content in hydrochars 2–5 is higher than in hydrochar 1.

HHVs were calculated according to Channiwala and Parikh (see the Supporting Information).²⁰ The diminished carbon contents of the hydrochars obtained in steps 2–5 also lead to a lower HHV as compared to step 1 (Table 1). Also HHV improvements of hydrochars vs paper decreased from 27% in step 1 to 14% in step 2 (Table 1). This finding can be attributed to a slower increase in carbon yields of 16% as compared to mass yields of 19% both with regard to solid feedstock input. Concomitantly, the energy yield increased

from 72% in step 1 to 84–89% in steps 2–5, which is due to the increase in solid mass yields.

FTIR spectra of the solid input substrate and of all hydrochars were recorded (Supporting Information Figure S1). Hydrochars produced in step 1 with fresh water differed from the input material and hydrochars 2–5. Hydrochar 1 showed signals with the highest intensity for aromatic groups. All hydrochar materials were rich in functional groups such as hydroxyl, ether, carboxyl, and carbonyl groups. The intensity of the OH stretching vibrations at 3400 cm^{-1} did not change significantly upon HTC showing the presence of hydroxyl groups in all chars. The band at 2902 cm^{-1} was assigned to stretching vibrations of aliphatic C–H groups. Its presence shows that aliphatic groups are still present in hydrochars. The broad band at 1630 cm^{-1} (aromatic C=C and C=O) indicates the formation of aromatic structures upon HTC.²³ The peak is more intense in hydrochar 1 than in hydrochars 2–5. Furthermore, a shoulder can be seen at around 1700 cm^{-1} suggesting the formation of C=O groups. The presence of a small band at 1509 cm^{-1} in hydrochar 1 can also be attributed to C=C double bonds. Another indication for the formation of aromatic structures is the band at 802 cm^{-1} ($\text{C}_{\text{aromatic}}\text{-H}$ out-of-plane). A comparative analysis of the spectra of the hydrochars and cellulose suggests that dehydration and aromatization reactions have taken place during HTC which is confirmed by elemental compositions presented in the van Krevelen diagram. This interpretation is in line with results published by Kang et al. and Sevilla and Fuertes.^{7,23,24} The aromatization is most pronounced in hydrochar 1 revealed by more intense bands in the FTIR and the lowest H/C and O/C ratios in the van Krevelen diagram. During dehydration, C–OH bonds are broken under formation of C=C bonds and C–O–C bonds. Thus, hydrogen and oxygen contents decrease. Additionally, C–O–C and C–OH functionalities can be found in hydrochars 2–5, as seen from the high intensities of bands at 1162 cm^{-1} (C–OH stretching) and 1110–1033 cm^{-1} (C–O stretching, O–H bending vibrations). These findings are in line with the relatively high O/C ratios of these hydrochars in the van Krevelen diagram. These could result from the formation of ether bridges due to bimolecular reactions of two hydroxyl groups.^{7,25} Ether formation could be catalyzed by general acid catalysis due to an increased acidity in the HTC solution caused by carboxylic acids in the reused PW. It could also be speculated that dissolved organic matter containing hydroxyl groups undergoes ether formation (or other

