On the selective desulphurization of biomass derivatives in supercritical water

David Baudouin a,*, Hang Xiang a, Frédéric Vogel a, b

a Laboratory for Bioenergy and Catalysis, Paul Scherrer Institute (PSI), 5232 Villigen PSI, Switzerland
b Institute for Biomass and Resource Efficiency, University of Applied Sciences Northwestern Switzerland (FHNW), 5210 Windisch, Switzerland

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ABSTRACT

The nature of organosulfur compounds formed during the reductive supercritical water treatment of sewage sludge, miscanthus and Spirulina was investigated by gas chromatography coupled to a sulphur chemiluminescence detector (GC-SCD). Methanethiol was found to be the dominating species after hydrothermal liquefaction and gasification of all process waters, along with its derivatives dimethyl disulphide and dimethyl trisulphide, likely formed upon quenching and/or after sampling. Various alkylthiophenes, short-chain sulphides and their corresponding disulphides were also found in varying amounts strongly depending on the biomass used. Various commercial sulphur absorbing materials and pure oxide nanoparticles were tested under supercritical water conditions to selectively desulphurize the various mixtures. Cu-based materials were found to be the most active in desulphurizing the organic mixture in hydrothermal conditions as well as absorbing sulphur. ZnO, MoO3, MnO and CeO2 were found to have an intermediate activity in decreasing organosulphur compounds concentration but had a good sulphur absorption capacity. Surprisingly, only Zn and Mn materials led to the formation of crystalline sulfide phases. Iron oxide showed intermediate desulphurization but surprisingly no sulphide absorption capabilities. All of these materials suffered various extents of sintering/coarsening under such harsh conditions, with cerium oxide showing very good structural and crystalline stability. All these results orientate further development of absorbing materials and/or catalysts for selective desulphurization of biomass under hydrothermal conditions.

1. Introduction

Hydrothermal processing of wet biomass aims at producing liquid bio-oils or gases in hot pressurized water (p ≈ 20–30 MPa, T ≈ 623–723 K) without the requirement for an energy-demanding drying step [1]. Hydrothermal liquefaction represents an interesting approach for the production of renewable liquid fuels, which remains unavoidable for aviation or sea and heavy-duty road transportation. In parallel, the production of synthetic natural gas (SNG) from hydrothermal gasification (HTG) brings a significant advantage over traditional technologies [2, 3]. It is particularly relevant when coupled with supercritical water-assisted recovery of inorganics for the production of fertilizer [4] such as phosphorus.

Catalytic hydrothermal gasification (cHTG) is a promising way to produce bio-methane from wet biomass with high-energy efficiency [5–7]. Ru/C catalyst is typically used to produce methane-rich biogas at low temperatures (653–723 K) [1, 7]. To protect the catalyst from poisoning by the sulphur present in biomass, a two steps process is typically applied. First, salts such as sulphates and sulphites are separated from the main stream thanks to their low solubility in supercritical water (SCW) [8, 9] or in subcritical water [10, 11]. This first step is necessary as sulphate can be reduced to H2S or organosulfur compounds via a thermochemical sulphate reduction (TSR) [12, 13]. The desalinated stream produced then goes through a desulphurization material ideally both to absorb H2S and desulphurize the stream, i.e. decompose organosulfur compounds, before it reaches the gasification catalyst downstream [7, 14].

Under the conditions used for hydrothermal liquefaction or gasification, the reductive (near)supercritical water conditions thermodynamically favour the full conversion of sulphur into H2S [25]. However, the kinetic of the many reactions involved can be rather slow. The chemistry of various organosulfur compounds present in fossil crudes has been studied under various hydrothermal conditions [26, 27]. Compounds such as alkylthiols, disulphides or with lower oxidation
states have shown low stability under hydrothermal conditions while aromatic or conjugated compounds such as aryl- or benzo-thiophenes, show rather high stability [26,28–30]. However, little is known about the nature of organosulphur compounds formed during the reductive hydrothermal treatment of biomass. Recent work identified several organosulphur compounds in the biogas produced during the hydrothermal treatment of sewage sludge [31]. Along with H₂S, the concentration of methanethiol, ethanethiol, dimethyl sulphide and dimethyl disulphide were found to increase with the temperature rising from 633 to 713 K. The characterization of the compounds present in the liquid phase indicates the presence of some thiophenes and thiols, but the identification of several compounds remains to be confirmed.

Under such conditions, absorption of sulphur is typically done using an absorbent based on zinc oxide [3,14], or using a nickel-based material [7,15] which increased the life expectancy of the Ru/C catalyst downstream when processing biomass. In parallel, various works on SCW desulphurization of fossil crudes have been made which outlined that some materials such as ZnO or MoO₂ could non-british desulphurization of model solutions such as dibenzothiophene in hexadecane under supercritical water [16]. Under these particularly harsh conditions, only a few metals or oxides have proved good long-term stability [17–20]. The commercial sulphur absorbents tested so far have low stability in SCW and consequently proved to have limited performance. Indeed, the porous network of commercial ZnO-based absorbent has shown to decrease significantly after exposure to SCW with a loss of material accumulating on the catalyst downstream [3,21], while nickel typically experiences important sintering and coarsening under such conditions [22–24]. MoO₂ material however suffered severe sintering and phase transformation [16].

