Chemical Engineering Journal 279 (2015) 715–724

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Combination of hydrothermal carbonization and wet oxidation of various biomasses

Gotthart Riedel, Robert Koehler, Juergen Poerschmann, Frank-Dieter Kopinke, Barbara Weiner *

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

HIGHLIGHTS

- Process waters from HTC of various biomasses were treated by wet oxidation.
- Iron-salts increased the efficiency of the wet oxidation.
- Chemical oxygen demand of the process waters was reduced by up to 55%.
- Oxidized waters showed improved biodegradability.
- Wet oxidation at mild conditions of 120 °C generates sufficient heat for HTC process.

ARTICLE INFO

Article history:
Received 2 February 2015
Received in revised form 6 May 2015
Accepted 25 May 2015
Available online 28 May 2015

Keywords:
Hydrothermal carbonization
Wet oxidation
Chemical oxygen demand
Dissolved organic carbon
Biochar

ABSTRACT

Wet oxidation (WO) treatment was performed on process waters obtained from hydrothermal carbonization (HTC) of sucrose, cellulose, wood, and brewer's spent grains with oxygen at 3 MPa and temperatures of 120–200 °C. The aim was to reduce the dissolved organic carbon (DOC) content and chemical oxygen demand (COD) of the process water in order to reduce toxicity, enhance biodegradability and supply heat to improve the preceding HTC process. Success of the treatment was evaluated on reduction of COD and DOC. Iron-salts were identified as suitable catalyst to increase the efficiency of the WO. At 200 °C DOC and COD elimination was for all biomasses around 40% and 55%, respectively. At 120 °C, DOC and COD reduction of sucrose, cellulose and wood process waters was around 20–30% and 40%, respectively. Products from brewer's spent grains HTC proved more resistant towards oxidation. The biodegradability of the process waters was improved as shown by increased BOD/COD ratios. The results provided evidence that WO at mild conditions of 120 °C can generate sufficient heat to sustain the HTC process in an autothermal regime. Moreover, WO showed the potential to degrade the recalcitrant chlorinated aromatics 2,4-dichlorophenol and 2-chloronaphthalene. In addition to HTC process waters, unseparated HTC slurries, *i.e.* hydrochars and process waters, were subjected to WO. At mild oxidation conditions of 120 °C, the dissolved organic matter was preferentially oxidized while the hydrochar retained its quality. However, oxidation temperatures of 200 °C led to a significant degradation of the hydrochars, while DOC and COD content were not reduced.

1. Introduction

Hydrothermal carbonization (HTC) is a promising method for upgrading waste biomass streams to valuable products. HTC can be used to produce solid carbonaceous materials (hydrochars) from various waste biomasses, *e.g.* municipal waste streams [1], sewage sludge [2–4], manure [5], fecal biomass [6], brewer's spent grain [7], or green/organic wastes. Several different uses for hydrochars from HTC are proposed and currently under investigation, *e.g.* as solid fuel, soil amendment, fertilizer, or designer nanomaterials [8]. Hydrochars can possess preferable properties over the untreated biomass, such as improved dewaterability and higher heating value. HTC is advantageous for waste treatment as the reaction temperatures >180 °C lead to hygienization of the materials by complete elimination of pathogens. Moreover, recalcitrant compounds found in waste streams like pharmaceuticals, pesticides, or industrial chemicals can be degraded under HTC conditions [9]. However, other chemicals such as chlorinated aromatics are found to be stable under the applied conditions [9].

There are some challenges that the HTC process needs to overcome prior to industrial scale application. Two of these are (i) the

---

* Corresponding author. Tel.: +49 3412351573; fax: +49 3412351471.
E-mail address: barbara.weiner@ufz.de (B. Weiner).

http://dx.doi.org/10.1016/j.cej.2015.05.086
1385-8947/

energy efficiency of the process and (ii) the process water (PW) treatment. The reaction enthalpy of HTC was calculated to be negative, *i.e.* heat will be released during the carbonization reactions [10]. Nevertheless, up to date no results have been reported, in which the process has been run de facto self-sustainingly [11].

Secondly, the PW is a bottleneck in the HTC process as it can contain toxic or recalcitrant substances. The PW has generally a high content of dissolved organic carbon (DOC) and a high chemical oxygen demand (COD). Values above 10 g-C L^{-1} and 20 g-O_2 L^{-1} are very common [12]. The carbon content equals about 15–40% of the feedstock carbon depending on HTC reaction conditions and feedstock source [4]. The carbon yield in the hydrochar can be increased by recirculation of the PW, which is also favorable for heat recovery [13,14]. The biodegradability seems to be mainly determined by the feedstock, HTC process parameters, and potential toxic substances. Nevertheless, the high COD precludes a dispose in urban wastewater treatment plants and requires a separate pretreatment.

A combination of HTC with a wet oxidation (WO) of the PW could solve both problems and enable HTC as a waste treatment technology especially for contaminated waste streams.

WO is an established technique for treatment of industrial wastewaters with high carbon contents (up to 100 g-C L^{-1}) [15–17]. It has been widely studied for the treatment of different wastewaters and degradation of pollutants [18,19]. Typical reaction conditions of the WO are elevated temperatures (100–320 °C) and pressures (0.5–20 MPa) using pure oxygen or air as an oxidizing agent. WO is capable to mineralize organic material to CO_2, H_2O, and inorganic salts. Short chain carboxylic acids such as acetic acid are typical products when incomplete DOC removal is achieved. In contrast to biological treatment methods, WO has no limitations with respect to toxicity or carbon content. The costs of WO are mainly determined by the reaction conditions, as high temperatures and pressures require expensive materials for the reactor. Air or oxygen as oxidizing agents are inexpensive and readily available. With chemical oxygen demands (COD) higher than 12–15 g-O_2 L^{-1}, WO generates enough heat to become self-sustaining [18]. Therefore, no continued heating is required after an initial heating phase. A combination of HTC and WO is favorable, as the reaction conditions of HTC and WO are alike and have similar requirements with respect to the reactor design. Furthermore, WO can treat the highly contaminated PW regardless of any toxic compounds. The oxidized PW is expected to be less toxic and could enable a subsequent biological treatment.