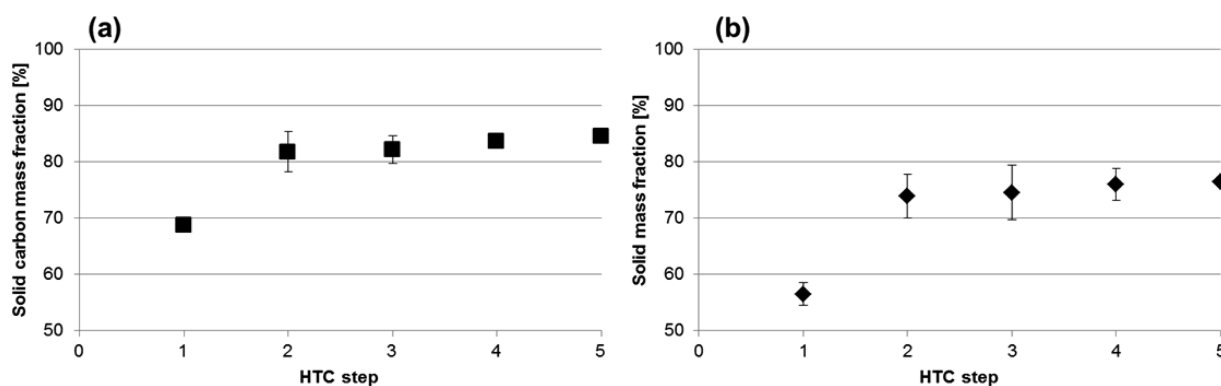


Figure 2. Hydrochar yields: (a) solid carbon fraction with regard to solid paper carbon input in each step, $m_{\text{carbon,hydrochar}}/m_{\text{carbon,paperinput}}$ (b) mass yield of hydrochars with regard to paper weight input, $m_{\text{hydrochar}}/m_{\text{paperinput}}$. Error bars correspond to standard deviations among individual experiments.

Table 1. Characterization of Solids^a

source	wt % C	wt % H	wt % O ^b	atomic H/C ratio	atomic O/C ratio	HHV [MJ kg ⁻¹] ^c	HHV improvement [%] ^d	energy yield [%] ^d
paper	44.3	5.77	49.6	1.56	0.839	17.1		
HTC-1	54.7 ± 1.1	5.68 ± 0.07	39.4 ± 1.1	1.25 ± 0.04	0.54 ± 0.03	21.7 ± 1.3	26.7 ± 1.6	71.6 ± 4.3
HTC-2	49.1 ± 0.8	6.00 ± 0.13	44.7 ± 0.8	1.47 ± 0.01	0.68 ± 0.02	19.6 ± 1.1	14.2 ± 0.8	84.5 ± 4.6
HTC-3	48.6 ± 0.9	5.99 ± 0.11	45.2 ± 0.9	1.48 ± 0.06	0.70 ± 0.03	19.3 ± 1.1	12.8 ± 0.8	84.1 ± 4.9
HTC-4	49.9 ± 1.5	6.07 ± 0.20	44.1 ± 1.3	1.46 ± 0.09	0.66 ± 0.04	20.0 ± 1.8	16.7 ± 1.5	88.7 ± 8.2
HTC-5	49.0	5.94	45.0	1.45	0.64	19.4	13.5	86.7

^aErrors correspond to relative standard deviations among individual experiments (steps 1–4). ^bCalculated as difference between 100% and the sum of C and H weight percent. ^cCalculated according to the work of Channiwalla and Parikh.²⁰ ^dCalculations of HHV improvement and energy yield can be found in the Supporting Information.

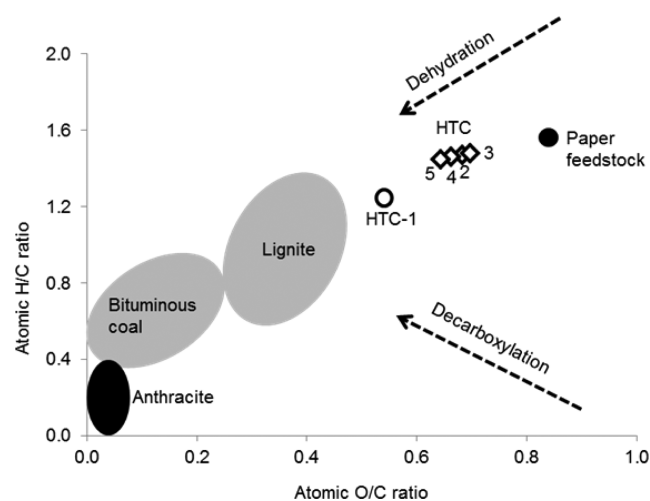


Figure 3. Van Krevelen diagram of paper feedstock and hydrochars compared with coals.

condensation reactions).^{7,25} This would also support the increase in mass yields of hydrochars.

