



Py-GC-MS of hydrochars produced from brewer's spent grains

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ABSTRACT

The aim of the study was to understand pyrolysis behavior and analyze the influence of hydrothermal carbonization (HTC) pretreatment on the volatile matter released during pyrolysis of hydrochars, produced from brewer's spent grains (BSG). The Py-GC-MS was used to analyze the pyrolysis products. The measurements were conducted for three hydrochars produced from BSG at different HTC conditions: (i) 180 °C, 4 h; (ii) 220 °C, 2 h; and (iii) 220 °C, 4 h, and the precursor BSG. The sample was pyrolyzed in the sequence at 300, 400, 500, and 600 °C with a heating rate of 500 °C min⁻¹ and residence time 15 s. Pyrolysis of BSG resulted in more phenolic compounds than hydrochars produced at mild conditions (HTC-180-4 and HTC-220-2). Pyrolysis of high-temperature hydrochar (HTC-220-4) showed the highest share of phenols due to the conversion of furan rings into benzene rings during HTC. Hydrochars (HTC-180-4 and HTC-220-2) produced more furans, and other cyclic oxygen compounds compared to the initial biomass. A significant amount of N-compounds was detected at low pyrolysis temperature for spent grains due to weakly bonded proteins into the biomass structure. However, hydrochars were characterized by fewer N-compounds compared to BSG because of the Maillard reaction occurred during hydrothermal pretreatment leading to more stable N-heterocycles structures. Increased severity during the HTC resulted in a higher share of N-compounds found during Py-GC-MS.

1. Introduction

Biomass is a potential source for overcoming the dependence of fossil resources for the production of energy, fuels, chemicals, and carbon materials. The transformations of the bio-based feedstock into several valuable products, via different thermochemical or biochemical technologies, are considered as the concept of the bio-refinery. One of the most developed biomass thermochemical conversion technology used since ancient times is pyrolysis. The process consists of material decomposition under elevated temperature in the absence of oxygen. It results in the production of a solid residue called biochar, condensable organic matter called bio-oil, and non-condensable gases. However, pyrolysis is considered as the dry conversion technology. Therefore, it is necessary to dry the feedstock before the process. The drying of biomass requires huge amounts of energy, due to this, the possible feedstock for the conversion is limited to a biomass with reasonable moisture content. There are many lignocellulose waste streams which are characterized by high moisture content, e.g., agricultural or food industry residues. These materials can be converted using hydrothermal carbonization (HTC) avoiding the drying process and related costs. The

advantage of the hydrothermal carbonization process is the utilization of liquid water as a reaction medium; therefore, wet feedstock with water content up to 90 wt. % can be converted without previous drying. HTC operates at relatively mild temperatures (180–260 °C) and elevated pressure (above saturated steam pressure) to keep the water in liquid phase [1–7]. During the HTC process, the series of complex reaction occurs including hydrolysis, dehydration, decarboxylation, condensation, aromatization, and polymerization [2]. It results in the conversion of biopolymers contained into biomass; the hemicelluloses start to decompose at 180 °C, then celluloses start the degradation at 200 °C while lignin is converted at very low extend [2]. The final solid product called hydrochar is created in two pathways: i) polymerization of solvated intermediates in the liquid phase, mainly 5-hydroxymethylfurfural (HMF) and ii) carbonization of the remaining solid [2,3,8]. Additionally, the liquid reaction medium eliminates/minimizes the heat transfer limitations compared to the dry conversion technologies.

In this work, brewer's spent grains (BSG) were selected for analysis as a potential feedstock for a cascaded hydrothermal carbonization followed by pyrolysis process due to high water content (after prior

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mechanical dewatering) 70–90 wt. % and huge worldwide production [9,10]. BSG is a waste lignocellulose stream generated by the brewing industry. The properties of BSG depend on used barley and the brewing technology. Nevertheless, typical reported [11,12] composition consists of hemicellulose (21.8–40.2), cellulose (12.0–25.4), lignin (4.0–27.8¹), proteins (14.2–26.7), and lipids (3.9–13.3) in the wt. % dry basis.

For all those purposes, fundamental pyrolysis study of volatile matter released during thermal decomposition of hydrochars and the initial brewer's spent grains is necessary to understand the pyrolysis mechanism, and, as a consequence, also the combustion behavior. Hydrochars were produced at different process conditions: i) 180 °C, 4 h residence time; ii) 220 °C, 2 h residence time; and iii) 220 °C, 4 h residence time, to investigate the influence of HTC pretreatment for released pyrolysis vapors. All materials were pyrolyzed using Py-GC-MS to minimize the effect of the secondary reaction of the volatiles.

2. Methodology

2.1. Materials

The biomass for the experiments was supplied by local brewery Hoepfner (Karlsruhe, Germany). The as-received brewer's spent grains (after prior mechanical dewatering) had a moisture content of ca. 78 wt. %. Part of the biomass was dried at 105 °C to constant mass and ground to achieve a particle size below 200 µm for further analysis. The biomass was labeled as BSG and collected in a plastic zip bag. The rest of the biomass, to be used for further hydrothermal carbonization, was stored in the freezer at -15 °C to avoid microbial attacks and keep the moisture content as close as possible to original biomass.

