Chemosphere 131 (2015) 71–77

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Organic breakdown products resulting from hydrothermal carbonization of brewer's spent grain

J. Poerschmann *, B. Weiner, R. Koehler, F.-D. Kopinke

Helmholtz Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstr. 15, D-04318 Leipzig, Germany

HIGHLIGHTS

- Organic components in HTC solutions of brewer's spent grain were analyzed by GC–MS.
- Phenols and carboxylic acids proved most abundant breakdown products.
- Acylglycerines were overwhelmingly hydrolyzed during the HTC process.
- Hydrophobic breakdown products are mostly sorbed onto the hydrochar.

ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form 3 February 2015
Accepted 21 February 2015
Available online 13 March 2015

Handling Editor: Caroline Gaus

Keywords:
Hydrothermal carbonization
Brewer's spent grain
Organic breakdown products
Hydrochar

ABSTRACT

Hydrothermal carbonization of brewer's spent grain resulted in a solid hydrochar and an aqueous phase rich in macromolecular dissolved organic matter. Both phases were analyzed with regard to low molecular weight organic compounds (MW < 500 Da) in lyophilized form by exhaustive solvent extraction followed by pre-chromatographic derivatization and GC/MS-analysis. Low molecular weight acids, O-functionalized phenols, cyclopentenone derivatives, and benzenediols accounted for the majority of organic analytes in both hydrothermal carbonization product streams while being absent in solvent extracts of the pristine biomass. The pattern of short chain functionalized acids in the pristine biomass and in the hydrothermally produced matrices turned out very different. Acylglycerines as the most abundant lipids in pristine brewer's spent grain were quantitatively hydrolyzed under hydrothermal conditions. The recovery of total fatty acids present in the pristine biomass amounted to 19%. The major fraction of hydrophobic breakdown products including fatty acids, fatty alcohols, and sterols was sorbed onto the hydrochar.

1. Introduction

Hydrothermal carbonization (HTC) has been successfully used to convert biomasses into highly carbonaceous hydrochars, which can be used for energetic purposes, for soil improvement or as sorbent in remediation processes (Funke and Ziegler, 2009; Meyer et al., 2011). HTC is an environmentally friendly, exothermic process in which wet biomass is hydrothermally converted in aqueous suspensions at moderate temperatures (180–250 °C) and self-generated, medium pressure into carbonaceous materials. In the HTC processes, subcritical water acts as the solvent and the reagent. Biomass decomposition is characterized by hydrolysis, defunctionalization, recondensation and aromatization (Libra et al., 2011). In addition to the desired char, an aqueous phase rich in dissolved organic matter (DOM) is produced as an undesired side product.

The solid residue brewer's spent grain (BSG) has mainly been used as cattle feed. Shortcomings of BSG application in animal nutrition include its insufficient degradation in rumen as well as its cyclic generation peaking in summer. Thus, BSG cannot be regarded as a marketable commodity today. A stabilization for storage (e.g. by drying) is necessary to prevent microbial degradation and chemical deterioration (Robertson et al., 2010). Hydrothermal treatment turned out an efficient route to utilize BSG. In the framework of a companion paper, BSG was successfully tested as biomass substrate for HTC (Poerschmann et al., 2014). It was demonstrated that around two thirds of the substrate's organic carbon (OC) were fixed into the energy-dense and volume-dense hydrochar, whereas almost 20% of the total OC were transferred to the aqueous product stream. However, the molecular characterization of organic breakdown products in the process water remains to be clarified yet. Thus, the first objective of this contribution was to study the product pattern of abundant analytes and to compare this pattern with precursor compartments

* Corresponding author. Tel.: +49 341 235 1761; fax: +49 341 235 2492.
E-mail address: juergen.poerschmann@ufz.de (J. Poerschmann).

http://dx.doi.org/10.1016/j.chemosphere.2015.02.057
0045-6535/

in the biomass (e.g. lipids, lignin). This scientifically demanding objective is embedded into two application-related issues:

- The production of potential value-added chemicals such as fatty acids as basis for biofuels, phenolics as valuable (antioxidative) chemicals, levulinic, lactic and succinic acid as platform chemicals, vanillin as flavoring agent in food industry.
- Breakdown products, which were sorbed onto the hydrochar, may limit its application for soil improvement due to their potential to impair plant and microbial growth, seed germination, etc. (Rillig et al., 2010; Meyer et al., 2011). Thus, a second objective of this contribution was associated with the determination of concentrations of the organic intermediates in both HTC slurry (consisting of char and DOM) and DOM itself, thus providing information about the sorption potential of hydrochar toward organic intermediates and giving finally information about the phytotoxic characteristics of the hydrochar.