In this paper, we aimed at studying the nature and concentration of organosulphur compounds present in samples produced from sewage sludge, Miscanthus and Spirulina under hydrothermal liquefaction and gasification conditions using. For that, the use of gas chromatography coupled to a sulphur chemiluminescence detector (GC-SCD) was decisive. In parallel, the identification of alternative or complementary materials for the desulphurization of biomass streams under supercritical water was carried out with both the aim to absorb H₂S and to catalyze the decomposition of organosulphur compounds.

2. Materials and methods

2.1. Process water from HTL

The feed used in this study is a process water produced from the hydrothermal liquefaction (HTL) of Spirulina at 623 K and 22 MPa following the conditions reported in Ref. [32]. Process waters produced from sewage sludge and Miscanthus were also used. In the case of Miscanthus, a KOH catalyst was co-fed with the slurry.

2.2. Sulphur absorption materials (sulphur scavengers)

The materials tested were provided by Sulphatrapp (R7N®1), Cabot (Norit RGM 3, Darco H2S). The commercial sample names used throughout the manuscript are based on their main constituents: Mn-Cu, Cu-Mo/AC and Fe-/AC respectively (AC stands for activated carbon). One commercially available ZnO-based material was also tested and is referred to as ZnO. All these materials are sometimes referred to here as sulphur scavengers.

Pure commercial metal oxide (MO₃) nanoparticles (NPs) were purchased from US Research Nanomaterials Inc (NP–ZnO, NP-CuO, NP-MoO₃, NP-MnO₂, NP-Fe₂O₃) and Riedel-de Haen (NP–CeO₂) as fine powder, dispersed and sonicated in water before use. The Ru mass fraction of Ru/AC catalyst was 5% and activated carbon support were purchased from BASF.

2.3. Batch reactor: stability tests and desulphurization of HTL process waters

The various sulphur absorption materials were aged in a supercritical water environment (718–728 K, 29–32 MPa) for 24 h (some for 36 h when indicated) in order to assess their stability.

The various HTL process waters with and without S-scavengers were tested under the same conditions in order to evaluate the nature and concentration of organosulphur compounds present under these conditions. For all experiments, 6.7 ml of water (pure or HTL process water) was added to the reactor, to which was optionally added an amount of sulphur scavenger or metal oxides nanoparticles so that the absorbing metal to total sulphur ratio was kept at M:S = 20 and 10, respectively. In the case of Ru/AC catalyst, a Ru:S ratio of 2 was used, while for activated carbon, about the same amount of material was used in the test as for Cu–Mo/AC and Ru/AC.

The tests were performed using a batch reactor (BR) with 28 ml volume, see details in Ref. [33]. Once closed, a fluidized sand bath (IPBS1, Teche) was used to quickly heat the BR within ca. 15 min. The total volume of the aqueous feed was always set at 6.7 ml in order to reach 29 ± 1 MPa at 723 K. The reaction time for all the experiments was 18 min (taken from when the BR temperature reached 623 K).

After the batch tests, the reactor was quenched by immersion in room temperature water. The volume of gas produced was calculated from the ideal gas law using the pressure and temperature measured within the reactor. The BR was then depressurized and the gas was discharged and sampled into a 3 L gas bag (Multi-Layer Foil, RESTEK) for immediate gas-phase analysis by a µGC (Micro GC Fusion, INFICON). 4 ml of iso-propanol were then added to the reactor to allow the dissolution of most organics and homogenization of the solution. The liquid was separated from the solid and sampled for further analysis. For metal oxide nanoparticles, the solids were washed with ethanol, and then water (3 times each), before drying at 383 K. Several blank tests (with 6.7 ml of pure water) were also performed from which no organic compounds could be detected by GC coupled to a flame ionization detector (FID) and a very small amount of organosulphur compounds were detected by GC-SCD (lower detection limit). These organoS compounds were left over from the most abundant compounds detected in the previous test (peak intensity in experiment n was less than 1% of that of experiment n-1). Reproducibility tests with ZnO and with the solution alone were performed two and three times, respectively, and showed less than 8% deviation.

2.4. Analytical procedures

Light organic sulphur compounds in the liquid samples were analyzed by gas chromatography (GC, Agilent 7890A) equipped with an Agilent J&W DB-Sulphur SCD column (Part No. G3903-63002; 40 m × 0.32 mm ID) with helium (quality 6.0) as the carrier gas. A sulphur chemiluminescence detector (SCD, Agilent 355) with a dual plasma burner was coupled for specific sulphur analysis [34]. The injector temperature was set at 528 K. A standard mixture of organosulphur compounds in an isopropanol/water mixture (40:67) was used to calibrate thiophene, dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), methyl propyl disulphide (MPDS), methanethiol and dimethyl sulphide (DMS). The concentration of the identified compounds or unassigned peaks was estimated on the basis of an “equimolar response” of the SCD detector towards S content in the molecule (semi-quantitative determination) [35]. For the quantitative analysis in part 3.3, a solution containing an internal standard dibenzothiophene was added to the sample.

Elemental screening and quantitative elemental analysis of aqueous samples were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 715). The analyzer was
calibrated with different dilutions of a multi-element standard solution prepared from certified standards. The standards of the individual elements were purchased either from Ultra Scientific or from Merck. To allow element concentrations to be within the calibrated range and to fit the matrix of the samples to the matrix of the standard solution, the samples were diluted with 1% HNO₃ (mass fraction) by a factor of 10–60 to compensate for the high potassium concentration of some samples. All the solutions were filtered (0.22 μm) before 1% HNO₃ solution was added. Each sample was injected three times and the mean value is reported. The standard deviation of the three repetitions did not exceed 5%.