The combined findings may point to a preferential carbonization of dissolved organic matter relatively rich in H and O atoms. Potential substrates include reactive organic compounds such as aldehydes, ketones, and carbohydrates.^{4–6} Baccile et al. have shown that residual 5-hydroxymethylfurfural was eliminated from the PW when it was reused in a second carbonization cycle.²⁶ Stemann et al. ascribed the increased dehydration reactions during HTC to carbonization of unknown organic compounds as well as to acid catalysis of PW constituents.¹⁶

Process Water Characterization. The pH of the PWs remained constant at 2.8 (Table 2). The DOC increased 1.8 times from step 1 to 5, namely from 9 to 15 g L⁻¹. Furthermore, no plateau of the DOC concentration was seen in the process water over the recycling steps. At the same time, the COD doubled from 25 to 48 g(O) L⁻¹. These findings

result in a slight increase of the COD to DOC ratio from step 1 to 2. Intriguingly, this ratio remained almost constant over further steps. It indicates the presence of more reduced species in the PW, which was in accordance with a simultaneous increase in O/C ratios of hydrochars. These findings could suggest that oxygen-rich species agglomerate and carbonize preferentially to form additional solid hydrochar, whereas components richer in H (which are “more saturated”) survive preferentially in the dissolved state.^{16,26}

The conductivity increased about 2.5 times from 1.6 to 4.6 mS cm⁻¹ indicating the presence of more ionic species such as carboxylates in the PW (Table 2). At the same time, the total concentration of acids doubled as determined by titration of the PWs against NaOH solution (Table 3). Ion chromatography revealed that the concentrations of C₁–C₃ organic acids increased (Table 3). In the employed method, only C₁–C₄ acids could be determined, namely lactic, acetic, formic, propionic, pyruvic and oxalic acid. The concentration of lactic acid increased from 11 to 50 mM, it being the most abundant identified organic acid. The acetic acid concentration roughly increased 2.5 times amounting to the second highest concentration of 32 mM. The concentration of formic acid roughly increased four times to 11 mM, while propionic acid doubled to 5.6 mM. Pyruvic and oxalic acid were only present in small amounts (<2 mM) and remained unchanged. Both acetic and formic acid can be regarded as relatively stable end-product in PWs.²⁷ The percentage of identified acids with regard to the titrimetrically determined total concentration increased from 50% in step 1 to 75% in the last recirculation step. At the same time the amount of identified acids made up 9% of the total DOC in step 1, while it increased to 19% in step 5. The number of carbon atoms per mol acid functionality decreased from 12.5 to 9 mol organic carbon per mol acid, remaining relatively constant from step 2–5. In order to bring the increase in COD to DOC ratio in accordance with these results, unidentified oxygen-rich and low molecular weight components, such as carbohydrates, furfurals, and phenols, should carbonize to form char-material.^{16,26} Some of the formed organic acids are relatively stable and enrich as end-

Table 2. Characterization of Process Waters^a

HTC step	DOC [g L ⁻¹]	COD [g _{O2} L ⁻¹]	COD/DOC	BOD ₂₀ [g L ⁻¹] ^b	BOD ₂₀ /COD	conductivity [mS cm ⁻¹]	pH
1	9.15 ± 0.8	24.8 ± 1.5	2.71 ± 0.11	13.5	0.544	1.64	2.7
2	9.9 ± 0.2	33.6 ± 5.9	3.39 ± 0.55	11.3	0.337	2.19	2.8
3	11.6 ± 0.4	35.3 ± 2.3	3.04 ± 0.29	13.5	0.383	2.77	2.8
4	13.1 ± 0.7	40.2 ± 3.0	3.07 ± 0.38	16.3	0.406	3.65	2.8
5	15.3 ± 0.1	47.9 ± 1.9	3.14 ± 0.22	18.0	0.376	4.61	2.8

^aErrors correspond to relative standard deviations among individual experiments. BOD, conductivity, and pH measurements were only performed on mixed PWs from individual experiments; thus, no standard deviations are reported. ^bDetermined with a 100-fold dilution.

