



Hydrothermal carbonization of olive mill wastewater



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HIGHLIGHTS

- ▶ The waste product olive mill wastewater was subjected to hydrothermal treatment.
- ▶ Biochar production is low due to low carbohydrate content.
- ▶ Simple biophenols are almost quantitatively released from aglycons during the process.
- ▶ Phenol, benzenediols, and carboxylic acids proved most abundant analytes.

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ABSTRACT

Hydrothermal carbonization (HTC) is an emerging technology to treat wet biomasses aimed at producing a biochar material. Herein, olive mill wastewater (OMW) was subjected to HTC. Mass balance considerations provide evidence that the yield of biochar is low (~30%, w/w), which is associated with a low fraction of carbohydrates in OMW.

The combination of different preparation schemes, pre-chromatographic derivatization reactions and GC/MS analysis for the analysis of organic compounds in aqueous HTC-solutions allowed to identify and quantify a wide array of analytes which belong either to intrinsic constituents of OMW or to characteristic HTC-breakdown products. Biophenols, such as hydroxyl-tyrosol (OH-Tyr), tyrosol (Tyr) account for the most abundant members of the first group. Most abundant breakdown products include phenol and benzenediols as well as short-chain organic acids. Secoiridoids, such as decarbomethoxy ligostride aglycon and decarbomethoxy oleuropein aglycon, all of them being typical components of OMW, are less abundant in HTC-solutions.

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1. Introduction

As a result of the olive oil production process, the waste product OMW is produced. It consists of vegetation water of olives, process water, and soft pulp tune in emulsified oil (Asses et al., 2009). The weight composition is 80–85% water, 14–18% organics and 1–2% minerals. As a rough estimate, the production process gives rise to an OMW yield of 0.5–1.5 m³ per 1000 kg of olives, which translates into an annual OMW-amount of over 30 million m³ worldwide (El-Abbassi et al., 2012). The wastewater is characterized by high chemical oxygen demand (COD), high biochemical oxygen demand (BOD), and high concentrations of (phytotoxic and antibacterial) phenols (Kavroulakis and Ntougias, 2010). Only 2% of the biophenolic fraction of OMW have passed into the desired olive oil phase, with remaining ~53% and ~45% being lost in OMW and the pomace (“olive cake”), respectively (Takac and Karakaya, 2009). Hydroxyl benzoic acids and their derivatives, hydroxyl

cinnamic acids and derivatives, phenyl ethyl alcohols, flavonols, flavones, lignans, and isochromans, as well as secoiridoids account for biophenolic compounds of both virgin olive oils and aqueous OMW (Bendini et al., 2007). Compounds with higher molecular weight, which account for phytotoxicity, antibacterial activity and the dark color of OMW and which are considered basically resistant to biodegradation, are generated as a result of condensation of monocyclic aromatic phenols and acids during processing and storage. Biophenols are promising targets for food and pharmaceutical industries due to their biological activities and natural abundance.

Challenges focussing on the utilization of OMW are bivalent: on the one hand the necessity to treat OMW to minimize environmental hazards, and on the other hand the necessity to capture reusable materials from the waste biomass. At present, conventional wastewater treatment methods are relatively ineffective to reduce environmental hazards, which is due to limited biodegradability of (phytotoxic) phenols (see (Sampedro et al., 2009) and references cited therein). The utilization of this feedstock for energy production, carbon sequestration, or improvement of soil fertility

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(Libra et al., 2011) is impeded by biomass-specific limitations, i.e. the high degree of heterogeneity in form, composition and water content, and OMW-specific limitations (phytotoxicity, biodegradation-resistant organics, seasonal nature of production, high regional scattering of olive mills). Thus, economically feasible conversion processes for more efficient utilization, which ought to be environmentally friendly and decentralized in operation, are necessary. This strategy gains further momentum if associated with preventing potential ecotoxicological hazards.

Following this line, a promising approach is HTC (Titirici et al., 2008). Wet biomasses are reacted in subcritical water at 180–250 °C in the presence of a catalyst such as citric acid to produce a highly carbonaceous biochar. The feedstock decomposition is dominated by hydrolysis as the initial degradation step, followed by dehydration, decarboxylation, and subsequent recondensation and aromatization reactions. The hot water acts as solvent and reactant. Its dielectric constant is lowered at higher temperatures, thus driving the solvation characteristics of water towards that of polar organic solvents (see (Yang et al., 1995) and references cited therein). In addition to the desirable solid, an aqueous solution rich in dissolved organic matter (DOM) is produced during hydrothermal treatment (Funke and Ziegler, 2009). The aqueous DOM-phase is an undesirable side-product, because valuable organic carbon (OC) is withdrawn from biochar formation. The characterization of a wide array of aqueous HTC-phases with regard to bulk parameters has been the subject of several publications (see (Libra et al., 2011) and references cited therein). However, data on the detailed characterization of aqueous HTC-matrices on the molecular level are scarce. In most cases quantitative data about the organic compounds in aqueous HTC-solutions are missing. Semi-quantitative data were given at best (Berge et al., 2011; Hoekman et al., 2011).