An elemental (C, H, N, S) analyzer (Vario EL cube, elementar) was also used to quantify the content of carbon, nitrogen, and sulphur in targeted solid and liquid samples.

The specific surface area (SSA), total pore volume (Vₚ) and pore size distribution were measured by N₂ physisorption (77 K) on an Autosorb-1 (Quantachrome). The samples were outgassed in a dynamic vacuum (10⁻³ Pa) for a minimum of 3 h at 573K. The SSA was calculated according to the Brunauer-Emmet-Teller (BET) model, and the total pore volume was determined at a relative pressure P/P₀ = 0.99. The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) model using the desorption branch of the isotherm.

Transmission Electron Microscopy (TEM) was performed on two microscopes: 1./a JEOL JEM 2010 microscope operated at 200 keV equipped with a LaB₆ electron source and with a slow scan charge-coupled device camera (4008 x 2672 pixels, Orios Gatan Inc.); 2./a probe-corrected JEOL JEM-ARM200F (NeoARM) microscope equipped with a cold field emission gun operated at 200 keV and with a OneView CMOS camera (IS-version; Gatan). The latter microscope was also used for Scanning TEM (STEM) using a high-angle annular dark field (HAADF) detector, and energy dispersive X-ray spectroscopy (EDS) investigations, for which a JEOL EDS detector “Centurio 100” was used. Samples were ground (when required) and dispersed in ethanol before being deposited on lacy carbon grids. For each sample, a thorough study was performed to ensure capturing micrographs representative of the sample. A particle size distribution (PSD) of the metallic particles was determined with a sample size of at least 200 particles. The histogram bin size for the PSD was selected by following the guidelines of Alxneit [36] to ensure a statistical representation of the measured particle size.

Ion chromatography was performed at ambient temperature using a Metrosep A Supp 10–100/4.0 column with a filtering pre-column composed of the same resin (Polystyrene/divinylbenzene copolymer resin, particle size 4.6 μm, quaternary ammonium). The eluent used for the analysis was composed of 4.0 mmol L⁻¹ sodium hydrogen carbonate, 6.0 mmol L⁻¹ sodium carbonate and 5 μmol L⁻¹ sodium perchlorate in purified water from a Milli-Q Advantage (Millipore) unit and was fed in at 1 mL min⁻¹ and 12 MPa. Recording of the data from the Metrohm 732 IC conductivity detector and analysis of chromatograms were performed with Metrohm Metrodata software. Prior to analysis, the samples were diluted to the calibrated sulphate concentration range, and filtered at 0.22 μm before being injected (20 μL).

X-ray powder diffraction (XRD) patterns were measured on a Bruker Advance D8 diffractometer (Cu-Kα radiation) in the 15–90° 2θ range with a 0.03° step scan.

3. Results and discussion

3.1. Stability tests of commercial sulphur scavengers in supercritical water

Changes in composition, elemental losses, crystallinity, pore volume/surface area and morphology in SCW were evaluated for several commercial sulphur absorption materials. Table 1 presents the composition and main characteristics of the sorbents selected for the stability tests. None of the sorbents showed changes in their mechanical integrity before and after the stability experiments in SCW except the Mn–Cu sorbent, which for the pellets fell apart during experimentation. This probably is a result of the production procedure (extrusion) and/or the nature of the binder used.

Leaching/material loss from various materials was evaluated by analyzing the solution by ICP-OES after the stability tests (Table 2). The amount of Al and Zn that leached out of the ZnO-based material is overall low, indicative of the low solubility of these elements in supercritical water [17]. Calcium is found to be significantly released from the material, which is consistent with the low adsorption capacity of the materials and porosity already observed [14]. The significant fluctuation of Ca and Al from the 24 h to the 36 h stability tests indicates a mechanical loss of sulphur scavenger fragments. This is in agreement with the accumulation of Ca and Al but also Zn on spent Ru/C catalyst downstream such ZnO-based scavenger during a continuous test [3,14].

The proportion of the main elements constituting Cu–Mo/AC that ended up in the water after the stability tests is rather low, in accordance with the good mechanical stability of the material in supercritical water. However, the total amount of elements that leached out of Mn–Cu is not negligible (0.38%), which is likely related to the observed lack of mechanical stability.

N₂ adsorption revealed an increase of BET surface area Cu–Mo/AC (Fig. 1), from 1300 to 1800 m² g⁻¹, the pore volume following the same proportional increase (30% increase). This increase is indicative of a transformation of the pore structure, and has been observed already on activated carbons under SCW [37]. This is supposedly originating from the partial gasification of the carbon (non-stable part) but could also originate from the migration of metals from inside the pores to the outer surface. This increase in pore volume and surface area did not coincide with any loss of mechanical integrity of the materials. On the opposite side, the pore volume and BET surface area of Mn–Cu (no carbon matrix) decreased significantly, in parallel to the loss of mechanical integrity observed. The same trend as for total surface area could be observed with the evolution of the total pore volume for the materials tested.

Table 1 Composition of the sorbents selected for the various tests performed determined by ICP-OES.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Binder/Matrix</th>
<th>Active phase content</th>
<th>ZnO</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Al₂O₃+CaO</td>
<td>&gt;-90°</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Mo/AC</td>
<td>Activated carbon</td>
<td>32 0 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–Cu</td>
<td>Al₂O₃</td>
<td>6 31 3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe/AC</td>
<td>Activated carbon</td>
<td>2°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* From the product specification sheet. Balance corresponds to the binder.