Table 3. Organic Acids in PW (Titration and Ion Chromatography)^a

HTC step	total acids from titration [mM]	lactic acid [mM]	acetic acid [mM]	propionic acid [mM]	formic acid [mM]	pyruvic acid [mM]	oxalic acid [mM]	% identified of total acids ($c_{\text{sumacids}}/c_{\text{totaltitration}}$)	% identified acids of DOC ($c_{\text{sumacid}}/c_{\text{DOC}}$)
1	60.0	11.4	12.4	1.94	2.71	0.942	1.43	51.4	9.6
2	72.5	21.7	24.5	2.97	5.87	1.03	1.42	79.3	16.4
3	102	22.6	23.3	3.23	7.80	0.955	1.64	58.3	14.3
4	111	37.0	31.4	4.60	7.82	1.13	1.57	75.3	18.5
5	135	49.8	31.7	5.65	11.4	1.18	1.33	75.9	19.4

^aRelative standard deviations were not reported as measurements were only performed on mixed PWs from individual experiments.

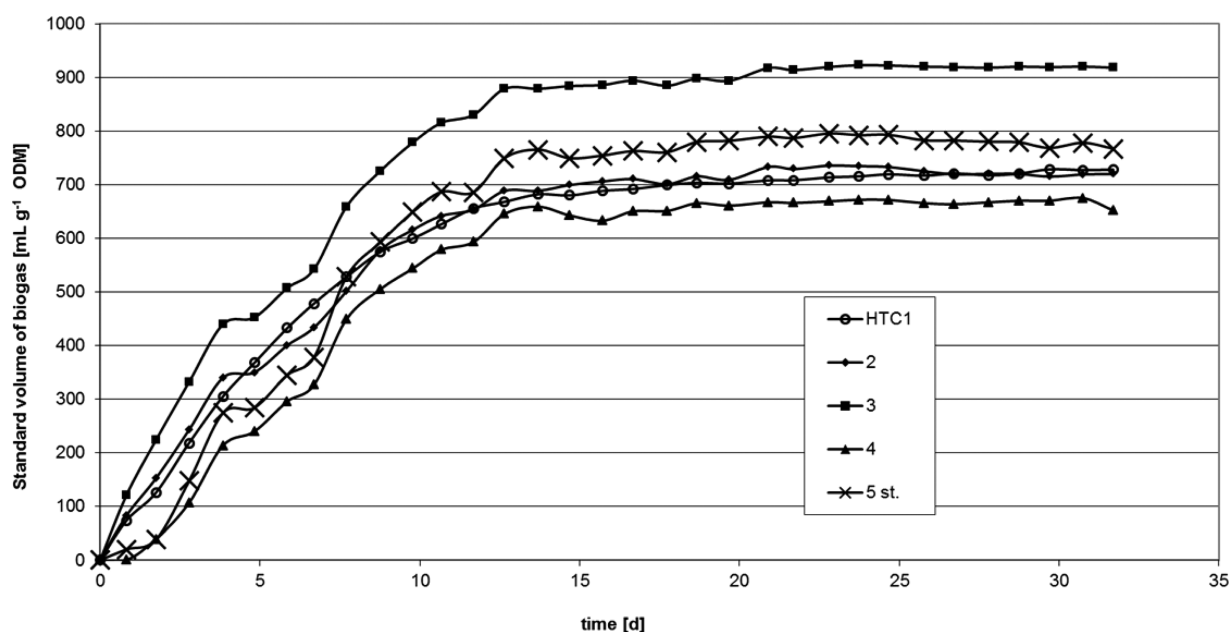


Figure 4. Specific standard volume of biogas over 32 days. ODM = organic dry matter.

products in PW.^{16,27} The presence of acids leads to accelerated cellulose dissolution.²⁸ Next to hydrolysis and dehydration reactions acid catalysis may also accelerate condensation reactions, thus leading to the formation of a greater proportion of solid material.²⁹ Acid catalyzed ether formations between DOM and dissolving cellulose feedstock may also occur as suggested from the FTIR results. As hydrochars with higher O/C ratios (and somewhat higher H/C ratios) were obtained after recirculation of PW, it was assumed that reactions of feedstock with the PW components might have had an influence on carbonization. These findings differ from the ones of Stemann et al.¹⁶ It could have been caused by higher concentrated PW solutions in our recirculation experiments. Taken all observations together, only some mechanistic hypotheses can be deduced as the PW is a very complex mixture of which the composition is largely unknown.^{6,16,30} The core of our findings is (i) an acceleration of carbonization reactions of the fresh feedstock catalyzed by organic acids present in the PW and (ii) additional carbonization of the dissolved organic matter itself.