The HTC of BSG was carried out in a batch stainless steel autoclave of the volume of 250 mL, equipped with temperature and pressure sensor. Around 150 g of wet BSG (adjusted moisture content with deionized water to 80 wt. %) was filled into the reactor for each experiment. The biomass was mixed and slightly pressed in the reactor with a spatula to cover the biomass with water. The reactor was placed in a GC oven (Hewlett Packard, GC 5890) and heated up to the desired temperature inside of the reactor in around 1 h. Then, the reactor was kept at the desired temperature for a set residence time. When the reaction time was completed, the reactor was removed from the GC oven and quenched in cold water to the room temperature. Subsequently, the hydrochars were filtered using a paper filter (Qualitative filter paper 413, 5–13 µm, VWR European Cat, France) and a Büchner funnel. No extra water was added during the filtration. Afterward, the hydrochars were dried overnight at 105 °C and next ground to achieve particle size below 200 µm. The hydrochars were produced in three different process conditions: (i) 180 °C, 4 h residence time; (ii) 220 °C, 2 h; and (iii) 220 °C, 4 h. The hydrochars were labeled as HTC-180-4, HTC-220-2, HTC-220-4, respectively, and stored in plastic zip bags.

Additionally, a series of pyrolysis experiments were carried out using a thermogravimetric analyzer STA Jupiter 449 F5 (Netzsch, Germany). The biomass and the hydrochars were pyrolyzed at 500 °C with a heating rate of 10 °C min⁻¹, nitrogen flow of 70 mL min⁻¹, and a residence time of 10 min. Around 40 mg of each sample was used for each experiment. The obtained pyrochars were named Py-BSG, Py-HTC-180-4, Py-HTC-220-2, and Py-HTC-220-4, respectively.

2.2. Characterization of the materials

The elemental analysis of pyrochars was conducted using CHNS-O analyzer Euro EA 3000 Serie (EuroVector, Italy). Properties of biomass and hydrochars used for Py-GC-MS study were published elsewhere [13]. Additional information about hydrothermal carbonization products (HPLC of HTC liquid, TGA of hydrochars, ultimate, and proximate

analysis) as well as the detailed characterization methodology are described therein [13].

2.3. Py-GC-MS

The decomposition studies of brewer's spent grains and hydrochars were carried out using pyrolysis and gas chromatography coupled to mass spectrometry (GC-MS) technique. Pyrolysis experiments were carried out using a Pyroprobe model 5200 (CDS Analytical), while the evolved during pyrolysis mixtures analyses were performed on GC-MS Agilent type GC 7890B equipped with an MS 5977 A mass spectrometer. The pyrolysis tests were conducted at four different temperatures (300, 400, 500, and 600 °C) with a heating rate of 500 °C s⁻¹ and held time 15 s. The mass of a sample used for each experiment was around 2.4–2.6 mg. The sample was placed inside a quartz tube, which was subsequently plugged from both sides with quartz wool and set at platinum filament. Before pyrolysis tests, the sample was purged from air with an inert gas (Helium) for ca. 10 min. The pyrolysis was carried out in the direct mode, so the GC analysis was started when the Pyroprobe filament was begun heating up. The sample was pyrolyzed in sequence, starting at 300 °C, and following (the same sample) was heated to 400 °C, 500 °C, and 600 °C. After each pyrolysis step, the platinum filament with the sample inside was kept at 50 °C in inert gas atmosphere waiting for GC-MS apparatus to be ready for the next measurement. When the GC-MS measurement was accomplished, the Pyroprobe started the next pyrolysis step. The analytes evolved during each decomposition step were transferred for the analysis to GC-MS via a transfer line. Pyrolysis interface and the transfer line were kept at 300 °C. The Agilent HP-5MS capillary column of dimensions of 30 m × 0.25 mm × 0.25 µm was used. Helium of a grade of 6.0 was used as a carrier gas at a flow rate of 1.0 mL min⁻¹. The GC injector temperature was kept at 300 °C. The analysis was performed at a split ratio of 25:1. The oven temperature was initially set to 40 °C with a hold time of 7 min, and then increased to 4 °C min⁻¹ until 250 °C. The ion source temperature was 230 °C, electron ionization was set at 70 eV, and spectra were scanned from 10 to 350 m/z. The obtained MS spectra were interpreted based on the reference MS library (chemical base G1034C). The threshold for the match factor calculated based on electronic library search routines was equal to 75%.

Additionally, the results were checked manually. Each analysis was repeated at least twice. The detected compounds were classified into seven groups (i.e., phenols, furans, carboxylic acids and esters, other aliphatic oxygen compounds, other cyclic oxygen compounds, N-compounds, hydrocarbons, complex compounds) and their relative shares for a single pyrolysis step were calculated as the ratio of peak area of all compounds within the group to the summary peak area of all detected compounds. The accumulative share at 500 °C were calculated as the ratio of the sum of peak areas of each group to the summary peak area of all groups at three pyrolysis steps (300, 400, and 500 °C). The presented results were calculated as an arithmetic mean (AM) value of all repetitions including the standard deviation (SD) to present the precision. Peak area was determined in the total ion mode. The permanent gases were excluded from the results to increase the visibility of changes occurred in the non-condensable volatiles.

3. Results

3.1. Materials characteristic

The hydrochar yields were 67.5, 58.0, and 55.0 wt. % on dry basis, for HTC-180-4, HTC-220-2, and HTC-220-4, respectively [13]. There are currently a few studies related to hydrothermal carbonization of brewer's spent grains. Velebil et al. [14] presented the hydrochar yield of 72.9 and 71.7 wt. % at 180 °C for 2 h, and 5 h residence time, respectively. On the other hand, experiments carried out at 215 °C resulted in 64.8 and 59.2 wt. % for 2 h and 5 h, respectively. Ulbrich et al.

¹ This value seems to be high.

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