Table 2 Elemental loss of various commercial sulphur scavengers observed after stability tests in supercritical water. Conditions: H₂O, 683 K, 25 MPa, 24 h or 36 h (when indicated). Confidence intervals are 10%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element loss from material (%)</th>
<th>Al</th>
<th>Ca</th>
<th>Zn</th>
<th>Cu</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td></td>
<td>11</td>
<td>0.01</td>
<td>0.9</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–Cu</td>
<td></td>
<td>0.11</td>
<td>0.05</td>
<td>0.10</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Mo/AC</td>
<td></td>
<td>0.05</td>
<td>0.05</td>
<td>0.19</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• Element loss calculated from the amount of element quantified in the solution after the test divided by its quantity in the fresh material placed in the reactor. Elements at a low concentration in the starting materials have been neglected (–).

• Results for these three scavengers are approximate and were calculated using an estimated mass fraction of Al, Ca and Zn in the scavengers of roughly 3, 3 and 60% respectively [21].
3.2. Performance of commercial sulphur scavengers towards organosulphur compounds

The nature of organosulphur compounds present in various HTL process waters, their stability and the efficiency of various sulphur scavengers in selectively desulphurizing such biomass-based aqueous streams were evaluated using a batch reactor. The tests were performed in conditions close to these met in continuous catalytic hydrothermal gasification. The process developed at the Paul Scherrer Institute consists of a high-pressure pump feeding at 29 MPa biomass into a salt separation vessel heated with a gradient of temperature. The latter reaches ca. 723 K at its top outlet, from which the desalinated stream goes to the gasification Ru/C catalyst protected upstream by a sulphur scavenger [3,38]. A temperature and pressure of 723 K and 29 MPa, respectively, were hence used for the batch tests to mimic conditions the scavenger is exposed to. The hydraulic retention time in the sulphur scavenger bed during the continuous test was calculated to be in the range of 10–12 min. A reaction time of 18 min was defined as representative of that retention time, the higher value compensating for the much faster heating ramp on the continuous setup than on the batch system [38]. The solutions produced were then analyzed by GC-SCD to identify and semi-quantify volatile organosulphur compounds (boiling point < 623 K).

3.2.1. Identification of volatile organosulphur compounds formed in SCW

Fig. 2 presents GC-SCD chromatograms of three HTL process waters produced from Spirulina, Miscanthus and sewage sludge before and after being exposed to conditions close to these used in the cHTG process. The total sulphur content for all the solutions is respectively 354, 88, and 71 mg L\(^{-1}\).

First, it can be observed that the composition in organosulphur compounds of the various process waters varies significantly from one feed to another, along with the concentration of the compounds (see Table 3). As expected, Spirulina HTL process water contains the most diverse and most concentrated organosulphur compounds, followed by the HTL process water produced from sewage sludge, while process water from Miscanthus barely contains any volatile organosulphur compounds. Note that the high volatility of carbonyl sulphide, methanethiol, DMS and hydrogen sulphide, and the sensitivity of the latter towards oxidation in air, probably leads to an underestimation of their concentration.

Table 3 presents the concentration of the main organosulphur compounds identified and a sum of all volatile compounds detected. In all cases, the sulphur-based concentration of volatile organosulphur compounds (bp < 623 K) in solution decreased from 21, 2 and 3 mg L\(^{-1}\) to 9, 0.6, and 2 mg L\(^{-1}\) for Spirulina, Miscanthus and sewage sludge HTL process waters, respectively. Hydrogen sulphide was detected in the three HTL waters exposed to HTG conditions. The slight increase in H\(_2\)S concentration probably originates from the decomposition of organosulphur compounds (see equations 1 and 2) [31], but also possibly by the ex situ reaction of trisulphides with water (see reverse equation 4) [39]. Overall, it can be observed that HTL process waters produced from Miscanthus and sewage sludge did not experience dramatic changes after being exposed to HTG conditions. In the case of Miscanthus-sourced water, it can be noted that small quantities of DMS and thiophene are formed. For the sewage sludge-sourced water, thiophene and methyl ethyl disulphide (MEDS) appeared after the reaction at 723 K, while the peaks at 22.0 and 22.3 min could not be assigned increased in intensity. Thanks to the linear correlation between boiling point/molecular weight and the GC retention time, these two peaks are expected to have a molecular weight of 125–140 g mol\(^{-1}\) and a boiling point of 453–483 K. Based on the list of compounds detected, they can tentatively be assigned to C\(_4\)-disulphide (e.g. diisopropyl or ethyl tert-butyl disulphide) or C\(_5\)-thiophene (e.g. 2,5-diethyl disulphide).