Biogas. The idea to combine HTC of biomasses and anaerobic digestion has been described by several groups.^{11,30–33} High concentration of dissolved organic matter, as reflected by high DOC and COD values, could result in a good biological degradability. The BOD tests showed an initial lag phase in the consumption of oxygen indicating either the presence of inhibiting substances or a long adaptation period of the microorganisms. The initial oxygen consumption started after 32 to 36 h in PW of step 1 and the reused waters,

respectively. Biodegradability, expressed as BOD/COD ratios, strongly depended on dilution of the PW: 1:100 diluted PW showed better biodegradability (0.5–0.3) than 1:50 dilution (<0.3). Generally, the BOD₂₀/COD ratios were relatively low with ~0.5 for step 1 and ~0.4 for steps 2–5 (Table 2). The lower BOD/COD values for recirculated waters are unexpected with regard to the higher organic acid concentrations (Table 3). As known, short-chain organic acids are highly biodegradable. Our findings indicate an enrichment of hardly biodegradable components in recycled PW, other than simple organic acids, such as phenols, benzendiols, and higher molecular weight compounds.³⁴

Biochemical methane potential tests were performed for 32 days, and all PW samples showed biogas formation (Figure 4). The gas formation continued for a long period indicating that the PW either contained components that were hard to digest or compounds that inhibited biogas production. The biogas formation proved high: 675–923 mL standard volumes of biogas from 1 g organic dry matter (ODM), which translates to 344–477 mL methane per gram of ODM (Table 4). Surprisingly, there were no significant differences in methane production from the various recirculation steps. All PWs proved good substrates, comparable to carbohydrates and proteins for methane production.³⁵ According to our experience, the anaerobic digestion of HTC process waters from Brewer's spent grains resulted in methane yields 287 mL g⁻¹ ODM (HTC at 200 °C) and 405 mL g⁻¹ ODM (HTC at 240 °C).³² For reasons of comparison, carbohydrates give a methane yield

Table 4. Production of Biogas from Process Water^a

HTC step	biogas yield [mL g ⁻¹ _{ODM}]	methane yield [mL g ⁻¹ _{ODM}]	methane concentration [vol %]
1	730	402	55
2	736	374	51
3	923	477	52
4	675	344	51
5	795	400	50

^aRelative standard deviations were not reported as biogas experiments were only performed with mixed PWs from individual experiments. ODM = organic dry matter.

of ~390 mL g⁻¹ ODM, proteins of 470 mL g⁻¹ ODM, and lipids of 780 mL g⁻¹ ODM.³⁵

In conclusion, dissolved organic matter in process waters proved a very good substrate (or cosubstrate) for biogas generation, although the BOD/COD tests suggest a relatively poor aerobic biodegradability. Reuse of PW did not increase methane production, as it might be suggested by the increase in total organic acid content.

CONCLUSION

PW reuse is useful to increase the mass yields of hydrochars. However, the quality of the hydrochars slightly decreases in terms of carbon content and HHV as compared to HTC with fresh water. The obtained results differ from previous findings with poplar wood by Stemann et al. as therein an increase in carbon yield of hydrochars was observed but not in mass yield.¹⁶ Similarly to previous results by Blöhse,¹⁸ a continuous increase in DOC content of PW was observed in this project, when undiluted PW was recirculated, while Stemann showed the formation of a DOC-plateau (when diluted PW was reused). The dilution seems to have a significant influence on continued DOC increase in recirculated PW and on reaching the plateau concentrations of the PW components. At the same time, carbonization conditions (200 °C and 16 h vs 220 °C and 4 h) also influence carbon and mass distributions. By recirculation of PW the concentration of organic acids increases. Despite this, the aerobic biodegradability, i.e. the BOD/COD ratio, slightly decreased but the anaerobic biogas production proved to be good. Although the carbon load in the PW increases, these remain good substrates for methane production. Thus, PW recirculation is useful to decrease the amount of wastewater that needs to be treated. The residual water content of the employed biomass feedstock limits the extent of recirculation of PW, as the concept is only useful and applicable with relatively dry feedstock. In future experiments, other feedstock materials should be investigated to clarify the impact of the biomass source on PW recirculation. Furthermore, PW recirculation will be considered in terms of increasing the energy balance of the HTC process, e.g. with a combination of HTC and wet oxidation in future research.