Former work was directed to determine volatile organics sorbed onto dried chars of different biomass origin by means of headspace analysis coupled to GC at enhanced temperatures (Becker et al., 2013). To study the impact of organic sorbates toward their application as soil amendment, volatile organics sorbed onto char produced by pyrolysis of a wide variety of biomasses at around 500 °C were determined by headspace analysis (Spokas et al., 2011). However, headspace analysis as a partitioning method can only determine free concentrations in the vapor phase. Even in case of headspace analysis at elevated temperature of 100 °C (Becker et al., 2013), the analyte concentrations do not necessarily correspond to total analyte concentrations, nor do these concentrations reflect the sorbate fraction accessible for reversible partitioning. This limitation holds especially true for sorbates with high sorption coefficients such as long-chain, hydrophobic analytes. Another shortcoming of headspace analysis is that highly polar, as well as high-boiling sorbates elude headspace analysis to a large degree. More importantly, highly polar breakdown products are not accessible to conventional GC. Thus, it is not surprising that highly polar analytes such as benzenediols with high phytotoxic potential (Sampedro et al., 2007) and low molecular weight carboxylic acids (lactic acid, glycolic acid), as well as high boiling analytes such as sterols and long-chain carboxylic acids, could not be detected using the headspace analysis approach. Herein, concentrations of BSG-based organic HTC products in both hydrochar and process water were determined by exhaustive solvent extraction followed by derivatization and low resolution GC/MS analysis. This approach, which does not need highly sophisticated and expensive techniques such as MS/MS, may be adapted in every analytical laboratory equipped with GC/MS capabilities. Organics accessible to solvent extraction were considered equivalent in their capability of being mobilized in soil (Rillig et al., 2010). In the framework of this contribution, focus was given on fatty acids, fatty alcohols and sterols released from lipids as a result of HTC as well as on O-functionalized phenols and phenolic acids as hydrothermal breakdown products of lignin. The breakdown pattern of nitrogen organics – characterized by high abundances of pyrazines and 2,5-diketopiperazines – along with their precursors will be detailed in a forthcoming contribution.

2. Materials and methods

2.1. Chemicals

All chemicals and solvents were purchased from Sigma–Aldrich (Munich, Germany); their purity was reagent or analytical grade. Chemicals included derivatization agents N,O-bis(trimethylsilyl) trifluoroacetamide) (BSTFA), 14% w/w boron-trifluoride methanol (BF_3/Meth), and acetic anhydride, as well as authentic standards, the latter listed in (Poerschmann et al., 2013). Briefly, authentic standards included phenols (benzyl alcohol, phenylethyl alcohol), aromatic acids (4-OH-benzoic acid, caffeic acid), short-chain acids (lactic acid, adipic acid), heterocyclic compounds (2-M-furan, furfural), mono- and diacylglycerines, as well as cyclopenten-1-ones, all of them obtained from Sigma–Aldrich. Isotopically labeled internal standards included phenol-d_6, hydroquinone-d_4, 4-M-catechol-d_3 (M: methyl; correspondingly E: ethyl throughout the text), palmitic acid-d_2, succinic acid-d_4, and phenanthrene-d_{10}. These chemicals were purchased from Cambridge Isotope Laboratories (Andover/MA, US).

2.2. HTC

The experiments were performed in a 200 mL bench-top laboratory autoclave (Roth Co., Karlsruhe, Germany). Fresh BSG was obtained from a local brewery in 2012 and immediately used as received. Its composition was very close to that of the biomass which was delivered in 2011 and used in a former publication (Poerschmann et al., 2014). In a nutshell, dry matter content of BSG amounted to 23.5%, OC-content was 51.3% (w/w, referred to dry matter), H-content was 6.7%, ash content was 4.5% and elemental ratio was determined as $C/N = 13$ ($g\,g^{-1}$). For reasons of easier handling, the biomass was diluted 1:1 with deionized water. The bench-top autoclave was filled with 50 g BSG and 50 mL of distilled water. The HTC parameters were chosen according to findings from previous HTC experiments with a wide array of biomasses (Poerschmann et al., 2013): operating temperature of 200 °C, reaction time of 14 h, and 80 $\mu g\,mL^{-1}$ of citric acid as catalyst. The pH of the slurry obtained after carbonization was 2.8; that of the native slurry was 7.0. The shift indicated the formation of carboxylic acids. After cooling to room temperature, the phases were separated by filtration and the aqueous phase was allowed to pass through a 0.45 μm cellulose filter. The concentration of dissolved organic carbon (DOC), which was determined by a TOC (total organic carbon) analyzer (Shimadzu, Duisburg/Germany), amounted to 14.5 $g\,L^{-1}$. The aqueous phase was subjected to lyophilisation. Likewise, the slurry (char plus process water) was subjected to lyophilisation. Prior to lyophilisation, both matrices were spiked with the array of isotopically labeled standards described in Section 2.1. (concentration ranging from 500 μg of palmitic acid-d_2 per g BSG substrate as dry matter to 10 $\mu g\,g^{-1}$ for phenanthrene-d_{10}). The lyophilization time was 72 h, as a result of that the humidity of the samples was reduced to 2–3%. Potential losses of volatile target analytes such as formic acid, and acetic acid were circumvented by ion chromatographic analysis, which supplements GC/MS analysis. Potential losses of volatile phenols were outbalanced by referring to the internal standard phenol-d_6.

2.3. Sample pretreatment

Lyophilizates were subjected to accelerated solvent extraction (ASE 300, ThermoFisher, Dreeich, Germany). The general experimental ASE design as applied here was detailed in Hubert et al. (2001). Briefly, extraction cell cartridges (11 mL) were filled with Hydromatrix (Merck) to about 50%, then a 200 mg aliquot of the sample to be extracted was added, finally the cartridge was filled to capacity with Hydromatrix. Extraction was performed with chloroform/methanol (2:1, v/v) at 100 °C for 15 min at 12 MPa, two cycles. Both solvents were distilled prior to use, and solvent blanks were examined. Beyond, solvents were sparged with helium so as to avoid oxidative cleavage of susceptible fatty acids (18:3 in particular) during the extraction procedure. Extracts of the slurry lyophilizate represented the total analyte