Process water from Spirulina contains the largest amount and variety of volatile organosulphur compounds and is the one that shows the most important change after being exposed to HTG. Very importantly, the large majority of the high boiling point and high molecular weight volatile organosulphur compounds (boiling point above ca. 493 K) were decomposed after being exposed to hydrothermal conditions, and this is the reason for most of the total organosulphur loss. This is the case for the important and broad peak observed at ca. 27 min which can tentatively be assigned to dibutyl disulphide, benzyl methyl thiophene, nonane thiol or related compounds with similar boiling points. While the concentration of methanethiol in solution was found to decrease, those of DMS, thiophene and MEDS significantly increased. The peak at 22.0 min is present as well and its concentration increased after SCW treatment. The many peaks present between retention times of 20–25 min mostly remain unassigned, but can tentatively be assigned to dibutyl disulphide or C\(_6\)-thiophene. For Spirulina, Miscanthus and sewage sludge did not experience dramatic changes after being exposed to hydrothermal conditions, and this is the reason for most of the total organosulphur loss. This is the case for the important and broad peak observed at ca. 27 min which can tentatively be assigned to dibutyl disulphide, benzyl methyl thiophene, nonane thiol or related compounds with similar boiling points. While the concentration of methanethiol in solution was found to decrease, those of DMS, thiophene and MEDS significantly increased. The peak at 22.0 min is present as well and its concentration increased after SCW treatment. The many peaks present between retention times of 20–25 min mostly remain unassigned, but can tentatively be assigned to dibutyl disulphide or C\(_6\)-thiophene. For Spirulina, Miscanthus and sewage sludge did not experience dramatic changes after being exposed to hydrothermal conditions, and this is the reason for most of the total organosulphur loss. This is the case for the important and broad peak observed at ca. 27 min which can tentatively be assigned to dibutyl disulphide, benzyl methyl thiophene, nonane thiol or related compounds with similar boiling points. While the concentration of methanethiol in solution was found to decrease, those of DMS, thiophene and MEDS significantly increased. The peak at 22.0 min is present as well and its concentration increased after SCW treatment. The many peaks present between retention times of 20–25 min mostly remain unassigned, but can tentatively be assigned to dibutyl disulphide or C\(_6\)-thiophene.
trisulphide. The latter is indeed expected to be formed from methanethiol after the reaction. Indeed, these compounds are known to readily decompose in hydrothermal conditions [26], in line with the low stability of S(0) in supercritical water [40, 41]. The formation of di- and trisulphide likely results from the exposure of the solution to oxygen, or oxygen with hydrogen sulphide [39, 42].

The total amount of volatile organosulphur compound (bp < 623 K) accounts for approximately 6% of the total amount of sulphur present in the HTL process water produced from Spirulina.

### 3.2.2. Performance of sulphur scavengers for the removal of organosulphur compounds

Spirulina-sourced HTL process water was exposed to cHTG conditions in the presence of various commercial scavengers and the GC-SCD results are presented in Fig. 3 and Fig. 4. Note that for these tests, the molar ratio MO\textsubscript{x} : S (M = sum of all transition metals in the scavengers) was maintained at 20.

First, the test performed with the benchmark ruthenium-based catalyst (molar Ru:S ratio of ca. 2) showed that no volatile (bp < 623 K) organosulphur compounds are left after hydrothermal treatment, except for a small amount of H\textsubscript{2}S, likely coming from the gas headspace after quenching. An important decrease in the concentration of all organic compounds was observed by GC-FID indicating nearly complete gasification of organic compounds. This indicates that the gasification catalyst can efficiently but unselectively desulphurize such HTL process water, outlining the necessity for a sulphur scavenger upstream of the catalyst that is efficient towards organosulphur compounds. Interestingly, exposing Spirulina HTL process water to HTG conditions with activated carbon led to a redistribution of some organosulphur compounds: most importantly less methanethiol but more dimethyl disulphide are produced, while the thiophene peak disappeared. This might be related to the known partial gasification occurring at the surface of activated carbon and/or could be related to the adsorption of some organosulphur compounds on the AC. Note that sulphur mass balance was not performed for this series of tests, but was done in the series using pure oxide nanoparticles (part 3.3).

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**Table 3**

Semi-quantitative analysis of organosulphur compounds identified by GC-SCD on the three HTL water phases as received and after being exposed to HTG conditions. Estimated errors on the values are 30%.

<table>
<thead>
<tr>
<th>Organosulphur compound</th>
<th>Spirulina fresh</th>
<th>after HTG</th>
<th>Miscanthus fresh</th>
<th>after HTG</th>
<th>sewage sludge fresh</th>
<th>after HTG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg L\textsuperscript{-1})</td>
<td></td>
<td>(mg L\textsuperscript{-1})</td>
<td></td>
<td>(mg L\textsuperscript{-1})</td>
<td></td>
</tr>
<tr>
<td>Total volatile organosulphur\textsuperscript{a, b}</td>
<td>21</td>
<td>9</td>
<td>2</td>
<td>0.6</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>H\textsubscript{2}S\textsuperscript{b}</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>COS\textsuperscript{b}</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>0.3</td>
<td>0.04</td>
</tr>
<tr>
<td>CH\textsubscript{2}SH\textsuperscript{b}</td>
<td>7</td>
<td>2</td>
<td>0.5</td>
<td>0.2</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>CH\textsubscript{3}SSCH\textsubscript{3}</td>
<td>0.5</td>
<td>3</td>
<td>0.05</td>
<td>0.01</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>CH\textsubscript{4}SSCH\textsubscript{4}</td>
<td>0.8</td>
<td>0.6</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Thiophene</td>
<td>&lt;0.01</td>
<td>0.08</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{5}SSCH\textsubscript{3}</td>
<td>0.03</td>
<td>0.5</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>C\textsubscript{4}-thiophene</td>
<td>0.1</td>
<td>0.3</td>
<td>0.07</td>
<td>0.05</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Correspond to the sum of all the peaks observed on the GC-SCD chromatograms, on the basis of an “equimolar response” of the SCD detector.