ASSOCIATED CONTENT

Supporting Information

Details on the experimental procedure (Table S1), calculations of HHV, HHV improvement and energy yield (Table S2), FTIR spectra (Figure S1), and IC chromatograms (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: barbara.weiner@ufz.de. Phone: +49 3412351573.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank I. Baskyr for preliminary experiments, Ö. Tekinalp for technical assistance, K. Lehmann for elemental analysis, and M. Wunderlich for IC measurements.

ABBREVIATIONS

BOD, biochemical oxygen demand; COD, chemical oxygen demand; DOC, dissolved organic carbon; FTIR, Fourier transform infrared spectroscopy; HTC, hydrothermal carbonization; IC, ion chromatography; ODM, organic dry matter; PW, process water

REFERENCES

- Libra, J. A.; Kyoung, S. R.; Kammann, C.; Funke, A.; Berge, N. D.; Neubauer, Y.; Titirici, M.-M.; Fühner, C.; Bens, O.; Kern, J.; Emmerich, K.-H. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 89–124.
- Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuel. Bioprod. Bior.* **2010**, *4*, 160–177.
- Kruse, A.; Funke, A.; Titirici, M.-M. Hydrothermal conversion of biomass to fuels and energetic materials. *Curr. Opin. Chem. Biol.* **2013**, *17*, 515–521.
- Baugh, K. O.; McCarty, P. L. Thermochemical pretreatment of lignocellulose to enhance methane fermentation: I. Monosaccharide and furfurals hydrothermal decomposition and product formation rates. *Biotechnol. Bioeng.* **1988**, *31*, 50–61.
- Xiao, L.-P.; Shi, Z.-J.; Xu, F.; Sun, R.-C. Hydrothermal carbonization of lignocellulosic biomass. *Bioresour. Technol.* **2012**, *118*, 619–623.
- Becker, R.; Dorgerloh, U.; Paulke, E.; Mumme, J.; Nehls, I. Hydrothermal carbonization of biomass: major organic components of the aqueous phase. *Chem. Eng. Technol.* **2014**, *37*, 511–518.
- Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, D-xylose, and wood meal. *Ind. Eng. Chem. Res.* **2012**, *51*, 9023–9031.
- Hoekman, S. K.; Broch, A.; Robbins, C. Hydrothermal carbonization (HTC) of lignocellulosic biomass. *Energy Fuel.* **2011**, *25*, 1802–1810.
- Berge, N. D.; Ro, K. S.; Mao, J.; Flora, J. R. V.; Chappell, M. A.; Bae, S. B. Hydrothermal carbonization of municipal waste streams. *Environ. Sci. Technol.* **2011**, *45*, 5696–5703.
- Heilmann, S. M.; Jader, L. R.; Sadowsky, M. J.; Schendel, F. J.; von Keitz, M. G.; Valentas, K. J. Hydrothermal carbonization of distiller's grains. *Biomass Bioenergy* **2011**, *35*, 2526–2533.
- Mumme, J.; Eckervogt, L.; Pielert, J.; Diakité, M.; Rupp, F.; Kern, J. Hydrothermal carbonization of anaerobically digested maize silage. *Bioresour. Technol.* **2011**, *102*, 9255–9260.
- Antonietti, M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem. Soc. Rev.* **2010**, *39*, 103–116.
- Titirici, M.-M., Ed. *Sustainable carbon materials from hydrothermal processes*; John Wiley & Sons, Ltd: UK, 2013.
- Kläusli, T. M. Klärschlamm: eine globale Herausforderung. *Wasser und Abfall* **2014**, *5*, 44–48.
- Funke, A.; Ziegler, F. Heat of reaction measurements for hydrothermal carbonization of biomass. *Bioresour. Technol.* **2011**, *102*, 7595–7598.