In a previous study it has been shown that the oxidation of HTC slurries, *i.e.* unseparated PW and hydrochar, can provide a sufficient amount of heat to support the HTC [20]. However, a selective oxidation of the dissolved compounds in the presence of the particulate char has not been achieved [20]. The hydrochars were significantly oxidized and degraded while at the same time the DOC content in the PW was not reduced.

The aim of this work was to find suitable reaction conditions and catalysts to treat the PW from HTC efficiently by WO under mild conditions. Different feedstocks (sucrose, cellulose, brewer's spent grains, and wood) were investigated and compared among each other. The success of the oxidation was measured by changes in the sum parameters of DOC and COD. Ion chromatography was used to quantify acetic, formic and lactic acids in the process waters. The potential of the WO post-treatment to facilitate the degradation of recalcitrant chlorinated aromatic contaminants was examined for 2,4-dichlorophenol and 2-chloronaphthalene.

The HTC reaction mixture is complex and a change in heat during the reaction is difficult to measure *in situ* with current calorimetric methods. Therefore, the heat of reaction was estimated on basis of the COD using the Thornton rule (Eq. (1)). Furthermore, biodegradability was assessed on the basis of BOD/COD values.

2. Materials and methods

2.1. Hydrothermal carbonization

BSG was obtained from Reudnitzer Brewery Leipzig, Germany, and stored at −18 °C until use. BSG was dried at 105 °C for 24 h before use for long-term storage and easier handling. Household sugar was used as sucrose source. Microcrystalline cellulose was purchased from Aldrich. Chipped wood waste from a carpenter's workshop in Leipzig, Germany, was used as wood feedstock. The hydrothermal process was performed in an autoclave with a capacity of 200 mL (Roth, Germany) filled with 20 g biomass (10 wt.% dry mass) and 200 mL of 10 mM aqueous sulfuric acid solution. The operating temperature was 200 °C and reaction time 16 h.

The obtained HTC slurry was allowed to pass through filter paper (Whatman™ 595 ½, 4–7 μm, GE Healthcare, U.K.). The hydrochar was washed two times with deionized water (100 mL each) and dried at 110 °C for 24 h. The filtrate, in the following called process water (PW), was stored at 4 °C until further use.

2.2. Wet oxidation

2.2.1. Wet oxidation of separated process waters

The O_2 atmosphere in stainless steel autoclaves (in-house built, $V = 30$ mL, $d_{\text{inner}} = 24$ mm) was generated *in situ* by decomposition of H_2O_2. In-house designed glass inserts ($d_{\text{inner}} = 10$–12 mm, $h = 55$ mm) equipped with a magnetic stirring bar were used for WO experiments preventing direct contact between PW and peroxide. They were filled with the PW and the solid catalyst and put into the autoclaves. As catalyst $FeSO_4 * 7H_2O$ (Merck), $MnSO_4 * H_2O$ (Sigma–Aldrich), $FeCl_3 * 6H_2O$ (Merck), or $CuSO_4 * 5H_2O$ (Merck) were used. A calculated amount of 30% H_2O_2 solution was filled in the gap between glass insert and autoclave wall (Table S1). Then, 0.5% aqueous $FeCl_3$ solution (0.1 mL) was added to the H_2O_2 to catalyze the thermal degradation, and the autoclaves were quickly closed. The autoclaves were heated to 50 °C for 1 h to guarantee complete decomposition of H_2O_2 and then heated further to the desired WO temperature. The reaction mixture was continuously stirred. After the desired reaction time, the autoclaves were allowed to cool down to room temperature. The reaction slurry was removed with a syringe and filtered through a folded filter (MN 615 ¼, 4–12 μm, Macherey–Nagel, Germany). The filtrate was stored at 4 °C, and the solid was dried at 110 °C for 24 h. All WO experiments were performed two to four times under identical conditions. Scattering values correspond to standard deviations among individual runs ($n = 2$–4).

If not stated otherwise, reaction conditions were for HTC: 200 °C, 16 h, 10 wt.% dry mass, 200 mL of 10 mM H_2SO_4, and for WO: 1 h at 50 °C and 1 h at higher indicated temperature, 3 MPa of O_2 pressure, 4 mL of PW and 50 mM of Fe(II). The WO conditions ensure a large surplus of available oxygen ($\geqslant$threefold) related to the COD of the PW such that any oxygen limitation is prevented.

2.2.2. Wet oxidation of HTC slurries

A defined amount of dried char (see Table S2 for details) was weighed into the glass insert and a magnetic stirring bar was added. The inserts were closed leaving a small hole in the top to ensure that H_2O_2 would not spill into the HTC solution, but O_2–gas could pass through. The catalyst was added either as a solid or dissolved in water via a syringe together with the PW. The WO was performed as described in the previous section.

2.2.3. Degradation of chlorinated organic compounds

In the glass insert, 10 mM aqueous H_2SO_4 solution or sucrose PW were spiked with 100 μL of a 2000 mg L^{-1} stock solution of