\textsuperscript{b} Values of volatile compounds are underestimated and should be used for relative comparison only (before-after HTG).
As shown in Figs. 3 and 4, ZnO-based material had a very limited impact on organosulphur compounds concentration. Like for the solution exposed to HTG conditions without a sulphur scavenger, the amount of methanethiol, dimethyl disulphide and trisulphide represent about two-thirds of the volatile organosulphur compounds. Interestingly, while the use of this material decreased the H$_2$S concentration, 10–40% remained after the tests, which might be related to the production of H$_2$S after quenching, separation of the material from the solution (see reversed equation 4), and/or contamination from the headspace after quenching. In the case of iron-doped activated carbon Fe-/AC (nature of the iron unknown, no crystalline phase detected), a 50% increase of total volatile organosulphur is observed, all compounds being more or less affected the same way, except for H$_2$S/COS. This increase could be explained by a favored cracking of large/non-volatile sulphur-containing organic compounds in the presence of the material.

The Mn–Cu and Cu–Mo/AC led to very low levels of volatile organosulphur compounds in the remaining solution, decreasing by 73 and 85% in total, respectively. GC-FID analysis of the solutions produced indicated a limited impact of the scavengers on the organics’ concentration, proving the relative selectivity of Cu-based materials toward S-compounds decomposition. Copper is hence a promising element both for organosulphur compounds decomposition and sulphide absorption, but manganese and molybdenum could also be responsible for the performance of the scavengers.

### 3.3. Sulphur absorption with pure MO$_x$ nanoparticles in cHTG conditions

To further investigate the role of individual MO$_x$, excluding the effects of binder and other additives, pure MO$_x$ colloidal nanoparticles (NP-MO$_x$) were studied. The mean oxide particle diameter was 25, 30, 35, 70, and 40 nm for NP-ZnO, NP-CuO, NP-Fe$_2$O$_3$, NP-MnO$_2$, NP-MoO$_3$, and NP-CeO$_2$, respectively. After the desulphurization tests with HTL process water from Spirulina, the liquid, solid, and gas produced were analyzed. Note that the process water used for these tests aged for roughly 12 months. As a result, the concentration of various volatile organosulphur compounds varied but remained high, and the total dissolved sulphur concentration increased as a result of the formation of insoluble organic droplets.

The sulphur mass balance and the conversion of organosulphur compounds with and without adding NP-MO$_x$ are illustrated in Fig. 5 and Fig. 6, respectively. After exposing the HTL process water (solution alone) to SCW conditions, about 7% of the sulphur in the feed was converted (mostly sulphate), while the concentration of the other S categories in the liquid did not change. With all metal oxide nanoparticles, a decrease of volatile organosulphur and other S species in the liquid was observed. In terms of absorption capacity, the amount of S scavenged (absorbed or in an isopropanol-insoluble form) in the NPs was found to decrease in the following order ZnO $\approx$ CuO $>$ MoO$_3$$>$ CeO$_2$$>$ MnO$_2$$>$ Fe$_2$O$_3$. NP-ZnO and NP-CuO showed similar absorption capacity. The sulphur balance might have ended up in isopropanol-insoluble organic solids, on the reactor walls (CuO-NP) or in the gas phase, and overall increased with the desulphurization efficiency. The
absence of stirring in the batch reactor and its design limits gas to liquid/ supercritical fluid mass transfer and is expected to lead to the loss of gaseous sulphur species in the gas phase. Iron oxide did not absorb any sulphur. This is in line with the work of Liu et al. who observed that while FeS2 is chemically stable in pure SCW, it desulphurizes to H2S, Fe3S4 and FeS4O2 under SCW in the presence of H2 [13]. All metals were found to reduce the amount of unidentified sulphur in the liquid phase, but at very different levels. For NP-ZnO, NP-MnO2 and NP-CeO2, this decrease was comparable and reached 40-50%. For NP-CuO, a significant reduction of the amount of unidentified sulphur in the liquid phase (82%) was observed, producing supposedly more gaseous S or insoluble organosulphur compounds.

Comparing the total amount of volatile S compounds (bp < 623 K) in HTL process water before (feed) and HTG conditions (solution alone), the biggest volatile S component CH3SH in the feed seems to have been converted to CH3SSCH3 (Fig. 6) possibly during the quenching or sampling. The impact of the NP-MO on organosulphur compounds concentration varied significantly but not in the same way as the ab/adsorption of S in the material. Indeed, the efficiency of organosulphur removal goes in the following order: CuO >> ZnO > MnO2 ≈ CeO2 > FeO3 > MoO3. This observation indicates that Cu has the predominant role in the commercial S-scavengers Mn–Cu and Cu–Mo/AC in removing volatile organosulphur compounds described in part 3.2.2. It is surprising, though, to see the relatively high performance of NP-ZnO nanoparticles but the poor performance of the ZnO-based S scavengers. This was probably related to a reduced mass transfer within the grain as a result of the collapse of pore volume and surface area of the commercial material [14].

For all other NP-MO, methanethiol and dimethyl disulphide were the dominating compounds and were present in comparable ratios. However, copper was found to remove largely the most resilient organosulphur compounds under such conditions that are methanethiol and dimethyl disulphide. Interestingly, NP-CuO was the only oxide with which dimethyl sulphide was observed. Note that the Cu-based nanoparticles were the only ones that could not be fully recovered after the test as they experienced agglomeration and were deposited on the walls of the batch reactor (the deposit had the colour of reduced Cu(0)). This agglomeration and accumulation at the walls likely affected mass transfer limitation and/or lead to a decrease of active surface despite the high performance of Cu.