- (16) Stemann, J.; Putschew, A.; Ziegler, F. Hydrothermal carbonization: process water characterization and effects of water recirculation. *Bioresour. Technol.* **2013**, *143*, 139–146.
- (17) Blöhse, D.; Lehmann, H.-J.; Ramke, H.-G. Hydrothermale Carbonisierung von organischen Industrieabfällen und Klärschlamm im halbtechnischen Maßstab. *Müll und Abfall* **2012**, *12*, 644–653.
- (18) Blöhse, D. Anaerobe Verwertung von HTC-Prozesswässern. In *Tagungsband 73. ANS e.V. Symposium, Biokohle im Blick*, Berlin, Sep 19 and 20; Fricke, K., Bergs, C.-G., Kammann, C., Quicker, P., Wallmann, R., Eds.; 2012; pp 79–88.
- (19) Verband Deutscher Papierfabriken. *Papier total: Informationen zu Geschichte, Herstellung und Rohstoffen*, Bonn, 2004.
- (20) Channiwal, S. A.; Parikh, P. P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *84*, 1051–1063.
- (21) VDI (Verein Deutscher Ingenieure) 4630. *Fermentation of organic materials - characterization of the substrate, sampling, collecting of material data, fermentation tests*; Beuth Publ.: Berlin, 2006.
- (22) ASTM D5210-92. *Standard test method for determining the anaerobic biodegradation*; American Society for Testing and Materials: West Conshohocken, PA, 2007.
- (23) Sevilla, M.; Fuertes, A. B. The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* **2009**, *47*, 2281–2289.
- (24) Sevilla, M.; Fuertes, A. B. Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chem.—Eur. J.* **2009**, *15*, 4195–4203.
- (25) Areeprasert, C.; Zhao, P.; Ma, D.; Shen, Y.; Yoshikawa, K. Alternative solid fuel production from paper sludge employing hydrothermal treatment. *Energy Fuels* **2014**, *28*, 1198–1206.
- (26) Baccile, N.; Laurent, G.; Babonneau, F.; Fayon, F.; Titirici, M.-M.; Antonietti, M. Structural characterization of hydrothermal carbon spheres by advanced solid-state MAS ¹³C NMR investigations. *J. Phys. Chem. C* **2009**, *113*, 9644–9654.
- (27) Jin, Z.; Zhou, Z.; Moriya, T.; Kishida, H.; Higashijima, H.; Enomoto, H. Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass. *Environ. Sci. Technol.* **2005**, *39*, 1893–1902.
- (28) Lu, X.; Flora, J. R. V.; Berge, N. D. Influence of process water quality on hydrothermal carbonization of cellulose. *Bioresour. Technol.* **2014**, *154*, 229–239.
- (29) Ibbett, R.; Gaddipati, S.; Davies, S.; Hill, S.; Tucker, G. The mechanisms of hydrothermal deconstruction of lignocellulose: new insights from thermal-analytical and complementary studies. *Bioresour. Technol.* **2011**, *102*, 9272–9278.
- (30) Poerschmann, J.; Baskyr, I.; Weiner, B.; Koehler, R.; Wedwitschka, H.; Kopinke, F.-D. Hydrothermal carbonization of olive mill wastewater. *Bioresour. Technol.* **2013**, *133*, 581–588.
- (31) Mumme, J.; Srocke, F.; Heeg, K.; Werner, M. Use of biochars in anaerobic digestion. *Bioresour. Technol.* **2014**, DOI: 10.1016/j.biortech.2014.05.008.
- (32) Poerschmann, J.; Weiner, B.; Baskyr, I.; Koehler, R.; Wedwitschka, H.; Kopinke, F.-D. Characterization of biocoals and dissolved organic matter phases obtained upon hydrothermal carbonization of brewer's spent grain. *Bioresour. Technol.* **2014**, *164*, 162–169.
- (33) Oliveira, I.; Bloehse, D.; Ramke, H.-G. Hydrothermal carbonization of agricultural residues. *Bioresour. Technol.* **2013**, *142*, 138–146.
- (34) Chen, Y.; Cheng, J. J.; Craemer, K. S. Inhibition of anaerobic digestion process: a review. *Bioresour. Technol.* **2008**, *99*, 4044–4064.
- (35) Schmidt, T.; Proeter, J.; Scholwin, F.; Nelles, M. Anaerobic digestion of grain stillage at high organic loading rates in three different reactor systems. *Biomass Bioenergy* **2013**, *55*, 285–290.