Qualitative and quantitative data of organic compounds on the molecular level are expected to provide further insight in the HTC-reaction mechanisms, to provide information on surrogates formed in the hydrothermal process, and on potential ecotoxicological hazards of the aqueous HTC-phase. HTC of OMW should be evaluated both as a decontamination process, and as a process to produce biochar. Potential applications of the produced biochar include soil amelioration, as sorbent for wastewater treatment or an energetic utilization. A potential application of the aqueous HTC-phase includes its utilization as substrate for biogas or biofuel production. Due to decomposition of high molecular weight compounds into smaller units during hydrothermal treatment, the HTC-phase rich in DOM is expected to be less recalcitrant for microbial conversion than the feedstock OMW. The DOM may also be used as substrate for wet oxidation processes, e.g. for energetic reasons or to reduce the DOM-content.

Herein, the usefulness of HTC to treat OMW is studied. Special attention was put (i) to the structural identification of organic compounds occurring in the aqueous HTC-solution, and (ii) to elucidate the pathways of feedstock-OC and inorganic constituents during the hydrothermal procedure. To this end, the HTC-solutions were lyophilized, subsequently subjected to exhaustive solvent extraction, followed by derivatization of the extracts and GC/MS analysis. To the best of our knowledge, detailed HTC studies with OMW as substrate have not been reported up to date.

2. Methods

2.1. Chemicals

All chemicals applied in the framework of this contribution were reagent or analytical grade, and were used as received without any further purification. Isotopically labeled internal standards phenol-d₆, hydroquinone-d₄, 4-M-catechol-d₃ (M: methyl

throughout the text), n-amylalcohol-d₁₂, palmitic acid-d₂, capronic acid-d₁₁, succinic acid-d₄, and phenanthrene-d₁₀ were purchased from CIL (Cambridge Isotope Lab., Andover/MA). To facilitate structural identification and quantification, an array of authentic standards including 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), glucose, and glycerol was obtained from Sigma/Aldrich (Munich, Germany) and Merck (Darmstadt, Germany). The silylation agents BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) and MTBSTFA to generate trimethylsilyl (TMS) derivatives and tert-butyl dimethylsilyl derivatives, respectively, as well as boron trifluoride (BF₃) in methanol (14% w/w) to produce methyl esters, were purchased from Sigma/Aldrich.

2.2. HTC

HTC experiments were conducted in a 200 mL lab-scale autoclave Modell II (Carl Roth, Karlsruhe) equipped with thermometer and pressure gauge. The wastewater was used as received, i.e. in non-diluted form from an olive oil mill facility in the Tuscany region. Citric acid (100 mg L⁻¹) was used as catalyst. A temperature of 220 °C or 180 °C was applied for 14 h. The HTC-reaction in the closed vessel proceeds under self-generated (autogenous) pressures. The pressures were measured to be 24 bar (220 °C) and 9 bar (180 °C).

The pH of the HTC-slurry was 2.8 (pH of native OMW: 4.8) indicating the generation of carboxylic acids. The HTC-slurry was allowed to pass through a 0.45 μm cellulose filter. After phase separation, the aqueous phase was subjected to lyophilization, and the solid biochar was dried at 105 °C for 4 h for elemental analysis and X-ray fluorescence spectroscopy. If not otherwise specified, the results presented below refer to HTC-experiments performed at 220 °C.

2.3. Elemental analysis, RFA, bulk parameters

An automatic analyzer LECO model CHN 932 was used to determine C, H, N and S in the lyophilized matrix. Dried samples were ground in a mortar for homogenization. The oxygen concentration was calculated from the difference between the ash-free dry weight and the combined weight of the measured elements.

X-ray fluorescence measurements were performed using a WDXRF-spectrometer S4 PIONEER (Bruker-AXS), equipped with a 4 kW-Rh X-ray tube (75 lm Be window) and a 60 kV generator.

Total organic carbon (TOC) was analyzed by a TOC analyzer (Shimadzu, TOC 600, Duisburg, Germany). The determination of the chemical oxygen demand (COD) was carried out as a DIN-compatible micro-method with chromo-sulfuric acid (cuvette test kit from HACH LANGE GmbH, Duesseldorf, Germany). The BOD was measured manometrically with a WTW BOD-analyzer OxiTop® IS 6, according to the DIN-method 38 409 – H51/H52. All samples were dried at 105 °C prior to analysis due to their hygroscopic characteristics.

2.4. Solvent extraction/saponification/derivatization

The HTC-slurry, which contains both biochar and DOM, was allowed to pass through a 0.45 μm membrane filter. Afterwards, internal deuterated standards were spiked into the aqueous filtrate prior to lyophilization. Extraction of lyophilizates (~500 mg each) was performed by pressurized liquid extraction with methanol/chloroform (9:1, v/v) (2 cycles at temperatures of 80 °C, each 15 min). The combined extracts were gently evaporated, chloroform (~100 μL) was added to each of the “greasy” residues. The chloroform extracts were subjected to silylation according to

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