Compared to the “solution alone”, the use of NP-MOX showed overall little impact on either the distribution of gas products, the total amount of gas, or the conversion of the feed organics into gas (gasification rate). However, a small increase in CH4 and H2 concentration with NP-ZnO, NP-CuO, and NP-CeO2 was observed. This is in line with the observations made from GC-FID and indicates that the NP-MOx tested desulphurize selectively the organosulphur compounds without gasifying the organic matter.

Note that mixing the HTL process water exposed to HTG conditions with the pure metal oxide at room temperature barely led to any decrease in the concentration of the organosulphur compounds. This rules out the possibility of desulphurization by mere adsorption of organosulphur compounds on the metal particles.

The phases identified from XRD in the fresh and spent NP-MOx are summarized in Table 4. XRD analysis of the spent materials showed that all the NP-MOx excluding NP-ZnO, went through total or partial reduction after cHTG treatment with HTL process water. The conditions used are indeed reductive, the oxide could have hence been reduced by the hydrocarbons present in the feed and/or the H2 or CO produced during the treatment. CuO, MoO3, Fe3O4, and Mn(IV) oxide were fully reduced to Cu(0), Mo2O3, FeO4, and Mn(II) compounds, while CeO2 was only partially reduced to Ce2O3. Interestingly, manganese oxide was converted to manganese carbonate mainly, along with MnO and MnS.

Only the spent NP-ZnO and NP-MnO2 showed significant metal(II) sulphide reflexes, in agreement with their sulphur content after the test. Interestingly, NP-MoO3, NP-CeO2 and more importantly NP-CuO barely showed any crystalline metal sulphide despite significant ab/adsorption of sulphur by the materials (Fig. 5). Considering the sulphur content in the spent NP-CuO and NP-MoO3, they probably contained metal sulphides in amorphous form. This is in agreement with the literature (gas phase) where it is reported that the ad/absorption of H2S takes place more efficiently on Cu than on ZnO [45], but that ZnS (crystalline) forms readily while crystalline copper sulphide does not [46]. The spent Fe-based nanoparticles showed no S-rich phases, in accordance with their low capacity to scavenger sulphur. In the case of copper, the three reflections corresponding to copper(0) (fcc structure, space group Fm3m) were found to be at lower angles than those reported in the literature, 43.27°, 50.39°, 74.05/74.26° instead of 43.6°, 50.7° and 74.45° for [111], [200] and [220] planes, respectively. In parallel, the two main diffraction peaks present a shoulder and the smallest peak (220) has a distinct satellite diffraction peak, in both cases at larger scattering angles. This is indicative of larger Interplane distances, which can be explained by the presence of crystallites with varying degrees of lattice defects and of structural relaxation, possibly brought by the

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**Table 4**

<table>
<thead>
<tr>
<th>Material ID</th>
<th>Fresh materials</th>
<th>Spent materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP-ZnO</td>
<td>ZnO 1123</td>
<td>ZnO 1123</td>
</tr>
<tr>
<td>NP-CuO</td>
<td>CuO 803</td>
<td>Cu(0) 683</td>
</tr>
<tr>
<td>NP-FeO3</td>
<td>FeO3 903</td>
<td>FeO3 933</td>
</tr>
<tr>
<td>NP-MnO2</td>
<td>MnO2 583</td>
<td>MnO2 213</td>
</tr>
<tr>
<td>NP-MoO3</td>
<td>MoO3 533</td>
<td>MoO3 683</td>
</tr>
<tr>
<td>NP-CeO2</td>
<td>CeO2 1333</td>
<td>CeO2 1333</td>
</tr>
</tbody>
</table>

1. Dominating phases are shown in bold.
2. Tamman temperature ≈ one-half of the melting point (K).
3. Important deposition on the reactor walls.
4. From Ref. [44].

**Fig. 6.** Distribution of volatile S compounds (boiling point < 623 K) in the aqueous phases recovered after the batch tests, determined by GC-SCD. The * refers to compounds with a low boiling point whose concentrations most likely are underestimated.
presence of sulphur atoms. Note CeS does have a low resistance towards oxidation and will oxidize in the air which could partially explain the absence of diffraction peaks [47].

Note that the S:Zn ratio of NP-ZnO was 0.036, while the ratio of crystalline ZnS and ZnO was nearly 1:1, indicating a high crystallinity of the sulphide and surprisingly low crystallinity of the oxide.

TEM showed an increase in particle size and a change of shape for all materials but to very different extent (see Fig. 7). Zn- and Fe-based nanoparticles converted to more crystalline needle-like or cubic particles, respectively, while spent Cu and Mo-based materials, and to a lower extent Mn-based ones, contained particles significantly larger with an undefined shape. In the case of NP-CeO$_2$, little change in particle size and shape could be observed. Spent NP-MoO$_3$ material mostly consisted of large round hollow particles, the shell being composed of very small agglomerated crystalline particles. The structure of the Mo-based particles observed in Fig. 7 might originates from a severe coarsening of MoO$_3$ (Tammann point at 533 K), concomitant with or followed by its reduction to crystalline MoO$_2$ particles that are more stable (Tammann point at 683 K). As it can be seen in Table 4, the spent materials with the phases having the lowest Tammann point were the ones that coarsened most (Cu, Mo). In the case of Mn, there is an important difference between Tammann points of Mn(IV) oxide and MnCO$_3$ on one side, and MnO and MnS on the other side. In parallel, the absence of a clear correlation between particle size increase and material solubility [17] indicates that surface energy and diffusion of chemical species of the materials (kinetic aspect) have a more important impact on coarsening than solubility (thermodynamic aspect).

Spent NP-ZnO was very heterogeneous with some particles barely affected by the conditions, some crystalline needle-like particles, some large amorphous particles, but also particles with a core-shell structure were observed. STEM-EDS showed that most particles had a low S:O ratio while a few particles showed a rather high S:O ratio (Fig. 8). This indicates that sulphidation of zinc did not occur homogeneously throughout the material, which cannot be explained by the absence of stirring in the batch reactor (see description of Ce or Mo oxides). Interestingly, STEM-HAADF images revealed a rather porous structure for the S-rich particles, as opposed to the highly crystalline sulphur-free ZnO particles observed on the same sample. These S-rich particles often presented a core-shell structure with a denser core, the whole structure being homogeneously composed of Zn and S mainly, with low amounts of O.

Sulphidation mechanism at atmospheric pressure and room temperature involves Zn$^{2+}$ dissolution and reprecipitation as ZnS [48]. A parallel between this mechanism and the observations made after reductive supercritical water treatment cannot easily be made because of the extremely low solubility of Zn under such conditions [17], and because of the heterogeneity of the zinc sulphide formation throughout the sample. Results hence indicate a slow initiation of ZnO sulphidation that is followed by a fast propagation (sulphidation) of a particle, or else very high mobility of ZnS at the surface of the oxide. According to Pokrovski et al. [49], trisulphur radical ion S$_3$$^•$ is favored under the conditions applied in this work (coexistence of sulphate and sulphide,
temperature, and pressure) which might favor migration of chalcophilic metal, e.g. Cu, Mo or Zn. Indeed, in the case of Pt, the formation of Pt\(^{6+}\)(HS\(^{-}\))\(_2\)(S\(^{2-}\))\(_2\) and Pt\(^{6+}\)(HS\(^{-}\))(H\(_2\)O)(S\(^{2-}\)) \(_2\) species can enhance Pt\(^{6+}\) solubility by four to five orders of magnitude \([50]\). A complex formed from S\(^{2-}\) and Zn\(^{2+}\) might be involved during sulphidation.

In the case of Cu-based particles, EDS indicated the presence of large grains rich in sulphur, while others had none, similarly to NP-ZnO (see Fig. 8). Most of the particles were oxygen free indicating a rather complete reduction of CuO as indicated by XRD. For cerium oxide nanoparticles, a very homogeneous distribution of S through the CeO\(_x\) particles was observed without a single high S/O ratio particle/area. In the case of the spent Mo-based material, EDS also showed homogeneous distribution of Mo and S.

The homogeneity of S deposition throughout Ce samples, in opposition to Zn samples, excludes mass transfer limitation linked to the absence of stirring because both materials present similar desulphurization rate performance.

4. Conclusions

Removal of organosulphur compounds from biomass stream is highly relevant for biogas production (cHTG) in order to protect the gasification catalyst. It is also relevant for biofuels (HTL), for which a selective desulphurization is required without significant gasification of the organics. For that, understanding the nature and fate of organosulphur in a complex biomass-sourced stream under supercritical water is of great importance. In this work, alkylthiophenes, short sulphides and their corresponding disulphides were found to be dominant after the hydrothermal treatment (723 K, 29 MPa) of various HTL process waters, methanethiol and dimethyl disulphide being the main compounds. For that, understanding the nature and fate of organosulphur in a complex biomass-sourced stream under supercritical water is of great importance. In this work, alkylthiophenes, short sulphides and their corresponding disulphides were found to be dominant after the hydrothermal treatment (723 K, 29 MPa) of various HTL process waters, methanethiol and dimethyl disulphide being the main compounds.

Out of many materials, the Cu(0) was found to be the most active phase in selectively desulphurizing the organic compounds in hydrothermal conditions, as well as absorbing sulphur. ZnO, MoO\(_2\), CeO\(_2\) or MnO showed intermediate desulphurization performance and good sulphur absorption capacity. Hydrothermal conditions are harsh for metals and metal oxides, and most materials tested suffered various extent of coarsening. Most active phases tested presented the disadvantage to sinter under the rough hydrothermal conditions applied. This represents a serious problem for the regeneration of sulphur scavengers, as a regenerated material would likely have very low surface area and pore volume, and hence poor performance. However, cerium oxide showed remarkably high stability under reductive supercritical water confirming the predictions based on thermodynamic calculations \([17]\). More importantly, its performance was comparable to ZnO, making it a good candidate for the preparation of stable and regenerateable scavengers.

Upon sulphidation, porous pure oxides or metals will lose pore volume and surface area as a result of the increase of the molar volume. Activated carbon was here found to be a good support/binder, but another form of carbon structure with high meso and macroporous volume should be used instead to allow a high loading of absorbing material and good mass transfer. Alternatively, Fe\(_2\)O\(_4\) could be a good candidate to be used as a material binder as it shows intermediate desulphurization performance, does not suffer sulphidation (no volume expansion), and showed limited sintering for a low cost.

Overall, CeO\(_2\) for its stability on one side, and Cu(0) embedded with Fe\(_2\)O\(_3\) or carbon on the side, were identified as a promising combination of sulphur scavengers with costs comparable to zinc oxide or nickel. The potential regenerability of the former, and the deep desulphurization offered by the second should allow an overall more cost-effective cHTG process that shall ease its scale up and industrialization.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References


